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CHEM 110B: Topics in Physical Chemistry

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Preface

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These are the lecture notes for CHEM 110B, "Topics in Physical Chemistry", a course which centers on thermodynamics and statistical mechanics. The lecture topics are:

Week 1 Introduction to Statistical Mechanics, Probability, Distribution Functions

Week 2 Boltzmann's Law, Kinetic Theory, Maxwell-Boltzmann Distribution

Weeks 3,4 Boltzmann's Law, Partition Functions (PFs), Microstates, Ensembles

Weeks 4,5 Ideal Gas: Translational, Rotational, Vibrational partition functions, Energy Equipartition

Week 5 Statistical Thermodynamics, Equilibrium

Week 6 Black Body Radiation, Heat Capacity of Solids, Third Law

Week 7 Non-Ideal Gases, Liquid Structure: Hard Sphere Liquid

Weeks 8,9 Bose-Einstein & Fermi-Dirac Statistics, Electron Gas, Fermi Level, BE Condensation

Weeks 9,10 Transport Processes and Kinetics

The following textbooks are recommended:

- Kubo, Toda, Saito, Statistical Physics I
- Honerkamp, Statistical Physics
- McQuarrie, Statistical Mechanics

- Kittel, Thermal Physics

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Chapter 1

Probability

Experimental measurements in the laboratory are random variables (rv). Every time you measure a physical quantity you get a different number because of random fluctuations (random errors). The random fluctuations are related to random errors in experiments. To properly describe experimental errors, a statistical description is needed. In statistical mechanics we deal with a very large number of particles. Because we cannot possibly know everything about every particle, a statistical description is needed. Herein we introduce tools to study random variables. Random variables can be continuous or discrete, depending on whether they take continuous or discrete values, respectively. An example of a continuous random variable is the length of an object. Length is a random variable which can take positive real values in a continuous interval. An example of a discrete random variable is the number of counts within a time interval. Counts can only take discrete values $(1, 2, 3, \dots)$, in this case, the positive integers.

1.1. Motivation for Probability

Let A be an event associated with some experiment E, so that A might, or might not, occur when E is performed. Now consider a Super-experiment E^∞ which consists of an infinite number of independent performances of E, "independent" in that no performance is allowed to influence others. Write $N(A, n)$ for the number of occurrences of A in the first n performances of E within the super-experiment. Then the long-term relative frequency (LTRF) idea is that

$$\frac{N(A,n)}{n} \quad \text{converges to} \quad \mathbb{P}(A)$$

in some sense, where $\mathbb{P}(A)$ is the probability of A, that is, the probability that A occurs within experiment E. If our individual experiment E consists of tossing a coin with probability p of Heads once, then the LTRF idea is that if the coin is thrown repeatedly, then

$$\frac{\text{Number of Heads}}{\text{Number of tosses}} \to p$$

in some sense. Here, A is the event that "the coin falls Heads" in our individual experiment E, and $p = \mathbb{P}(A)$. Since the coin has no memory, we believe (and postulate in mathematical modelling) that it behaves independently on different tosses.

The **certain event** Ω (Greek Omega), the event that "something happens", occurs on every performance of experiment E. The **impossible event** $\emptyset$ ("nothing happens") never occurs. The LTRF idea suggests that

$$\mathbb{P}(\Omega) = 1, \qquad \mathbb{P}(\emptyset) = 0.$$

Note that in order to formulate and prove the Strong Law, we have to set up a model for the super-experiment E^∞, and we have to be precise about "in some sense".

Addition Rule for Two Events: If A and B are events associated with our experiment E, and these events are disjoint (or exclusive) in that it is impossible for A and B to occur simultaneously on any performance of the experiment, and if $A \cup B$ is the event that "A happens or B happens", then, of course,

$$N(A \cup B, n) = N(A, n) N(B, n).$$

The appropriateness of the set-theoretic "union" notation will become clear later. If we "divide by n and let n tend to ∞" we obtain LTRF motivation — but not proof — of the Addition Rule for Two Events: if A and B are disjoint, then $\mathbb{P}(A \cup B) = \mathbb{P}(A) + \mathbb{P}(B)$. This is normally taken as an axiom. If our individual experiment is that of tossing a coin twice, then

$$\mathbb{P}(\text{1 Head in all}) = \mathbb{P}(\text{HT}) + \mathbb{P}(\text{TH}),$$

where, of course, HT signifies "Heads on the 1st toss, Tails on the 2nd". If A is any event, we write A^c for the event "A does not occur". Then A and A^c are disjoint, and $A \cup A^c = \Omega$: precisely one of A and A^c occurs within our experiment E. Thus, $1 = \mathbb{P}(\Omega) = \mathbb{P}(A) + \mathbb{P}(A^c)$, so that $\mathbb{P}(A^c) = 1 - \mathbb{P}(A)$. Hence, for our coin, $\mathbb{P}(\text{it falls Tails}) = q : 1 - p$.

The LTRF motivation for conditional probability. Let A and B be events associated with our experiment E, with $\mathbb{P}(A) \neq 0$. The LTRF motivation is that we regard the conditional probability $\mathbb{P}(B|A)$ that B occurs given that A occurs as follows. Suppose again that our experiment is performed 'independently' infinitely often. Then (the LTRF idea is that) $\mathbb{P}(B|A)$ is the long-term proportion of those experiments on which A occurs that B (also) occurs, in other words, that both A and B occur: In other words, if $A \cap B$ is the event that 'A and B occur simultaneously', then we should have

$$\begin{aligned}\mathbb{P}(B|A) =& \text{limit in some sense of } \frac{N(A \cap B, n)}{N(A, n)}\\ =& \text{limit in some sense of } \frac{N(A \cap B, n)/n}{N(A, n)/n} = \frac{\mathbb{P}(A \cap B)}{\mathbb{P}(A)}\end{aligned}$$

in our experiment E. In the mathematical theory, we define

$$\mathbb{P}(B|A) := \frac{\mathbb{P}(A \cap B)}{\mathbb{P}(A)}.$$

Suppose that our experiment E has actually been performed in the real world, and that we are told only that event A has occurred. Bayesians would say that $\mathbb{P}(B|A)$ is then our 'probability as degree of belief that B (also) occurred'. Once the experiment has been performed, whether or not B has occurred involves no randomness from the Frequentist standpoint. A Frequentist would have to quote: 'the long-term proportion of those experiments on which A occurs that B (also) occurs is (whatever is the numerical value of) $\mathbb{P}(B|A)$'; and in this sense $\mathbb{P})(B|A)$ represents our 'confidence' that B occurred in an actual experiment on which we are told that A occurred.

With this Frequentist view of probability, we should explain to Homer that if the experiment 'Pick a person at random and test him or her for the disease' were performed independently a very large number of times, then on a proportion 11/12 of those occasions on which a person tested positively, he or she would not have the disease. To guarantee the independence of the performances of the experiment, we would have to pick each person from the entire population, so that the same person might be chosen many times. It is of course assumed that if the person is chosen many times, no record of the results of any previous tests is kept. This is an example of sampling with replacement.

General Multiplication Rule. We have for any 2 events A and B,

$$\mathbb{P}(A \cap B) = \mathbb{P}(A)\mathbb{P}(B|A),$$

this being merely a rearrangement of the previous formula. The latter does not exist when $\mathbb{P}(A) = 0$.

For any 3 events A, B and C, we have, for the event $A \cap B \cap C$ that all of A, B and C occur simultaneously within our experiment E,

$$\mathbb{P}(A \cap B \cap C) = \mathbb{P}((A \cap B) \cap C) = \mathbb{P}(A \cap B)\mathbb{P}(C|A \cap B),$$

whence

$$\mathbb{P}(A \cap B \cap C) = \mathbb{P}(A)\mathbb{P}(B|A)\mathbb{P}(C|A \cap B).$$

The extension to 4 or more events is now obvious.

A decomposition result. Let A and B be any two events. The events $G : A \cap B$ and $H := A^c \cap B$ are disjoint, and $G \cup H = B$. (Clarification. We are decomposing B according to whether or not A occurs. If B occurs, then either 'A occurs and B occurs' or 'A does not occur and B occurs'.) We have

$$\mathbb{P}(B) = \mathbb{P}(G) + \mathbb{H} = \mathbb{P}(A)\mathbb{P}(B|A) + \mathbb{P}(A^c)\mathbb{P}(B|A^c).$$

This, the simplest decomposition, is extremely useful.

Example on conditional probability. Suppose that 1 in 100 people has a certain disease. A test for the disease has 90% accuracy, which here means that 90% of those who do have the disease will test positively (suggesting that they have the disease) and 10% of those who do not have the disease will test positively. One person is chosen at random from the population, tested for the disease, and the test gives a positive result. That person might be inclined to think: "I have been tested and found 'positive' by a test which is accurate 90% of the time, so there is a 90% chance that I have the disease." However, it is much more likely that the randomly chosen person does not have the disease and the test is in error than that he or she does have the disease and the test is correct. Indeed, we can reason as follows, using 'K.' to signify 'thousand' (1000, not 1024) and 'M' for 'million'. Let us suppose that there are 1M people in the population. Suppose that they are all tested. Then, amongst the 1M people, and about 1M x 99% = 990K would not have the disease, of whom about (1M x 99%) x 10% = 99K would test positively; 1M x 1% = 10K would have the disease, of whom about (1M x 1%) x 90% = 9K would test positively. So, a total of about 99K + 9K = 108K would test positively, of whom only 9K would actually have the disease. In other words, only 1/12 of those who would test positively actually have the disease. Because of this, we say that the conditional probability that a randomly chosen person does have the disease given that that person is tested with a positive result, is 1/12.

Now consider the situation where the experiment has actually been performed: a real person with an actual name — let's say it is Homer Lagrange — has been chosen, and tested with a positive result. Can we tell Homer that the probability that he has the disease is 1/12? Do note that we are assuming that Homer is the person chosen at random; and that all we know about him is that his test proved positive. It is not the case (for example) that Homer is consulting his doctor because he fears he may have caught a sexually transmitted disease.

A Possible Frequency-School View. The problem is that there is no randomness in whether or not Homer has the disease: either he does have it, in which case the probability that he has it (conditional on any information) is 1; or he does not have it, in which case the probability that he has it (conditional on any information) is 0. All that we can say to Homer is that if every person were tested, then the fraction of those with positive results who would have the disease is 1/12; and in this sense he can be 11/12 'confident' that he does not have the disease. It is not very helpful to tell Homer only that the probability that he has the disease is either 0 or 1 but we don't know which.

The Bayesian-School View. If we take the contrasting view of the Bayesian School of Statistics, then we can interpret 'probability that a statement is true' as meaning 'degree of belief in that statement'; and then we can tell Homer that the probability (in this new sense) that he has the disease is 1/12.

In this example, let B be 'chosen person has the disease' and A be 'chosen person tests positively'. We want to find $\mathbb{P}(B|A)$. We are given that $\mathbb{P}(B) = 1\%$, $\mathbb{P}(B^c) = 99\%$, $\mathbb{P}(A|B) = 90\%$, $\mathbb{P}(A|B) = 10\%$. We have, keeping the calculation in the same order as before,

$$\mathbb{P}(A) = \mathbb{P}(B^c \cap A) + \mathbb{P}(B \cap A) = \mathbb{P}(B^c)\mathbb{P}(A|B^c) + \mathbb{P}(B)\mathbb{P}(A|B)$$
$$= (0.99 \times 0.10) + (0.01 \times 0.90) = 0.108 \qquad (= 108K/1M)$$

We now know $\mathbb{P}(A \cap B)$ and $\mathbb{P}(A)$, so we can find $\mathbb{P}(B|A)$.

’Independence means Multiply’. If A and B are two events, then we say that A and B are independent if

$$\mathbb{P}(A \cap B) = \mathbb{P}(A)\mathbb{P}(B),$$

one of several assertions which we shall meet that ’Independence means Multiply’. If $\mathbb{P}(A) = 0$, no comment is necessary. If $\mathbb{P}(A) \neq 0$, then we may rearrange the expression as

$$\mathbb{P}(B|A) = \frac{\mathbb{P}(A \cap B)}{\mathbb{P}(A)} = \mathbb{P}(B),$$

which says that the information that A occurs on some performance of E does not affect ‘our degree of belief that B occurs’ on that same performance.

If we consider the experiment ’Toss a coin (with probability p of Heads) twice’, then, we believe that, since the coin has no memory, the results of the two tosses will be independent. (The laws of physics would be very different if they are not!) Hence we have

$$\mathbb{P}(\text{HT}) = \mathbb{P}(\text{Heads on first toss}) \times \mathbb{P}(\text{Tails on second}) = pq,$$

where q, the probability of Tails, is $1 - p$; and, using the addition rule, we get the familiar answer that the probability of ’exactly one Head in all’ is $pq + qp = 2pq$.

The Multiplication Rules for n independent events follow from the General Multiplication Rules similarly. If we toss a coin 3 times, the chance of getting HTT is, of course, pqq.

Counting. We now begin a discussion (continued in the next section) of various ’counting’ and ’conditioning’ aspects of the famous binomial-distribution result for coin tossing. The ’counting’ approach may well be familiar to you; but, in the main, we want you to condition rather than to count.

Lemma. For non-negative integers r and n with $0 \leq r \leq n$, the number $\binom{n}{r}$, also denoted by ${}^cC_r$, of subsets of $\{1, 2, \ldots, n\}$ of size r is

$$\binom{n}{r} =^n C_r = \frac{n!}{r!(n-r)!},$$

where, as usual,

$$n! := n(n-1)(n-2)\ldots 3.2.1, \qquad 0! := 1.$$

If $r < 0$ or $r > n$, we define ${}^nC_r := \binom{n}{r} := 0$. Note: there is a standard convention in math that ‘set’ means ’unordered set’: $\{1, 2, 3\}\{3, 1, 2\}$. There are indeed ${}^4C_2 = 6$ subsets of size two of $\{1, 2, 3, 4\}$, namely, $\{1, 2\}, \{1, 3\}, \{1, 4\}, \{2, 3\}, \{2, 4\}, \{3, 4\}$. The empty set is the only subset of $\{1, 2, ..., n\}$ of size 0, even if $n = 0$.

Lemma. (a) The number of ordered r-tuples $(i_1, i_2, \ldots, i_r)$ where each i_k is chosen from $\{1, 2, \ldots, n\}$ is n^r. (We know from Set Theory that the set of all such r-tuples is the

Cartesian product $\{1, 2, \ldots, n\}^r$.) (b) For $0 \le r \le n$, the number ${}^nP_r$ of ordered r-tuples $(i_1, i_2, \ldots, i_r)$ where each i_k is chosen from $\{1, 2, \ldots, n\}$ and $i_1, i_2, \ldots, i_r$ are distinct is given by

$$ {}^nP_r = n(n-1)(n-2)\ldots(n-r+1) = \frac{n!}{(n-r)!}. $$

(c) The number of permutations of $\{1, 2, \ldots, n\}$ is $n!$. (d) The previous Lemma is true. *Proof.* In Part (a), there are n ways of choosing i_1, and, for each of these choices,n ways of choosing i_2, making $n \times (n-1)$ ways of choosing the ordered pair (i_1, i_2). For each of these n^2 choices of the ordered pair (i_1, i_2), there are n ways of choosing i_3; and so on. In Part (b), there are n ways of choosing i_1, and, for each of these choices, $n-1$ ways of choosing i_2 (because we are now not allowed to choose it again), making $n \times (n-1)$ways of choosing the ordered pair (i_1, i_2). For each of these $n(n-1)$ choices of the ordered pair (i_1, i_2), there are $n-2$ ways of choosing i_3; and so on. Part (c) is just the special case of Part (b) when $r = n$. Now for Part (d). By Part (c), each subset of size r of $\{1, 2, \ldots, n\}$ gives rise to $r!$ ordered r-tuples $(i_1, i_2, \ldots, i_r)$ where $i_1, i_2, \ldots, i_r$ are the distinct elements of the set in some order. So it must be the case that $r! \times^n C_r =^n P_r$;and this leads to our previous formula for ${}^nC_r$.

National Lottery. One can however obtain clearer intuitive understanding of this Lemma by using conditioning rather than counting as follows. Yes, a certain amount of intuition goes into the argument too. A gambler (who clearly knows no Probability) pays 1 pound to choose a subset of size r of the set $\{1, 2, \ldots, n\}$. ($n = 49$, and $r = 6$.) The Lottery Machine later chooses 'at random' a subset of size r of the set $\{1, 2, \ldots, n\}$. If the machine chooses exactly the same subset as our gambler, then our gambler wins the 'jackpot'. It is clear that our gambler wins the 'jackpot' with probability $1/\binom{n}{r}$, and we can find $\binom{n}{r}$ from this probability.

Now, the probability that the first number chosen by the machine is one of the numbers in our gambler's set is clearly r/n. The conditional probability that the second number chosen by the machine is in our gambler's set given that the first is, is clearly $(r-1)/(n-1)$, because, given this information about the first, at the time the machine chooses its second number, there are $n-1$ 'remaining' numbers, $r-1$ of which are in our gambler's set. By the multiplication rules the probability that the first two numbers chosen by the machine are in our gambler's set is

$$ \frac{r}{n} \times \frac{r-1}{n-1}. $$

By extending the idea, we see that the probability that the machine chooses exactly the same set as our gambler is

$$ \frac{r}{n} \times \frac{r-1}{n-r} \times \frac{r-2}{n-2} \times \cdots \times \frac{1}{n-r+1} = \frac{r!}{{}^nP_r} = \frac{r!(n-r)!}{n!}. $$

(In Britain, then, the probability of winning the jackpot is very roughly 1 in 14 million.) We have proved the Lemma.

Binomial(n, p) distribution. If a coin with probability p of Heads is tossed n times, and we write Y for the total number of Heads obtained, then Y has the probability mass function of the binomial(n, p) distribution:

$$\mathbb{P}(Y = r) = b(n, p; r) := \binom{n}{r} p^r (1-p)^{n-r}.$$

Proof. Because of the independence of the coin's behavior on different tosses, we have for any outcome such as HTHHHTTHH with exactly r Heads and $n - r$ Tails,

$$\mathbb{P}(\text{HTHHHTTRH...}) = pqpppqqpp... = p^r q^{n-r},$$

where $q = 1 - p$. Now the typical result with r Heads in all is a sequence such as HTHHHTTHH ... in which the set of positions where we have H is a subset of $\{1, 2, \ldots, n\}$ of size r. Every one of these $\binom{n}{r}$ subsets contributes $p^r q^{n-r}$ to $\mathbb{P}(Y = r)$, whence the result follows.

Stirling's Formula. This formula, proved in 1730, states that

$$n! \sim \left(\frac{n}{e}\right)^n \sqrt{2\pi n} \quad \text{as} \quad n \to \infty,$$

with the precise meaning that, as $n \to \infty$, the ratio of the two sides of this expression converges to 1. For $n = 10$, LHS/RHS $= 1.0084$.

As an exercise, show that for the probability $n(2n, \frac{1}{2}; n)$ that we would get n Heads and n Tails in $2n$ tosses of a fair coin satisfies

$$n(2n, \tfrac{1}{2}; n) \sim \frac{1}{\sqrt{\pi n}}.$$

Check that when $n = 10$, the left-hand side is 0.1762 (to 4 places) and the right-hand side is 0.1784 (to 4 places).

A very useful inequality.

$$1 - x \leq e^{-x} \qquad \text{for } x \geq 0.$$

To prove this, integrate $1 \geq e^{-y}$ $(y \geq 0)$ from 0 to x, getting $x \geq 1 - e^{-x}$. Note that therefore, the probability that no two of our 23 people have the same birthday is at most

$$\exp\left(-\frac{1 + 2 + \cdots + 22}{365}\right) = \exp\left(-\frac{253}{365}\right) = 0.499998.$$

1.2. Events and Probabilities

Probability $\mathbb{P}$ is just a function which assigns numbers to events in a manner consistent with the Addition Rule (and with conditional-probability considerations) — and nothing more. And events are just (technically, 'measurable') subsets of a certain set, always denoted by Ω. This set is called the sample space and it represents the set of all possible outcomes ω of our experiment. In Statistics, the experiment has been performed, and we have some information — in many cases, all information — about the actual outcome ω^{act}, the particular point of Ω actually ‘realized’. The relation between ’sample’ in Statistics and our ’sample point’ and ’sample space’ will become clear as we proceed.

1.2.1. Possible outcome ω, actual outcome ω^{act}; and Events.

1.2.1.1. *Sample space of possible outcomes ω.* Probability considers an experiment before it is performed, and Statistics considers an experiment after it has been performed. Probability considers an abstract set Ω, the sample space, which represents the set of all possible outcomes of our experiment. A possible outcome, or sample point, ω is mathematically a point of the ’abstract’ set Ω.

1) For example, for the experiment of tossing a coin three times,

$$\Omega = \{\text{HHH, HHT, HTH, HTT, THH, THT, TTH, TTT}\}, \tag{1.1}$$

a finite set.

2) For the experiment of choosing a point at random between 0 and 1, we naturally take $\Omega = [0, 1]$, an uncountable set.

3) For the experiment of tossing a coin until the first time we obtain MI, we can justify taking

$$\Omega = \{\text{HH, THH, HTHH, TTHH}, \dots\},$$

a countable set. However, there is the difficulty, which must be addressed, that there are uncountably many ‘crazy’ outcomes in which the pattern HH never occurs. The set of all such crazy outcomes must be proved to have probability 0 before we can reduce to the desired Ω.

1.2.2. Crystallization of actual outcome; realization. Our picture is that Tyche, Goddess of Chance, chooses a point ω^{act} of Ω ‘at random and in accordance with the probability law $\mathbb{P}$’ in a sense explained below. This is Tyche’s ’experiment’, and it determines the actual outcome ω^{act} in the real world. The whole sample space Ω is a nebulous, abstract thing. Tyche’s choice, as it were, ’crystallizes into existence’ one sample point ω^{act} which becomes real. It is important that we regard Tyche’s single choice of ω^{act} as determining the entire outcome, the entire realization, of the real-world experiment. If the real-world experiment consists of many stages (for example, many coin tosses), then Tyche is in a sense revealing her choice to us in instalments. But she made just the one choice ω^{act}.

1.2.3. Event as (measurable) subset of Ω. For the ’Toss coin three times’ experiment, the real-world event ’2 Heads in all’ occurs if and only if ω^{act} belongs to the subset $\{\text{HHT, HTH, THH}\}$ of Ω at (1.1) consisting of those possible outcomes ω which would produce 2 Heads in all. In the mathematical theory, the event ’2 Heads in all’ is regarded as the subset $\{\text{HHT, HTH, THH}\}$ of the sample space Ω. And so for any event for any experiment.

Technical note: Except in simple cases, essentially those in which Ω is finite or countable, we have to restrict the type of subset of Ω which constitutes an 'event': an event is a 'measurable' subset of Ω. We therefore have the following table in mind:

Table 1.1. Correspondence between Mathematical and Real-world Concepts in Probability

Event	Real-world interpretation
Sample space Ω	Set of all outcomes
Point ω of Ω	Possible outcome of experiment
(No counterpart)	Actual outcome ω^{act}
Event F, measurable subset of Ω	The real-world event corresponding to F occurs if and only if $\omega^{act} \in F$
$\mathbb{P}$, a number	Probability that F will occur for an experiment yet to be performed

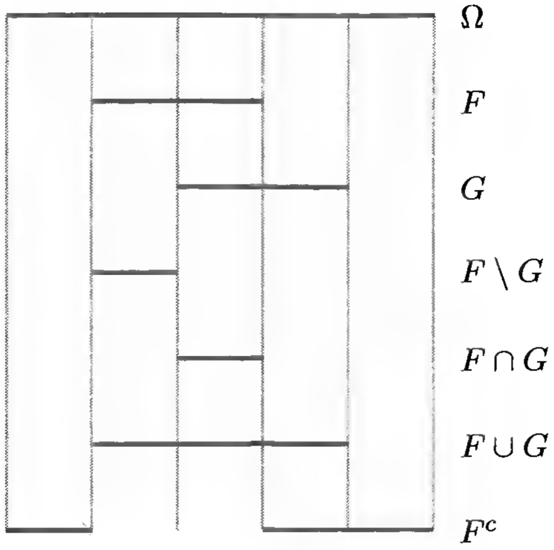
We see that Tyche must perform her experiment in such a way that she will choose ω^{act} to be in the set F 'with probability $\mathbb{P}(F)$'. This is what is meant by 'Tyche chooses in accordance with the law $\mathbb{P}$'. Because we are now regarding events F, G, etc, as subsets, we can extend this table:

Table 1.2. Correspondence between Mathematical Events and Real-world Interpretations

Event	Real-world interpretation
Ω, the entire sample space	The certain event 'something happens'
The empty subset $\emptyset$ of Ω	The impossible event 'nothing happens'
The intersection $F \cap G$	'Both F and G occur'
$F_1 \cap F_2 \cap \cdots \cap F_n$	'All of the events $F_1, F_2, \ldots, F_n$ occur simultaneously'
The union $F \cup G$	'At least one of F and G occurs'
$F_1 \cup F_2 \cup \cdots \cup F_n$	'At least one of $F_1, F_2, \ldots, F_n$ occurs'
Complement F^c of F	'F does not occur'
$F \setminus G$	'F occurs, but G does not occur'
$F \subseteq G$	If F occurs, then G must occur

1.2.4. Set theory and Probability.

Combining events is exactly the same as combining sets in elementary set theory. I am sure that you know about Venn diagrams. The figure below illustrates parts of the table just considered.



The amazing fact that the Fundamental Experiment

Choose a number between 0 and 1 uniformly at random

is Universal in that every other experiment is contained within it makes the 1-dimensional pictures particularly appropriate, especially for constructing counterexamples.

You should practice giving probabilistic interpretations of set-theoretic results. For example, one of de Morgan's rules states that

$$(F_1 \cap F_2 \cap \cdots \cap F_n)^c = F_1^c \cup F_2^c \cup \cdots \cup F_n^c.$$

In real-world terms, with L for the left-hand side and R for the right-hand side, L: it is not true that all of the events $F_1, F_2, \ldots, F_n$ do occur; R: it is true that at least one of the events $F_1, F_2, \ldots, F_n$, does not occur. Thus this relationship is obvious.

Or again, consider the distributive law:

$$A \cap (B \cup C) = (A \cap B) \cup (A \cap C).$$

An (B U C) = (A n B) U (AnC). Exercise. Use 'event' language (so that the left-hand side signifies ' A definitely occurs and at least one of B and C occurs') to make the distributive law 'obvious'.

1.2.5. Probabilities. Mathematically, probability is just a function $\mathbb{P}$ which assigns to each event F a number $\mathbb{P}(F)$ in [0, 1] such that

$$\mathbb{P}(\Omega) = 1$$

and the so-called Addition Rule holds. One important part of the Addition Rule states the following.

1.2.5.1. *Addition Rule, an Axiom.* For events F and G,

$$F \cap G = \emptyset \quad \text{implies} \quad \mathbb{P}(F \cup G) = \mathbb{P}(F) + \mathbb{P}(G).$$

If $F \cap G = \emptyset$, then F and G are called disjoint or exclusive. In the mathematical theory, this rule is an axiom that the probability laws $\mathbb{P}$ which we use must satisfy: and we do not prove this rule. We can only motivate it with examples.

1.2.5.2. *Lemma.* (a) For any event F, $\mathbb{P}(F^c) = 1 - \mathbb{P}(F)$. (b) For any two events F and G, we have the Inclusion-Exclusion Principle

$$\mathbb{P}(F \cup G) = \mathbb{P}(F) + \mathbb{P}(G) - \mathbb{P}(F \cap G).$$

Proof. Part (a) is obvious. Part (b) may be seen as follows. The event F may be written the disjoint union of F
G and $F \cap G$. So,

$$\mathbb{P}(F) = \mathbb{P}(FG) + \mathbb{P}(F \cap G);$$

and, since $F \cup G$ is the disjoint union of F
G and G,

$$\mathbb{P}(F \cup G) = \mathbb{P}(FG) + \mathbb{P}(G) = \mathbb{P}(F) - \mathbb{P}(F \cap G) + \mathbb{P}(G),$$

the desired result.

1.2.5.3. *Lemma.* We have the extended Addition Rule: if the events $F_1, F_2, \ldots, F_n$ are disjoint (that is, $F_i \cap F_j = \emptyset$ whenever $i \neq j$),

$$\mathbb{P}(F_1 \cup F_2 \cup \cdots \cup F_n) = \mathbb{P}(F_1) + \mathbb{P}(F_2) + \cdots + \mathbb{P}(F_n).$$

In shorthand:

$$\mathbb{P}\left(\cup_{k=1}^{n} F_k\right) = \sum_{k=1}^{n} \mathbb{P}(F_k).$$

Proof. If A, B and C are disjoint events, the $A \cup B$ is disjoint from C, so that two applications of the Addition Rule for disjoint sets give

$$\mathbb{P}(A \cup B \cup C) = \mathbb{P}((A \cup B) \cup C) = \mathbb{P}(A \cup B) + \mathbb{P}(C) = \mathbb{P}(A) + \mathbb{P}(B) + \mathbb{P}(C).$$

It is not worth dignifying the 'n-event' case with a proof by induction.

1.2.5.4. *General Inclusion-Exclusion Principle.* What about the Inclusion- Exclusion Principle for n events? For 3 events A, B, C, it would say

$$\mathbb{P}(A \cup B \cup C) = \Sigma_1 - \Sigma_2 + \Sigma_3,$$

where

$$\begin{gathered} \Sigma_1 := \mathbb{P}(A) + \mathbb{P}(B) + \mathbb{P}(C), \\ \Sigma_2 := \mathbb{P}(A \cap B) + \mathbb{P}(A \cap C) + \mathbb{P}(B \cap C), \\ \Sigma_3 := \mathbb{P}(A \cap B \cap C). \end{gathered}$$

1.2.5.5. *Lemma: General Inclusion-Exclusion Principle.* Let $F_1, F_2, \ldots, F_n$ be any events. Then

$$\mathbb{P}(F_1 \cup F_2 \cup \cdots \cup F_n) = \Sigma_1 - \Sigma_2 + \Sigma_3 - \cdots + (-1)^{n+1}\Sigma_n,$$

where Σ_r is the sum of terms

$$\mathbb{P}(F_{i_1} \cap F_{i_2} \cap \cdots \cap F_{i_r})$$

over all subsets $\{i_1, i_2, \ldots, i_r\}$ of size r from $\{1, 2, \ldots, n\}$.

1.2.5.6. *Example: The Hat-Matching Problem.* In this well-known problem, n absent-minded hat-wearing professors attend a meeting. At the end of the meeting, each picks a hat at random. We want to show that the probability at least one of them gets the right hat is

$$1 - \frac{1}{2!} + \frac{1}{3!} - \cdots + (-1)^{n+1}\frac{1}{n!}.$$

Thus the probability that none of them gets the right hat, namely 1 minus the above expression, is exactly the sum of the first $n + 1$ terms in the expansion of e^{-1}, and so is extremely close to $1/e$ even for moderate n.

Solution. Let F_k be the probability that the k-th professor to leave (Prof. k) gets the right hat. Now, it is all just as if someone shuffled the whole 'pack' of hats and gave them out randomly to the various professors. So, for every k, the chance that the k-th professor to leave gets the right hat is $1/n$. For $i \neq j$, the chance that Prof i and Prof j both get the right hat is $(1/n) \times (1/(n-1))$.

Since there are $n!$ permutations of the n numbers $\{1, 2, \ldots, n\}$, there are $n!$ ways of 'giving out the hats'. We need to know how many ways there are of giving out the n hats such that Prof i and Prof j both get the right hats (others being allowed to get the right hats too). In other words, we need to know how many permutations of $\{1, 2, \ldots, n\}$ keep i and j fixed. But this is just the total number of permutations of the remaining numbers. Hence for $i \neq j$,

$$\mathbb{P}(F_i \cap F_j) = \frac{(n-2)!}{n!} = \frac{1}{n(n-1)},$$

and, more generally, for any subset $\{i_1, i_2, \ldots, i_r\}$ of $\{1, 2, \ldots, n\}$,

$$\mathbb{P}(F_{i_1} \cap F_{i_2} \cap \cdots \cap F_{i_r}) = \frac{(n-r)!|}{n!}.$$

Hence, since there are (7) subsets of size r from $\{1, 2, \ldots, n\}$,

$$\Sigma_r = \frac{n!}{r!(n-r)!} \times \frac{(n-r)!}{n!} = \frac{1}{r!},$$

1.2.6. Probability and Measure.

1.2.6.1. *The Full Addition-Rule Axiom.* If $F_1, F_2, \dots$ is an infinite sequence of disjoint events, then

$$\mathbb{P}\left(\cup_{k=1}^{\infty} F_k\right) = \sum_{k=1}^{\infty} \mathbb{P}(F_k).$$

It is impossible to prove this by 'letting $n \to \infty$ in the Lemma for the extended Addition Rule. That is the whole point. Except in very simple cases, we cannot arrange that this property (full addition-rule axiom) will hold if we insist that *all* subsets of Ω are events. We will need the concept of σ-algebra.

1.2.6.2. *Full Axiomatization.* In the general theory then, not all subsets of Ω need be events. We axiomatize things again. The class $\mathcal{F}$ of all subsets of Ω which are events must be what is called a σ-algebra: this means that

- $\Omega \in \mathcal{F}$,
- $F \in \mathcal{F}$ implies that $F^c \in \mathcal{F}$,
- $F_1, F_2, \dots \in \mathcal{F}$ implies that $\cup F_n \in \mathcal{F}$.

Then $\mathbb{P}$ is a map $\mathbb{P} : \mathcal{F} \to [0, 1]$ such that $\mathbb{P}(\Omega) = 1$ and the Full Addition-Rule Axiom Property holds whenever the F_k are disjoint elements of $\mathcal{F}$. We now have the full axiomatization of the Addition Rule. We say that $\mathbb{P}$ is a probability measure on $(\Omega, \mathcal{F})$, and that $(\Omega, \mathcal{F}, \mathbb{P})$ is a probability triple.

What makes things work is that we can always set up an $(\Omega, \mathcal{F}, \mathbb{P})$ triple for the experiment which we wish to model in which is large enough to contain every event of which we could ever wish to find the probability. In the remainder of this section, $(\Omega, \mathcal{F}, \mathbb{P})$ is a probability triple used to model some experiment.

1.2.6.3. *Fact: Monotone-Convergence Properties.* (a) Suppose that we have events $F_1 \subseteq F_2 \subseteq F_3 \subseteq \dots$ and that $F = \cup F_n$. Then $\mathbb{P}(F_n) =\uparrow \mathbb{P}(F)$: the sequence $\{\mathbb{P}(F_n)\}$ is non-decreasing with limit $\mathbb{P}(F)$.

(b) Suppose that we have events $G_1 \supseteq G_2 \supseteq G_3 \supseteq \dots$ and that $G = \cap G_n$. Then $\mathbb{P}(G_n) \downarrow \mathbb{P}(G)$: the sequence $\{\mathbb{P}(G_n)\}$ is non-increasing with limit $\mathbb{P}(G)$. (This uses the fact that $\mathbb{P}(\Omega)$ is finite.)

This is important in that, for example, F_n might be 'population is extinct at time n' and then F is 'population is eventually extinct'.

1.2.6.4. *Almost surely.* A statement S about outcomes is said to be almost surely true or to be true with probability 1 if the truth set T of S, the set of outcomes ω for which S is true, is an element of $\mathcal{F}$ and $\mathbb{P}(T) = 1$. If a statement is certain, true for every ω, then, of course, its truth set is Ω and, since $\mathbb{P}(\Omega) = 1$, it is *almost surely* (a.s.) true. The important point is that many of the things in which we are most interested are *almost surely* true without being 'absolutely certain'. Do note that the probability of an almost sure event is exactly 1, not 99.9% or anything similar.

1.2.6.5. *Null set, null event.* An event N is called a *null event* or null set if $N \in \mathcal{F}$ and $\mathbb{P}(N) = 0$. We see that a statement about outcomes is almost surely true if the outcomes for which it is false form a null event.

1.2.6.6. *Fact.* If $N_1, N_2, \dots$ is a sequence of null sets, then $\cup N_k$ is a null set. If $H_1, H_2, \dots$ is a sequence of events each of probability 1, then $\cap H_k$ has probability 1.

1.2.6.7. *The Fundamental Model.* Consider the experiment 'Choose a (real) number uniformly between 0 and 1. The outcome must be a real number between 0 and 1, so we take Ω to be [0, 1]. For each x in [0,1], we wish the statement 'chosen number is less than or equal to x' to have a probability and for that probability to be x. It is a theorem of Borel and Lebesgue that if $\mathcal{F}$ is the smallest σ-algebra of subsets of $\Omega = [0, 1]$ containing every interval $[0, x]$ where $0 < x < 1$, then there is a unique probability measure $\mathbb{P}$ on $(\Omega, \mathcal{F})$ such that $\mathcal{P}([0, x]) = x$ whenever $0 < x < 1$. We therefore have our complete model for choosing a point at random between 0 and 1. Let's call the resulting triple $(\Omega, \mathcal{F}, \mathbb{P})$ the Fundamental Triple.

1.2.6.8. *Null sets for the Fundamental Model.* This most fundamental model contains all other models in a certain sense. It is therefore good that we can understand easily what 'almost sure' or 'with probability 1' means for this model. As explained previously, we need only understand what is a null set for the Fundamental Triple. A set N in $\mathcal{F}$ is a null set (it has measure 0) if and only if, for every $\epsilon > 0$ we can find a sequence of disjoint open subintervals $I_n = (a_n, b_n)$ of [0,1] (such an open interval is also allowed to have the form $[0, b)$ or $(a, 1]$ to deal with the endpoints) such that

$$N \subseteq \cup I_n \qquad \text{and} \qquad \sum \ell(I_n) < \epsilon,$$

where $\ell(I_n)$ is the length of I_n. In short, for any $\epsilon > 0$, you can find an open subset G of $[0, 1]$ containing N and of length at most ϵ.

1.2.6.9. *Remark.* For $X \in \Omega = [0, 1]$, let $N_x = \{x\}$. Then each N_x a null event. (For $\epsilon > 0$, $G_\epsilon = (x - \frac{1}{3}\epsilon, x + \frac{1}{3}\epsilon) \cap [0, 1]$ is an open subset of [0,1] of length less than ϵ and containing N_x.) However, $\Omega = \cup_{n \in \Omega} N_x$, and Ω is certainly not a null event. The point here is that the set $Q = [0, 1]$ is not countable, i.e., we cannot write $\Omega = \{x_1, x_2, x_3, \dots\}$ for some sequence (x_k) of points of Ω; Ω is too large a set to allow us to do this. Otherwise, we would have a contradiction with Lemma 1.2.6.6. The set of all subsequences of the sequence of positive integers is also uncountable.

1.2.6.10. *Fact: First Borel-Cantelli Lemma.* Let $J_1, J_2, \dots$ be a sequence of events. If $\sum \mathbb{P}(J_k) M < \infty$, then it is almost surely true that only finitely many of the events J_k occur (Assumed fact). This First Borel-Cantelli Lemma is a very useful result. In the next chapter,

1.2.6.11. *Borel sets and functions.* The Borel σ-algebra $\mathcal{B}(S)$ on a topological space S is the smallest σ-algebra of subsets of S which contains all open subsets of S (equivalently, the smallest σ-algebra of subsets of S which contains all closed subsets of S). A Borel subset of S is an element of this Borel σ-algebra.

If $S = \mathbb{R}$, then the Borel σ-algebra is the smallest σ-algebra containing every set of the form $(-\infty, x]$, where $x \in \mathbb{R}$. This is just what is needed to study distribution functions in Probability and Statistics. If $S = \mathbb{R}^n$, then the Borel σ-algebra is the smallest σ-algebra containing every subset of the form

$$\{(x_1, x_2, \ldots, x_n) : x_k \leq a\}$$

where $a \in \mathbb{R}$ and $k \in \{1, 2, \ldots, n\}$. For the Fundamental Model $\mathcal{F} \in \mathcal{B}([0, 1])$.

Recall that a continuous function $f : S \to \mathbb{R}$ is one such that the inverse image $f^{-1}(B) := \{s \in S : f(s) \in B\}$ of any open subset B of $\mathbb{R}$ is open in S. Analogously, we define a function $f : S \to \mathbb{R}$ to be a Borel function if the inverse image $f^{-1}(B)$ of any Borel subset B of $\mathbb{R}$ is Borel in S: equivalently, if, for every $x \in \mathbb{R}$, $\{s \in S : f(s) \leq x\}$ is Borel in S.

Every subset of $\mathbb{R}^n$ and every function on $\mathbb{R}^n$ you are ever likely to meet will be Borel. Continuous functions are Borel. Limits, limsups, what-have-you of sequences of Borel functions are Borel. You need to be clever to construct explicitly a function which is not Borel; but it can be done.

Remark: It was previously stated that there exists a unique measure $\mathbb{P}$ on what we now know to be $\mathcal{B}[0, 1]$ such that $\mathbb{P}([0, x]) = x$ for every x in [0,1]. The hard thing is to prove the existence of $\mathbb{P}$. But it matters greatly that $\mathbb{P}$ is unique. Uniqueness can easily be proven.

1.3. Random Variables, Means and Variances

1.3.1. Random Variables. Intuitively, a Random Variable (r.v.) is 'a number determined by Chance'; but this is hardly adequate for a mathematical theory. The formal definition is as follows.

1.3.1.1. *Mathematical formulation of Random Variable (RV)..* A Random Variable is defined to be a function (strictly, an $\mathcal{F}$-measurable function) from Ω to $\mathbb{R}$.

Question: Why is it appropriate to axiomatize the notion of Random Variable as being a function on our sample space ft?

Answer. Suppose that our r.v. Y is 'total number of Heads' if I toss my coin 3 times. We can make the picture:

Table 1.3. Random variable Y is a mapping from ω to $Y(\omega)$

ω:	HHH	HHT	HTH	HTT	THH	THT	TTH	TTT
$Y(\omega)$:	3	2	2	1	2	1	1	0

and this already displays Y as a function on Ω. Any 'intuitive r.v. X' will assign a value $X(\omega)$ to every possible outcome ω.

Here's another example. Suppose that our experiment consists of throwing a die twice, that X is the score on the first throw, Y that on the second, and Z is the sum of the scores. A typical possible outcome w has the form (i, j), where i is the first score and j

the second. Then $X(\omega) = i$, $Y(\omega) = j$, and $Z(\omega) = i + j$, and we have the picture

$$\begin{array}{|c|cccc|c|cccc|}
\hline
 & (1,1) & (1,2) & \cdots & (1,6) & & 1 & 1 & \cdots & 1 \\
\Omega: & (2,1) & (2,2) & & (2,6) & X: & 2 & 2 & & 2 \\
 & \cdot & \cdot & & \cdot & & \cdot & \cdot & & \cdot \\
 & (6,1) & (6,2) & \cdots & (6,6) & & 6 & 6 & \cdots & 6 \\
\hline
 & 1 & 2 & \cdots & 6 & & 2 & 3 & \cdots & 7 \\
Y: & 1 & 2 & & 6 & Z: & 3 & 4 & & 8 \\
 & \cdot & \cdot & & \cdot & & \cdot & \cdot & & \cdot \\
 & 1 & 2 & \cdots & 6 & & 7 & 8 & \cdots & 12 \\
\hline
\end{array}$$

For an r.v. X, we wish to be able to talk about its Distribution Function (DF) $F_X : \mathbb{R} \to [0,1]$ (of which more, of course, later) defined by

$$F_X(x) := \mathbb{P}(X \leq x) \qquad (x \in \mathbb{R}).$$

We therefore require that, for every $x \in \mathbb{R}$, the subset $L_x := \{\omega : X(\omega) < x\}$ of Ω (the mathematical formulation of the 'event that $X < x$') be a true mathematical event, that is, an element of the class $\mathcal{F}$ of events; and then, of course, we interpret $\mathbb{P}(X < x)$ as $\mathbb{P}(L_x)$.

Question: Why the restriction to 'measurable' functions in the proper theory?

Saying that for every x in $\mathbb{R}$, $L_x \in \mathcal{F}$ is exactly saying in Measure Theory that X is an $\mathcal{F}$-measurable map from Ω to $\mathbb{R}$.

The point is that sums, products, pointwise limits (if they exist), etc, of measurable functions are measurable. You cannot break out of the world of measurable things without being rather clever. So, we shall ignore measurability questions.

1.3.1.2. *Crystallization, Pre-Statistics and actual statistics.* Again let Y be the number of Heads in 3 tosses of my coin. In Probability, we consider the experiment before it is performed, and Y is a function on the nebulous, abstract set Ω. Tyche's choice 'crystallizes into existence' the actual outcome ω^{act}. Suppose that $\omega^{act} = \{HHT\}$. Then the observed, or realized, value y^{obs} of Y is $y^{obs} = Y(\omega^{act}) = 2$. We may call

- Y, the r.v., a Pre-Statistic,
- y^{obs}, the observed value of Y, an *actual statistic*,

and regard the crystallization of ω^{act} as changing Y to $y^{obs} = Y(\omega^{act})$.

A Pre-Statistic is a special kind of Random Variable: a Random Variable Y is a Pre-Statistic if the value $Y(\omega^{act})$ will be known to the observer (it may have to be calculated from things directly observed) after the experiment is performed; and then $Y(\omega^{act})$ becomes the observed value y^{obs} of Y. Thus,

A Pre-Statistic is an Observable Random Variable.

The model may involve r.v.'s the actual values of which cannot be determined after the experiment: these r.v.'s are not Pre-Statistics. We refer to ω^{act} rather than ω^{obs} precisely because full information about may never be known.

1.3.1.3. *Indicator function I_F of an event F.* For an event F, we define

$$I_F(\omega) := \begin{cases} 1 & \text{if } \omega \in F, \\ 0 & \text{if } \omega \notin F. \end{cases}$$

Intuitively, $I_F = 1$ if F occurs, 0 if it doesn't. Note: For any x, $\{\omega : I_F(\omega) < x\}$ can only be one of three things: $\emptyset$, F^c, Ω, depending on where x lies in relation to 0 and 1. Hence I_F is certainly measurable.) We use indicator functions to do our counting. The number Y of Heads I get in n tosses of a coin is

$$Y = X_1 + X_2 + \cdots + X_n,$$

where X_k is the indicator function of the event 'Heads on k-th toss': for the sum counts 1 for every Head, 0 for every Tail.

Exercise. Let F and G be events. Prove that

$$I_{F^c} = 1 - I_F, \qquad I_{F\cap G} = I_F I_G,$$

as function identities ('true for every ω'). Deduce from de Morgan's rule that $I_{F\cup G} = I_F + I_G - I_F I_G$, and explain why this is otherwise obvious.

1.4. Distribution Functions, PMFs and PDFs

1.4.1. Continuous Random Variables. As mentioned earlier, a random variable X is not a simple variable; it is better described by associating it with a function that encodes all of its statistical properties.[1] We associate with X a probability density function (PDF), $p(x)$. As a matter of convention, we shall use capital letters (X) to denote random variables and lowercase letters (x) for the value of X in some particular experiment ω, i.e., $x = X(\omega)$.

1.4.2. Probability Density Function. The probability density function (PDF) of a random variable X, denoted $p(x)$, is everywhere non-negative: $p(x) \geq 0$ and is normalized to 1:

$$\int_{-\infty}^{\infty} p(x)\mathrm{d}x = 1.$$

We note that the PDF refers to a particular random variable (say, X). This is sometimes emphasized by adding a subscript, e.g., $p_X(x)$ instead of $p(x)$. When working with a single random variable we do not need the subscript because it should be clear that there is only one possible random variable that $p(x)$ refers to. However, when the problem involves

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[1] Think of an experiment performed on Monday. The value measured on Tuesday may be slightly different than the one obtained on Monday because of random errors. Same story for measurements performed on subsequent days — these values will also be different due to fluctuations.

more than one random variable, we should use a subscript to avoid confusion between the different PDFs.

1.4.3. Cumulative Distribution Function. We define the *cumulative distribution function* (CDF) as the integral of the PDF:

$$\boxed{\mathbb{P}(X \leq x) \equiv \int_{-\infty}^{x} p(x')\mathrm{d}x'}$$

The event $\{X \leq x\}$ is interpreted as $\{\omega : X(\omega) \leq x\}$, i.e. the set of all random outcomes ω such that $X(\omega) < x$. The CDF is the probability that X takes a value less than or equal to x. The quantity $\{X \leq x\}$ is an example of a *random event*; the function $\mathbb{P}(\cdot)$ associates a number between 0 and 1 to this random event. We note that if $p(x)$ is continuous, then there is no distinction between $\mathbb{P}(X \leq x)$ and $\mathbb{P}(X < x)$. When discontinuities are present, we should be careful about the equality.

From this definition, we can solve for p in terms of P:[2]

$$p(x) = \left.\frac{\mathrm{d}\mathbb{P}(X \leq x)}{\mathrm{d}x}\right|_{x}.$$

We note that for $a \leq b$

$$\mathbb{P}(a < X \leq b) = \int_{a}^{b} p(x)\mathrm{d}x = \left(\int_{-\infty}^{b} - \int_{-\infty}^{a}\right) p(x)\mathrm{d}x = \mathbb{P}(X \leq b) - \mathbb{P}(X \leq a).$$

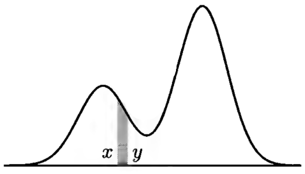
The events $\{X \leq a\}$ and $\{a < X \leq b\}$ are disjoint with union $\{X \leq b\}$.

1.4.4. Interpretation of PDF. The PDF, $p(x)$, has the following interpretation. The quantity $p(x)\mathrm{d}x$ is the probability that the random variable X lies in the interval $[x, x+\mathrm{d}x]$:

$$p(x)\mathrm{d}x = \mathbb{P}(x \leq X \leq x + \mathrm{d}x) \equiv \mathbb{P}(X \in \mathrm{d}x),$$

where $\mathrm{d}x$ is an infinitesimally small quantity. In the last equality, $\mathrm{d}x$ refers to the interval $[x, x + \mathrm{d}x]$. $\mathbb{P}(\cdot)$ denotes the probability of the event $\cdot$ occurring.

$\mathbb{P}(a \leq X \leq b)$



$\mathbb{P}(X \in \mathrm{d}x)$ $(y = x + \mathrm{d}x)$

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[2] To differentiate the integral with respect to x, apply the Leibniz formula (see Section 9.9) for differentiation of integrals. In the expression $\int_{-\infty}^{x} p(x')\mathrm{d}x'$, the only dependence on x comes from the upper limit of the integral. Thus, $\frac{\mathrm{d}}{\mathrm{d}x}\int_{-\infty}^{x} p(x')\mathrm{d}x' = p(x)$.

The quantity $p(x)\mathrm{d}x$ by itself is rarely used, except under the integral sign. Instead, one integrates this expression to find the probability that X will take some value in a finite interval $[a, b]$:

$$\mathbb{P}(a \le X \le b) = \int_a^b p(x)\mathrm{d}x.$$

The last step follows from[3]

$$\mathbb{P}(x \le X \le x + \mathrm{d}x) = \mathbb{P}(X \le x + \mathrm{d}x) - \mathbb{P}(X \le x) = \mathrm{d}\mathbb{P}(X \le x),$$

integrating $\mathbb{P}(x \le X \le x + \mathrm{d}x) = \mathrm{d}\mathbb{P}(X \le x)$ from a to b yields $\int_a^b \mathrm{d}\mathbb{P}(X \le x) = \mathbb{P}(X \le b) - \mathbb{P}(X \le a) = \mathbb{P}(a \le X \le b)$ whereas integrating $p(x)\mathrm{d}x$ yields $\int_a^b p(x)\mathrm{d}x$. Since the two are equal, we have that $\mathbb{P}(a \le X \le b) = \int_a^b p(x)\mathrm{d}x$.

1.4.5. Limit value of CDF. We note that the CDF approaches 1 in the limit of large x. This follows from the normalization condition on the PDF.

1.4.6. Experimental Data: The Empirical Distribution. Suppose that our knowledge of the rv X is not its PDF, $p(x)$ but instead a series of data points obtained experimentally:

$$x_1 = X(\omega_1), x_2 = X(\omega_2), \ldots, x_n = X(\omega_n).$$

(An equivalent description that will be used in subsequent chapters is to take n independent rv's $X_1, \ldots, X_n$ of the same distribution as X and fix ω. The order in which rv's are measured is immaterial since they are assumed independent. Fixing ω implies that all random variables are measured simultaneously. The data is $\{x_i = X_i(\omega)\}_{i=1}^n$.)

We define the empirical PDF as follows:

$$\hat{p}(x) = \frac{1}{n}\sum_{i=1}^n \delta(x - x_i),$$

where $\delta(x)$ is the Dirac delta function. It is trivial to verify that $\int \hat{p}(x)\mathrm{d}x = 1$ and $\hat{p}(x) \ge 0$. The CDF corresponding to $\hat{p}(x)$ is:

$$\mathbb{P}(X \le x) = \int_{-\infty}^x \hat{p}(x)\mathrm{d}x = \frac{1}{n}\#\{i : x_i \le x\}.$$

Here, $\#\{i : x_i \le x\}$ denotes the number of data points x_i satisfying the condition $x_i \le x$. The empirical distribution $\hat{p}(x)$ is an approximation to the true PDF $p(x)$. This fact follows from the Law of Large Numbers (see Problem 16).

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[3] In calculus, recall that $\mathrm{d}f(x) = f(x + \mathrm{d}x) - f(x)$.

1.4.7. Mean Value of Continuous Random Variable. Let X be a continuous rv. The mathematical expectation of X, denoted $\langle X\rangle$, is defined as:

$$\boxed{\langle X\rangle \equiv \int_{-\infty}^{\infty} x\, p(x)\mathrm{d}x.}$$

where the integral is over all values taken by the rv X (here, over the entire real line). If the random variable takes values in the interval $[0,1]$ then the limits of the integral range from 0 to 1.

That is, to obtain the mean value of X, we replace the rv X by a regular variable x that represents its value, then multiply by $p(x)$ and integrate over all x.

Other names for $\langle X\rangle$ include "mean value" (of X), or "expectation value" or "average value". Other symbols you may encounter in the literature include $\overline{X}$, μ_X, $\langle X\rangle$ or $m(X)$.

We note that this expression differs from the *sample mean* $\hat{\mu}_X = \frac{1}{n}\sum_{i=1}^{n} x_i$. The sample mean is an *estimate* of the mean.[4] Substitution of the empirical distribution (Eq. 1.2)

$$\hat{p}(x) = \frac{1}{n}\sum_{i=1}^{n}\delta(x-x_i) \tag{1.2}$$

into the above definition for $\langle X\rangle$ gives the sample mean:

$$\int_{-\infty}^{\infty} x\,\frac{1}{n}\sum_{i=1}^{n}\delta(x-x_i)\mathrm{d}x = \frac{1}{n}\sum_{i=1}^{n} x_i.$$

Here $\{x_i\}_{i=1}^{n}$ denotes experimental measurements of X.

1.4.8. Indicator Functions. An *indicator function*, $\mathbf{1}_{\{x<y\}}(x)$ is a function that takes the value 1 when $x<y$ and 0 otherwise. Indicator functions can also be applied to random events. Let X be a rv and A is a random event. The indicator function for the random event $X\in A$ is defined as:

$$\mathbf{1}_A(X) = \begin{cases} 1 & \text{if } X\in A \\ 0 & \text{otherwise} \end{cases}$$

where $X\in A$ refers to the value of the rv X taken after a random experiment. Another notation for $\mathbf{1}_A(X)$ you may encounter is $\mathbf{1}_{X\in A}$. You may also encounter $\mathbb{I}_{X\in A}$ or $\chi_A(X)$ instead of $\mathbf{1}_{X\in A}$. Taking the mathematical expectation of $\mathbf{1}_{X\in A}$ and applying the definition of probability,

$$\langle \mathbf{1}_{X\in A}\rangle = \int_{-\infty}^{\infty}\mathbf{1}_{x\in A}(x)p(x)\mathrm{d}x = \int_A p(x)\mathrm{d}x = \mathbb{P}(A).$$

where A is a random event and the integral $\int_A$ means integral over all points x that meet the condition $x\in A$ (for example, X could be a coordinate, and $A=(-\infty,y]$ indicates an event where the coordinate is less than y). Indicator functions are useful when dealing with

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[4] More specifically, the sample mean is the best estimate of the mean in the sense of least squares.

experimental measurements. See Problems 15, 10 and 17 for example uses of the indicator function.

1.4.9. Variance. The *variance* of X, denoted $var(X)$ or σ_X^2, is defined as the sum of square differences between X and its mean, $\mu_X \equiv \langle X \rangle$, weighted by the PDF:

$$\boxed{\sigma_X^2 \equiv var(X) = \int_{-\infty}^{\infty} p(x)(x-\mu_X)^2 \mathrm{d}x}$$

The square can be expanded to give $\int_{-\infty}^{\infty} p(x)(x^2+\mu_X^2-2x\mu_X)\mathrm{d}x$ and thus

$$\sigma_X^2 = \langle X^2 \rangle - (\mu_X)^2.$$

The square root of the variance is called the standard deviation and is commonly denoted σ.

1.4.10. Example PDFs.

1.4.10.1. *Point Distribution.* Let X be a rv and $p(x)$ its distribution (PDF). The simplest known PDF is one concentrated at a single point x_0:

$$p(x) = \delta(x - x_0).$$

It is trivial to verify that $p(x) \geq 0$ and $\int_{-\infty}^{\infty} p(x)\mathrm{d}x = 1$. The CDF is easily found:

$$\boxed{\mathbb{P}(X < a) = \int_{-\infty}^{a} \delta(x-x_0)\mathrm{d}x = \theta(a - x_0),}$$

where

$$\theta(x) = \begin{cases} 1 & \text{if } x > 0 \\ 0 & \text{otherwise} \end{cases}$$

is the Heaviside step function. We note that the Heaviside function can be expressed in terms of the indicator function as $\theta(x) = \mathbf{1}_{(0,\infty)}(x)$. We also note that $\delta(x) = \frac{\mathrm{d}}{\mathrm{d}x}\theta(x)$.

1.4.10.2. *Discrete Distribution.* Let X be a rv that can take values $\{x_i\}_{i=1}^N$ in a set $\mathcal{X}$. N is the number of possible values that X can take. The PDF

$$p(x) = \sum_{i=1}^{N} p_i \delta(x - x_i), \qquad p_i \geq 0, \qquad \sum_{i=1}^{N} p_i = 1$$

is called discrete distribution because it can be used to describe discrete rv. The set of number $\{p_i\}_{i=1}^N$ is called the probability mass function (PMF). The x_i represent the discrete values taken by the rv X. p_i is the probability of observing the discrete outcome $x_i \in \mathcal{X}$. The mean of X is:

$$\mu_X \equiv \langle X \rangle = \int_{-\infty}^{\infty} x \sum_{i=1}^{N} p_i \delta(x - x_i)\mathrm{d}x = \sum_{i=1}^{N} p_i x_i.$$

The variance is

$$var(X) = \sum_{i=1}^{N} p_i (x_i - \mu_X)^2.$$

1.4.10.3. *Distribution After Rescaling Of Random Variable.* Let X be a rv. What is the distribution of $2X$? Since we are multiplying all values of X by 2, we at least expect the mean to be twice as large. What about the remaining details of its distribution? First of all we note that:

$$\mathbb{P}(2X < a) = \mathbb{P}(X < a/2) = \int_{-\infty}^{a/2} p_X(x)\mathrm{d}x.$$

Next, we differentiate this integral with respect to a to get the PDF:

$$\frac{\mathrm{d}}{\mathrm{d}a}\mathbb{P}(2X < a) = p_X(a/2) \cdot \frac{1}{2}.$$

We conclude that the PDF of $2X$ is half as high and twice as spread out compared to the distribution of X. If the mean of X is μ_X then the mean of $Y = 2X$ is

$$\langle Y \rangle = \frac{1}{2}\int_{-\infty}^{\infty} y p_X(y/2)\mathrm{d}y = \frac{1}{2}\int_{-\infty}^{\infty} (2x) p_X(x)(2\mathrm{d}x) = 2\mu_X.$$

The variance is:

$$var(Y) = \frac{1}{2}\int_{-\infty}^{\infty} (y - \mu_Y)^2 p_X(y/2)\mathrm{d}y = \frac{1}{2}\int_{-\infty}^{\infty} (2x - 2\mu_X)^2 p_X(x)(2\mathrm{d}x) = 2^2 var(X).$$

1.4.10.4. *Cauchy Distribution.* Let X be a rv with the Cauchy (or Lorentzian) distribution. Its PDF is defined as:

$$\boxed{p_X(x) = \frac{1}{\pi}\frac{1}{(1+x^2)}.}$$

The CDF is:

$$\mathbb{P}(X < x) = \int_{-\infty}^{x} \frac{1}{\pi}\frac{1}{(1+x^2)}\mathrm{d}x.$$

We know from calculus that the derivative of $\tan^{-1}(x)$ is $1/(1+x^2)$. Therefore, the last expression can be integrated:

$$\boxed{\mathbb{P}(X < x) = \frac{1}{\pi}\tan^{-1}(x) + \frac{1}{2}.}$$

1.4.10.5. *Rayleigh Distribution.* Let X be a rv with Rayleigh distribution ($X \sim$ Rayleigh). The Rayleigh distribution has a PDF:

$$\boxed{p(x) = \frac{x}{\sigma^2}e^{-x^2/(2\sigma^2)},}$$

where $x \geq 0$ and σ is a parameter of the distribution. The CDF can be shown to be:

$$\boxed{\mathbb{P}(X < x) = 1 - e^{-x^2/(2\sigma^2)},}$$

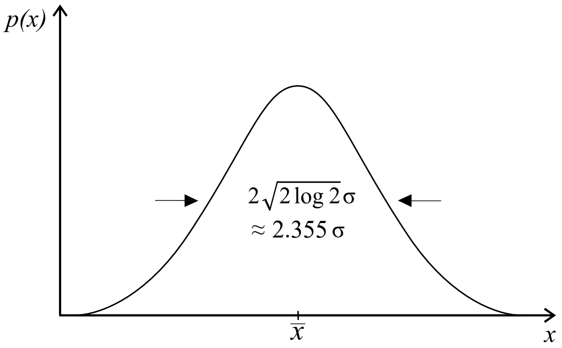

Figure 1.1. Gaussian (bell shaped) distribution. The PDF has full width at half-maximum of approximately 2.355σ.

where $x \geq 0$. The reader can check that the mean of X is $\sigma\sqrt{\pi/2}$ and its variance is $\sigma^2\frac{4-\pi}{2}$.

1.4.10.6. *Gaussian (Normal) Distribution.* The normal distribution $\mathcal{N}(\mu, \sigma^2)$ with parameters μ and σ^2 is defined by the density:

$$\boxed{p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}},}$$

where $x \in (-\infty, \infty)$. The prefactor $\frac{1}{\sqrt{2\pi\sigma^2}}$ is such that $p(x)$ adds up to 1:

$$\int_{-\infty}^{\infty} p(x)\mathrm{d}x = 1.$$

This can be verified using the well-known result for a Gaussian integral $\int_{-\infty}^{\infty} e^{-ax^2}\mathrm{d}x = \sqrt{\pi/a}$, where $a > 0$. As an exercise, you should check that this PDF is normalized to 1, the mathematical expectation of $X \sim \mathcal{N}(\mu, \sigma^2)$ is μ and its variance is σ^2, i.e. $\langle X \rangle = \mu$ and $\langle X - \mu \rangle^2 = \sigma^2$.

This probability density is plotted below. It is centered on μ and the width is proportional[5] to σ.

If a rv X follows a Gaussian distribution (Fig. 1.1) with mean μ and variance σ^2 we write $X \sim \mathcal{N}(\mu, \sigma^2)$. For a Gaussian distribution, the CDF is called the *error function.* See Figure 1.2.

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[5] In fact, the full width at half maximum of the Gaussian is $2\sqrt{2\log 2}\sigma \approx 2.355\sigma$. You can check this by finding the values of x for which $\frac{1}{2}\frac{1}{\sqrt{2\pi\sigma^2}} = \frac{1}{\sqrt{2\pi\sigma^2}}e^{-\frac{x^2}{2\sigma^2}}$ or $\frac{1}{2} = e^{-\frac{x^2}{2\sigma^2}}$, since the maximum of the function is $\frac{1}{\sqrt{2\pi\sigma^2}}$ (set $x = 0$). Taking logs of both sides gives $x = \pm\sqrt{2\sigma^2 \log 2}$.

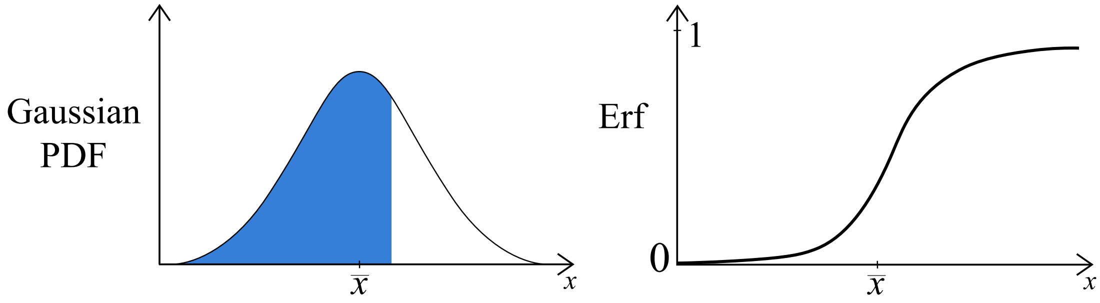

Figure 1.2. Error function is defined as the (cumulative) area under the Gaussian PDF.

$$\boxed{\operatorname{erf}(x)_{\mu,\sigma} = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{x} e^{-\frac{(x-\mu)^2}{2\sigma^2}}\,\mathrm{d}x.} \tag{1.3}$$

The error function is an integral which cannot be evaluated analytically. Instead it must be solved numerically. Values of the error function can be obtained from tables, calculators or computer programs. The error function for standard normal rv (mean 0, variance 1) is often tabulated in books. In MATLAB the command `normcdf(x,mu,sigma)` will return values for $\operatorname{erf}(x)_{\mu,\sigma}$. See Section 1.4.11 for a discussion of the error function.

1.4.10.7. *Multivariate Normal Distribution.* Let $\xi_1, \ldots, \xi_n$ be n random variables whose joint distribution is given by the density $p(x_1, \ldots, x_n)$, of the form

$$p(x) = p(x_1, \ldots, x_n) = Ce^{-\frac{1}{2}(A(x-m),(x-m))}.$$

Here C is a normalization constant, $x = (x_1, \ldots, x_n)$ is an n-dimensional vector, $m = (m_1, \ldots, m_n)$ is another n-dimensional vector and A is a symmetric matrix. This density is convenient because it depends on simple parameters: a n-dimensional vector m and a symmetric matrix A of order n.

Since $p(x)$ is integrable, $p(x) \to 0$ as $x \to \infty$. This is possible only in the case when A is a positive definite matrix. We now find the value of the constant C. By the normalization condition we have

$$\frac{1}{C} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\frac{1}{2}(A(z-m),(x-m))} dx_1 \ldots dx_n.$$

We first make the change of variables $y = x - m$:

$$\frac{1}{C} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\frac{1}{2}(Ay,y)} dy.$$

We now find an orthogonal matrix S such that $S^*AS = D$, where D is a diagonal matrix with elements d_i on the diagonal. We also have $\det D = \det A$. We now make the linear change of variables $y = Sz$. Then $(Ay, y) = (ASz, Sz) = (S^*ASz, z) = (Dz, z)$ (for an orthogonal matrix $S^* = S^{-1}$) and

$$\begin{aligned}\frac{1}{C} =& \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\frac{1}{2}(Dz,z)} dz = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\frac{1}{2}\sum_{i=1}^{n} d_i z_i^2} dz_1 \dots dz_n \\ =& \prod_i \int_{-\infty}^{\infty} e^{-\frac{1}{2} d_i z_i^2} dz_i = \prod_i \sqrt{2\pi d_i^{-1}} = (2\pi)^{n/2} \left(\prod_i d_i \right)^{-1/2} \\ =& (2\pi)^{n/2} (\det D)^{-1/2} = (2\pi)^{n/2} (\det A)^{-1/2}.\end{aligned}$$

Therefore $C = (2\pi)^{-n/2}\sqrt{\det A}$. We now elucidate the probabilistic meaning of the vector m and the matrix A. Let us find the expectation $\langle \xi_i \rangle$:

$$\begin{aligned}\langle \xi_i \rangle =& \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} x_i p(x_1, \dots, x_n) dx_1 \dots dx_n \\ =& C \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} x_i e^{-\frac{1}{2}(A(x-m),(x-m))} dx_1 \dots dx_n \\ =& C \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} (x_i - m_i) e^{-\frac{1}{2}(A(x-m),(x-m))} dx_1 \dots dx_n + m_i \\ =& C \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} y_i e^{-\frac{1}{2}(Ay,y)} dy + m_i.\end{aligned}$$

Here we made the change of variable $x - m = y$. The resulting integral is equal to 0, since the integrand is an odd function of y_i. Thus, $m_i = \langle \xi_i \rangle$.

We now find $cov(\xi_i, \xi_j)$. We have

$$\begin{aligned}cov(\xi_i, \xi_j) =& \langle (\xi_i - m_i)(\xi_j - m_j) \rangle \\ =& C \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} (x_i - m_i)(x_j m_j) e^{-\frac{1}{2}(A(x-m),(x-m))} dx \\ =& C \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} y_i y_j e^{-\frac{1}{2}(Ay,y)} dy_1 \dots dy_n.\end{aligned}$$

As before, we make the change of variable $y = Sz$ or, more explicitly $y_i = \sum_{k=1}^{n} s_{ij} s_z$. Then

$$\begin{aligned}cov(\xi_i, \xi_j) =& C \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \sum_{k,l} s_{ik} s_{jl} z_k z_l e^{-\frac{1}{2}\sum_i d_i z_i^2} dz_1 \dots dz_n \\ =& C \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \sum_{k} s_{ik} s_{jk} z_k^2 e^{-\frac{1}{2}\sum_i d_i z_i^2} dz_1 \dots dz_n \\ =& \sum_{k=1}^{n} s_{ik} s_{jk} d_k^{-1}\end{aligned}$$

Here we used the fact that $\int_{-\infty}^{\infty} z_k z_l e^{-1/2 \sum_i d_i z_i^2} dz_1 \dots dz_n = 0$ for $k \neq l$ and equals $\sqrt{2\pi} d_k^{-3/2}$ for $k = l$. We now note that $\sum_k s_{ik} d_k^{-1} s_{jk}$ is an element of the matrix $SD^{-1}S^* =$

$SD^{-1}S^{-1} = A^{-1}$. Thus the matrix A^{-1} has en immediate probabilistic meaning. Its elements are the covariances of the random variables ξ_i, ξ_j. Let us assume that the covariances of the random variables ξ_i, ξ_j are equal to 0 for $i \neq j$. This means that A^{-1} is a diagonal matrix. Then A is also a diagonal matrix, and $p(x_1, \dots, x_n) = p_1(x_1) \dots p_n(x_n)$ is the product of one-dimensional normal densities, i.e. the random variables $\xi_1, \dots, \xi_n$ are independent. Thus in the case of the multivariate normal distribution, if the covariances reduce to zero, independence flow.

1.4.10.8. *Log-Normal Distribution.* In Section 1.4.10.6, we have introduced the error function as the CDF of the Gaussian PDF (Eq. 1.3):

$$\mathrm{erf}(x)_{\mu,\sigma} = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{x} e^{-(x-\mu)^2/2\sigma^2} \mathrm{d}x.$$

If $X \sim \mathcal{N}(\mu, \sigma^2)$ and $Y = e^X$, then

$$\mathbb{P}(Y < y) = \mathbb{P}(e^X < y) = \mathbb{P}(X < \log y),$$

which leads to the CDF:

$$\boxed{\mathbb{P}(Y < y) = \int_{-\infty}^{\log y} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2} \mathrm{d}x = \mathrm{erf}(\log y)_{\mu,\sigma}.} \tag{1.4}$$

This is called the log normal distribution ($Y \sim$ log-normal). You can check, using the Leibniz formula (see Section 9.9) for differentiation, that the PDF of the log-normal distribution is:

$$\boxed{p_Y(y) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(\log(y)-\mu)^2/2\sigma^2} \cdot \frac{1}{y}.}$$

1.4.11. Tabulated Values of Error Function. It is important to be able to use tabulated values of the error function. Let $X \sim \mathcal{N}(\mu, \sigma^2)$. Then,

$$\begin{aligned}\phi_{\mu,\sigma}(x) \equiv \mathrm{erf}(x)_{\mu,\sigma} = \mathbb{P}(X < x) = & \underbrace{\frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{x} e^{-(\xi-\mu)^2/(2\sigma^2)} \mathrm{d}\xi}_{\text{let } \zeta=(\xi-\mu)/\sigma,\, \mathrm{d}\zeta=\mathrm{d}\xi/\sigma} \\ = & \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{(x-\mu)/\sigma} e^{-\zeta^2/2} \mathrm{d}\zeta = \Phi\left(\frac{x-\mu}{\sigma}\right),\end{aligned}$$

where $\Phi(\cdot)$ denotes the *normalized error function*:

$$\boxed{\Phi(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{z} e^{-\zeta^2/2} \mathrm{d}\zeta.}$$

The latter is the CDF of the standard normal distribution, $\mathcal{N}(0, 1)$. z is known as the z-score:

$$z = \frac{x-\mu}{\sigma}. \tag{1.5}$$

As an example, Eq. (1.4) can be expressed in this notation as:

$$\operatorname{erf}(\log y)_{\mu,\sigma} = \Phi\left(\frac{\log y - \mu}{\sigma}\right).$$

You should beware that there exist other conventions for the error function. For example, MATLAB and EXCEL softwares define the error function as:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \mathrm{d}t. \tag{1.6}$$

This is related to the normal CDF according to:

$$\phi_{\mu,\sigma}(x) = \operatorname{erf}(x)_{\mu,\sigma} = \Phi\left(\frac{x-\mu}{\sigma}\right) = \frac{1}{2}\left(1 + \operatorname{erf}\left(\frac{x-\mu}{\sigma\sqrt{2}}\right)\right).$$

This expression can be used to calculate $\operatorname{erf}(x)_{\mu,\sigma}$ using data from tables, where μ is the mean of the population and σ is the standard deviation of the population. First, we form the "z-score" (Eq. 1.5). Then we use tabulated values of the error function for this particular value of z.

For example, suppose that a manufacturer produces electrical resistors whose nominal value is $(100 \pm 2)\ \Omega$, where $2\ \Omega$ is the standard deviation (both could be estimated, for example, using sample mean and sample variance). Assuming that the distribution of the resistance X is Gaussian (i.e. $X \sim \mathcal{N}(100, 2^2)$), what is the probability that choosing a resistor at random will yield a resistance of 95 Ω or less? We want to show that

$$\mathbb{P}(X \leq 95\ \Omega) = \operatorname{Erf}(95)_{100,2} \approx 0.0062.$$

Method 1 uses MATLAB:

```
>> normcdf(95,100,2)

ans =

    0.0062
```

Method 2 uses tabulated values of $\Phi(z)$: The z-score is:

$$z = \frac{x-\mu}{\sigma} = \frac{95-100}{2} = -2.5,$$

which is negative. Unfortunately, tables of error function do not list negative z values. However, notice that negative z values can be obtained from positive ones:

$$\boxed{\Phi(-z) = 1 - \Phi(z).}$$

Here, for positive $z = 2.5$ the value $\Phi(2.5)$ is 0.993790. Taking $1 - \Phi(2.5)$ gives 0.00621, the result we sought. Most books on statistics will have such a table. Tables can also be generated in MATLAB by typing:

```
normcdf(linspace(0,3,50)',0,1)
```

x	$\Phi(x)$	x	$\Phi(x)$	x	$\Phi(x)$	x	$\Phi(x)$	x	$\Phi(x)$	x	$\Phi(x)$
0	0.5000	0.5056	0.6934	1.0112	0.8440	1.5169	0.9353	2.0225	0.9784	2.5281	0.9943
0.0337	0.5134	0.5393	0.7052	1.0449	0.8520	1.5506	0.9395	2.0562	0.9801	2.5618	0.9948
0.0674	0.5269	0.5730	0.7167	1.0787	0.8596	1.5843	0.9434	2.0899	0.9817	2.5955	0.9953
0.1011	0.5403	0.6067	0.7280	1.1124	0.8670	1.6180	0.9472	2.1236	0.9831	2.6292	0.9957
0.1348	0.5536	0.6404	0.7391	1.1461	0.8741	1.6517	0.9507	2.1573	0.9845	2.6629	0.9961
0.1685	0.5669	0.6742	0.7499	1.1798	0.8810	1.6854	0.9540	2.1910	0.9858	2.6966	0.9965
0.2022	0.5801	0.7079	0.7605	1.2135	0.8875	1.7191	0.9572	2.2247	0.9869	2.7303	0.9968
0.2360	0.5933	0.7416	0.7708	1.2472	0.8938	1.7528	0.9602	2.2584	0.9880	2.7640	0.9971
0.2697	0.6063	0.7753	0.7809	1.2809	0.8999	1.7865	0.9630	2.2921	0.9891	2.7978	0.9974
0.3034	0.6192	0.8090	0.7907	1.3146	0.9057	1.8202	0.9656	2.3258	0.9900	2.8315	0.9977
0.3371	0.6320	0.8427	0.8003	1.3483	0.9112	1.8539	0.9681	2.3596	0.9909	2.8652	0.9979
0.3708	0.6446	0.8764	0.8096	1.3820	0.9165	1.8876	0.9705	2.3933	0.9917	2.8989	0.9981
0.4045	0.6571	0.9101	0.8186	1.4157	0.9216	1.9213	0.9727	2.4270	0.9924	2.9326	0.9983
0.4382	0.6694	0.9438	0.8274	1.4494	0.9264	1.9551	0.9747	2.4607	0.9931	2.9663	0.9985
0.4719	0.6815	0.9775	0.8358	1.4831	0.9310	1.9888	0.9766	2.4944	0.9937	3.0000	0.9987

Table 1.4. Numerical values of the error function $\Phi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{x} e^{-x^2/2} \mathrm{d}x$.

The results $\{(x, \Phi(x))\}$, $x \in [0, 3]$ are shown in Table 1.4.

1.4.12. The *z*-score. Let's view the z-score as a random variable:

$$Z(\omega) = \frac{X(\omega) - \mu}{\sigma}$$

where $\mu \equiv \langle X \rangle$, $\sigma \equiv \sqrt{var(X)}$ and $Z \sim \mathcal{N}(0, 1)$. The statement that $Z \sim \mathcal{N}(0, 1)$ follows automatically when X is normal with mean μ and variance σ^2. In that case,

$$\begin{aligned} \mathbb{P}(X \leq x) &= \mathbb{P}(\sigma Z + \mu \leq x) = \mathbb{P}(Z \leq \frac{x - \mu}{\sigma}) \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{(x-\mu)/\sigma} e^{-\zeta^2/2} \mathrm{d}\zeta = \Phi\left(\frac{x - \mu}{\sigma}\right). \end{aligned} \tag{1.7}$$

This is result identical to the one in the previous section, but its derivation did not require us to change variables of integration. Using the probability function $\mathbb{P}(\cdot)$ can sometimes save you a step.

1.4.13. Confidence Limits and Error Bars. Recall the Gaussian probability density which has a bell shape centered on $\langle X \rangle = \mu_X$ and full width at half-maximum $\approx 2.355\sigma$ (Fig. 1.3). The area under the curve bounded by the interval $x \in [\mu_X - \sigma, \mu_X + \sigma]$ is given by:

$$\frac{1}{\sqrt{2\pi\sigma^2}} \int_{\mu_X - \sigma}^{\mu_X + \sigma} e^{-\frac{(x - \mu_X)^2}{2\sigma^2}} \mathrm{d}x = \mathrm{erf}(\mu_X + \sigma)_{\mu_X, \sigma} - \mathrm{erf}(\mu_X - \sigma)_{\mu_X, \sigma} \approx 0.683$$

where

$$\mathrm{erf}(x)_{\mu, \sigma} = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{x} e^{-\frac{(x - \mu)^2}{2\sigma^2}} \mathrm{d}x.$$

About 2/3 of the total area under the curve is within $\pm\sigma$ of the mean. Recall that:

$$(\text{value of } x) = x_{best} \pm \delta x$$

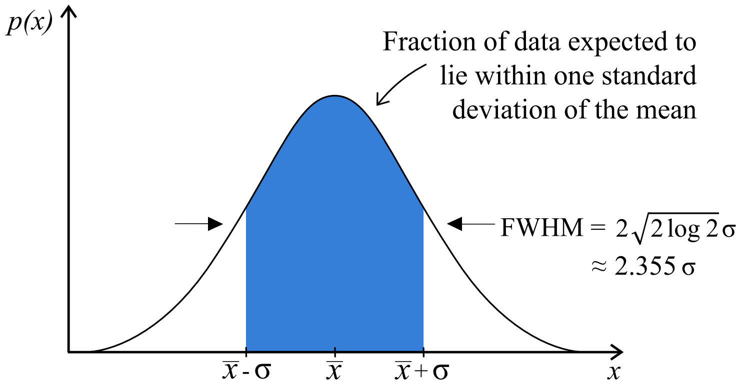

Figure 1.3. Confidence limits. The Gaussian distribution has a full width at half-maximum of approximately 2.355σ.

where we often take $\delta x = \sigma$. This choice for δx corresponds to the "68% confidence level". This means that we are confident, at the 68% level, that were we to take another measurement, the value would lie within one standard deviation of the mean. There are other possible conventions for choosing δx. Common choices for δx are:

$$\begin{aligned} \pm\sigma &\quad\to\quad 68\% \text{ level} \\ \pm 2\sigma &\quad\to\quad 95\% \text{ level} \\ \pm 3\sigma &\quad\to\quad 99.7\% \text{ level} \end{aligned}$$

1.4.14. Example: From CDF to PDF. It is important to be able to convert from PDF to CDF and vice versa. Suppose that we have a CDF:

$$\mathbb{P}(Y < a) = \int_{-\infty}^{a} \frac{1}{\pi} \frac{\mathrm{d}y}{(1+y^2)} \tag{1.8}$$

To get the PDF from this CDF we use the formula

$$\frac{\mathrm{d}\mathbb{P}(Y \le a)}{\mathrm{d}a} = p_Y(a).$$

The result is:

$$p_Y(y) = \frac{1}{\pi} \frac{1}{(1+y^2)},$$

(We renamed a as y.) The differentiation is always with respect to the upper bound of the integral. Another way to look at it is to write $F(x) = \mathbb{P}(X \le x)$ and

$$\frac{\mathrm{d}F(x)}{\mathrm{d}x} = p_X(x) \quad \text{or} \quad \frac{\mathrm{d}F(a)}{\mathrm{d}a} = p_X(a).$$

Inspection of the Leibniz formula (see Section 9.9) for differentiation shows that the differentiation step is completely trivial and amounts to simply identifying the integrand. This is consistent with the definition of CDF:

$$\mathbb{P}(Y < a) = \int_{-\infty}^{a} p_Y(y)\mathrm{d}y. \tag{1.9}$$

1.4.15. Calculating Probabilities: Single Variable. Probabilities of random events of the type $\{a \leq X \leq b\}$ are calculated by integrating the PDF from a to b:

$$\mathbb{P}(a \leq X \leq b) = \int_{a}^{b} p(x)\mathrm{d}x.$$

More generally, we deal with *random events*, which are statements of the type $\{X \in A\}$ where A is a set of points. The quantity $\mathbb{P}(X \in A)$ is a number between 0 and 1, which gives the probability that the rv X will take values in the set A:

$$\mathbb{P}(X \in A) = \int_{\{x|x\in A\}} p(x)\mathrm{d}x,$$

where $\{x|x \in A\}$ is the set of points x that belong to the set A. The integral is a Riemann summation over the set of points $\{x|x \in A\}$ on the real line. This notation is useful because we can transform the statement $\{x \in A\}$ into any equivalent statement, including one that involves a change of variables. For example, the two following statements are equivalent:

$$\{X < a\} = \{\log(X) < \log(a)\}.$$

This is useful if another rv Y is defined as $Y = \log(X)$. In that case, evaluating the probability of $\{Y < b\}$, $b = \log(a)$, gives the same numerical result as evaluating the probability of $\{X < a\}$.

1.4.16. Average of $f(X)$. The average (or mean, or expectation value) of a function f of a rv X is defined as:

$$\boxed{\langle f(X)\rangle \equiv \int_{-\infty}^{\infty} f(x)p(x)\mathrm{d}x.}$$

1.4.17. Statistical Moments, Deviation and Dispersion.

1.4.18. Moments: Mean, Variance, Skewness, Kurtosis. Let X be a rv. Take $f(x) = x^n$ in the above formula. This gives the *n-th moment* of X:

$$\langle X^n\rangle \equiv \int_{-\infty}^{\infty} p(x)x^n\mathrm{d}x.$$

The case $n = 1$ (*first moment*) is called the mathematical expectation or mean value of X:

$$\langle X\rangle \equiv \int_{-\infty}^{\infty} xp(x)\mathrm{d}x. \qquad \text{“mathematical expectation”}$$

We assumed that X takes values in the range $(-\infty, \infty)$. When X takes values in a set $\mathcal{X}$ the limits of integration in all our integrals must be changed accordingly:

$$\boxed{\langle X\rangle \equiv \int_{\mathcal{X}} x p(x)\mathrm{d}x.}$$

We shall often write as shorthand:

$$\mu_X \equiv \langle X\rangle.$$

As we have seen in the previous lecture, the *variance* of X is defined as:

$$\sigma^2 \equiv \int_{-\infty}^{\infty} p(x)(x-\mu_X)^2\mathrm{d}x,$$

which also equals $\sigma^2 = \langle X^2\rangle - \mu_X^2$. Thus, the variance is the second moment of X minus the square of the average of X. Variance is also known as the second *central* moment of X.

The n-th *central moment* of X is defined as:

$$\langle X-\mu_X\rangle^n \equiv \int_{-\infty}^{\infty} p(x)(x-\mu_X)^n\mathrm{d}x.$$

Why are moments important? Moments describe the probability distribution. There is a theorem of mathematics that says if we know the moments of all orders, we can reconstruct the entire distribution function. You already know how to obtain the sample mean and variance. The mean is just the center of mass of the distribution whereas the variance is related to its width (about the mean).

Also of interest are the skewness (3rd central moment)

$$Skew[X] = \frac{\langle X-\mu_X\rangle^3}{\langle X-\mu_X\rangle^2]^{3/2}} = \frac{\langle X-\mu_X\rangle^3}{\sigma^3},$$

and the kurtosis (4th central moment):

$$Kurt[X] = \frac{\langle X-\mu_X\rangle^4}{[\langle X-\mu_X\rangle^2]^2} = \frac{\langle X-\mu_X\rangle^4}{\sigma^4}.$$

The skewness measures the asymmetry of the distribution about its mean whereas the kurtosis is often used to assess by how much a distribution deviates from the bell-shape. For example, if a distribution looks like a bell shape but has much longer tails, the kurtosis will reflect this.

1.4.19. Median, Percentile. The median of a rv X is the value of x_{50} such that

$$\mathbb{P}(X \geq x_{50}) = \mathbb{P}(X \leq x_{50}) \equiv \int_{-\infty}^{x_{50}} p(x)\mathrm{d}x = \frac{1}{2}.$$

The median is a special case of *percentile*. The 10-th percentile of X is the value of x_{10} such that:

$$\mathbb{P}(X \leq x_{10}) \equiv \int_{-\infty}^{x_{10}} p(x)\mathrm{d}x = 0.10.$$

The n-th percentile of X is the value x_n such that:

$$\boxed{\mathbb{P}(X \leq x_n) \equiv \int_{-\infty}^{x_n} p(x)\mathrm{d}x = \frac{n}{100}.}$$

1.4.20. Mode. The mode is the value that appears most often in a set of data values. If X is a discrete rv, the mode is the value that is most likely to be sampled. For example, in a sample $\{1, 1, 6, 7, 5, 9, 10, 1\}$ the mode is 1. In a sample $\{1, 1, 6, 5, 7, 7\}$ there are two modes: 1 and 7. A distribution with more than one mode is called multimodal. The most extreme case of a multimodal distribution occurs for uniform distributions, where all values occur equally often. This definition can be adapted for continuous rv by discretizing the PDF into a histogram and finding the value(s) of x for which the histogram is highest.

Another definition of mode for continuous distribution is the set of local maxima. When the PDF of a continuous distribution has multiple local maxima those are called the modes of the distribution (any peak is a mode). It may be tempting to define the mode of a PDF $p(x)$ as the set of points x for which $\mathrm{d}p(x)/\mathrm{d}x = 0$; however, this method does not always work. There are shapes of PDFs that have a mode, but at which the derivative of the PDF is not zero. The Laplace distribution being an obvious example:

$$p(x) = \frac{1}{2b} \exp\left(-\frac{|x-\mu|}{b}\right).$$

The mode is μ but the derivative at μ does not exist since the derivative of $|x|$ does not exist at $x = 0$. We note that a continuous rv's mode is not the value of X most likely to occur, as was the case for discrete rv. Furthermore, for some densities, even when the derivative is 0, it doesn't imply there's a mode there. Consider the beta density as an example, where setting $p'(x) = 0$ will find a local minimum rather than a maximum.

1.4.21. Average Absolute Deviation (AAD). We have seen that the center of a distribution can be quantified by the mathematical expectation (mean), the mode and the median. There are likewise many possible descriptors of the dispersion of a rv. The variance is one example. Another example is the average absolute deviation (AAD). AAD of a data set is the average of the absolute deviations from a central point. The central point can be a mean, median, mode or any other point of reference. The two most common AADs are the mean absolute deviation and the median absolute deviation (MAD).

Let X be a rv. The mean absolute deviation of a random sample $\{x_i = X(\omega_i)\}_{i=1}^{n}$ of X is

$$MAD(x_1, \ldots, x_n) = \frac{1}{n}\sum_{i=1}^{n} |x_i - m(X)|,$$

where $m(X)$ is the reference value (typically, the mean or median). This arithmetic average provides an estimate of the expectation value $\langle |X - m(X)| \rangle$ given a random sample. The median absolute deviation is defined similarly, except that we compute the median of $|X - m(X)|$ instead of its mean.

More generally, a dispersion can be defined by

$$\mathcal{D}_p(x_1, \ldots, x_n) = \sqrt[p]{\langle |X - m(X)| \rangle^p} \approx \sqrt[p]{\frac{1}{n} \sum_{i=1}^{n} |x_i - m(X)|^p},$$

where $p = 0, 1, 2, \ldots, \infty$ and $\{x_1, \ldots, x_n\}$ is a random sample of X. For $p = \infty$ we get the maximum absolute deviation. For $p = 1$ we get the average absolute deviation. For $p = 2$ we get the mean squared error.

1.4.22. Remark: $\langle f(X) \rangle$ is NOT the Same as $f(\langle X \rangle)$.

1.4.22.1. *Example 1:* Suppose that the kinetic energy, $K(v) = \frac{1}{2}mv^2$, of an object of mass m is to be calculated using experimentally measured values of the velocity v. Thus, v is a rv. Since v is a random variable, $K(v)$ is also a random variable. We may denote it as V. You determine from experiments that the velocities, V, are Gaussian-distributed around 100 m/s, with a standard deviation of 1 m/s, i.e. $p(v) = \frac{1}{\sqrt{2\pi}} e^{-(v-100)^2/2}$. What is the average kinetic energy, $\langle K(V) \rangle$? You expect that $\langle K(V) \rangle$ should be close to $K(100) = \frac{1}{2}m(100)^2$. However, the exact value of $\langle K(V) \rangle$ will depend on the distribution $p(v)$. We need to calculate:

$$\begin{aligned}\langle K(V) \rangle =& \int_{-\infty}^{\infty} \frac{1}{2} mv^2 \frac{1}{\sqrt{2\pi}} e^{-(v-100)^2/2} \mathrm{d}v \\ =& \frac{m}{2\sqrt{2\pi}} \int_{-\infty}^{\infty} v^2 e^{-(v-100)^2/2} \mathrm{d}v \approx \frac{m}{2} 1.0001 \cdot 10^4.\end{aligned}$$

So fairly close to $K(100)$ but slightly higher.

1.4.22.2. *Example 2:* Suppose that $f(\theta) = \cos(\theta)$ and $p(\theta) = 1$ for $\theta \in [-\frac{1}{2}, \frac{1}{2}]$ and $p = 0$ elsewhere (uniform distribution). Denote the random variable as Θ. Using $p(\theta)$ you can easily check that $\overline{\Theta} = \int_{-1/2}^{1/2} \theta \, \mathrm{d}\theta = 0$. The average of $\cos(\Theta)$ is:

$$\overline{\cos(\Theta)} = \int_{-1/2}^{1/2} \cos(\theta) \mathrm{d}\theta \approx 0.9589.$$

Note: it is not equal to 1 even though the average of Θ is 0.

1.4.22.3. *Example 3:* In physics and chemistry, the notations $\langle r \rangle$ and $\overline{r}$ are used interchangeably to denote the mathematical expectation. Consider the dipole-dipole interaction between two electric dipoles. The energy of interaction depends on $1/r^3$, where r is the distance separating the two point dipoles. It is easy to show that in general, $\left\langle \frac{1}{r^3} \right\rangle \neq \frac{1}{\langle r \rangle^3}$.

r is a rv due to molecular diffusion. It has an average value $\overline{r}$ and deviation δr:

$$r = \overline{r} + \delta r,$$

where $\overline{r}$ is deterministic and δr is random with zero mean. The average of $1/r^3$ is Taylor-expanded about the mean $\overline{r}$:

$$\left\langle \frac{1}{r^3} \right\rangle = \left\langle \frac{1}{(\overline{r}+\delta r)^3} \right\rangle = \left\langle \frac{1}{\overline{r}^3} \right\rangle - \left\langle \frac{3}{\overline{r}^4}\delta r \right\rangle + \left\langle \frac{12}{\overline{r}^5}(\delta r)^2 \right\rangle + O(|\delta r|^3)$$

The first term is $1/\overline{r}^3$ since $\overline{r}$ is deterministic. In the second term, $\frac{3}{\overline{r}^4}$ can come out of the angle bracket because it is a deterministic quantity. Similarly for $\frac{12}{\overline{r}^5}$ in the third term. Thus,

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{\langle r\rangle^3} - \frac{3}{\langle r\rangle^4}\langle \delta r\rangle + \frac{12}{\langle r\rangle^5}\langle(\delta r)^2\rangle + O(|\delta r|^3)$$

and you can see that $\left\langle \frac{1}{r^3} \right\rangle$ is in general different from $\frac{1}{\langle r\rangle^3}$. Since $\langle \delta r\rangle = 0$ we have:[6]

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{\langle r\rangle^3} + \underbrace{\frac{12}{\langle r\rangle^5}\langle(\delta r)^2\rangle + O(|\delta r|^3)}_{\text{extra terms (nonzero)}}.$$

We sometimes see in the literature $\frac{1}{\langle r\rangle^3}$ in lieu of $\left\langle \frac{1}{r^3} \right\rangle$. This is technically incorrect. However, for small values of $\langle|\delta r|\rangle/\langle r\rangle$, it is a good approximation.

1.4.23. Jensen's Inequality. A topic related to the previous section is Jensen's inequality. Let $\varphi(x)$ be a convex function, i.e.

$$\varphi(tx_1 + (1-t)x_2) \leq t\varphi(x_1) + (1-t)\varphi(x_2), \qquad x_1 < x_2, \quad t \in [0,1]$$

This can be generalized for $\lambda_1 + \cdots + \lambda_n = 1$, $\lambda_i \geq 0$ as:

$$\varphi(\lambda_1 x_1 + \lambda_2 x_2 + \cdots + \lambda_n x_n) \leq \lambda_1\varphi(x_1) + \lambda_2\varphi(x_2) + \cdots + \lambda_n\varphi(x_n),$$

for any $x_1, \ldots, x_n$. Let X be a rv. Then,

$$\boxed{\varphi(\langle X\rangle]) \leq \langle\varphi(X)\rangle}$$

Proof:

$$\begin{aligned}\varphi(\langle X\rangle) =&\varphi\left(\int_0^1 xp(x)\mathrm{d}x\right) = \lim_{n\to\infty}\varphi\left(\sum_{j=0}^{2^n} 2^{-n}(j\cdot 2^{-n}p(j\cdot 2^{-n}))\right)\\ &\leq \lim_{n\to\infty}\sum_{j=0}^{2^n} 2^{-n}\varphi\left(j\cdot 2^{-n}p(j\cdot 2^{-n})\right) = \int_0^1 \varphi(xp(x))\mathrm{d}x = \langle\varphi(X)\rangle].\end{aligned}$$

As an example application of this inequality we have:

$$(\langle|X-\mu_X|\rangle)^2 \leq \langle|X-\mu_X|^2\rangle = var(X).$$

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[6] For our definition $r = \overline{r} + \delta r$ to hold, we need $\langle\delta r\rangle = 0$.

Taking the square root of both sides:

$$\langle |X - \mu_X| \rangle \leq \sqrt{var(X)}.$$

We conclude that the mean absolute deviation from the mean is less than or equal to the standard deviation.

1.4.24. Remark: Discrete Random Variables as Special Case. Suppose that we roll a die and a rv X (i.e. value of the top face of die) takes values in a discrete set, such as $\mathcal{X} = \{1, 2, 3, 4, 5, 6\}$. It is said to be a discrete rv because the set $\mathcal{X}$ is countable. In the general case X may take values in a discrete set $\{x_1, \ldots, x_N\}$. Let $p_i \geq 0$ be the probability of observing the value x_i. Define the PDF in terms of Dirac delta functions and PMF $\{p_i\}_{i=1}^{N}$:

$$p(x) = \sum_{i=1}^{N} p_i \delta(x - x_i)$$

Since the PDF is normalized, we must have:

$$\int_{-\infty}^{\infty} p(x)\mathrm{d}x = \int_{-\infty}^{\infty} \sum_{i=1}^{N} p_i \delta(x - x_i)\mathrm{d}x = \sum_{i=1}^{N} p_i = 1.$$

All of our previous definitions hold if we replace integrals by summations. For example:

$$\mu_X \equiv \langle X \rangle = \int_{-\infty}^{\infty} x \cdot p(x)\mathrm{d}x = \int_{-\infty}^{\infty} x \cdot \sum_{i=1}^{N} p_i \delta(x - x_i)\mathrm{d}x = \sum_{i=1}^{N} p_i x_i.$$

The variance:

$$var(X) = \int_{-\infty}^{\infty} (x - \mu_X)^2 p(x)\mathrm{d}x = \sum_{i=1}^{N} p_i (x_i - \mu_X)^2.$$

Similarly,

$$\langle f(X) \rangle = \int_{-\infty}^{\infty} f(x) \cdot p(x)\mathrm{d}x = \sum_{i=1}^{N} p_i f(x_i).$$

Here, $x_i \in \mathcal{X}$ are the possible values X can take, whereas $p_i \equiv \mathbb{P}(X = x_i)$ are the corresponding probabilities.

1.4.25. Two (Continuous) Random Variables. If we are to compute the average of an expression that is a function of more than one rv, we need to use the *joint probability density* $p_{XY}(x, y)$, which is everywhere non-negative ($p_{XY}(x, y) \geq 0$) and integrates to 1:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_{XY}(x, y)\mathrm{d}x\mathrm{d}y = 1.$$

The joint PDF is obtained from the joint CDF analogously to the single-variable case:

$$p_{XY}(x, y) = \frac{\partial^2}{\partial x \partial y} \mathbb{P}(X < x, Y < y). \tag{1.10}$$

The average of a function $g(X,Y)$ would be:

$$\langle g(X,Y)\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p_{XY}(x,y)g(x,y)\mathrm{d}x\mathrm{d}y.$$

Given a joint probability density function, $p_{XY}(x,y)$, the *marginal density* function for X is obtained by integrating over y:

$$\boxed{p_X(x) = \int_{-\infty}^{\infty} p_{XY}(x,y)\mathrm{d}y.}$$

Similarly, the marginal density for Y is obtained by integrating over all x:

$$\boxed{p_Y(y) = \int_{-\infty}^{\infty} p_{XY}(x,y)\mathrm{d}x.}$$

Note: you can easily check that both marginals $p_X(x)$ and $p_Y(y)$ are bona fide densities, i.e. nonnegative and normalized to 1.

1.4.26. Statistical Independence. The marginal density is a useful concept if you are asked to check whether or not two rv are statistically independent. Two rv X and Y are *statistically independent* if the joint probability density is written as the product of densities of each variable:

$$\boxed{p_{XY}(x,y) = p_X(x)\cdot p_Y(y),}$$

where $p_X(x)$ and $p_Y(y)$ are the marginal densities of X and Y, respectively. They can be computed from $p_{XY}(x,y)$ by integrating.

There are at least two consequences of statistical independence that we can immediately point out. First, one concerns expectation values. Consider the average of a function $g(X,Y)$ of two rv X and Y:

$$\begin{aligned}\langle g(X,Y)\rangle &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p_{XY}(x,y)g(x,y)\mathrm{d}x\mathrm{d}y\\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p_X(x)p_Y(y)g(x,y)\mathrm{d}x\mathrm{d}y.\end{aligned}$$

If g factors as a product of a function of X times a function of Y, for example $g(X,Y) = XY$ then the expectation value of XY is equal to the product of expectation values of X and that of Y:

$$\begin{aligned}\langle XY\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p_X(x)p_Y(y)xy\,\mathrm{d}x\mathrm{d}y &= \int_{-\infty}^{\infty} p_X(x)x\mathrm{d}x\cdot\int_{-\infty}^{\infty} p_Y(y)y\mathrm{d}y\\ &= \langle X\rangle\cdot\langle Y\rangle.\end{aligned}$$

Thus, the expectation value of a product of rv's factorizes as a product of expectation values for each rv:

$$\boxed{\langle XY\rangle = \langle X\rangle\cdot\langle Y\rangle.}$$

The second consequence pertains to the calculation of probabilities in general, which also factors as a product. For example, the joint probability:

$$\begin{aligned}\mathbb{P}(X \in A, Y \in B) &= \int_{\{(x,y)|x\in A, y\in B\}} p_{XY}(x,y)\mathrm{d}x\mathrm{d}y\\ &= \int_{\{(x,y)|x\in A, y\in B\}} p_X(x)p_Y(y)\mathrm{d}x\mathrm{d}y\\ &= \int_{\{x|x\in A\}} p_X(x)\mathrm{d}x \cdot \int_{\{y|y\in B\}} p_Y(y)\mathrm{d}y\\ &=\mathbb{P}(X\in A)\cdot\mathbb{P}(Y\in B).\end{aligned}$$

As a special case, take the intervals $A = (-\infty, x]$ and $B = (-\infty, y]$ and we get the result that the CDFs also factorize:

$$\boxed{\mathbb{P}(X \le x, Y \le y) = \mathbb{P}(X \le x)\cdot\mathbb{P}(Y \le y).}$$

1.4.27. Calculating Probabilities: Two Variables. Probabilities of an event A are calculated by integrating the PDF over the relevant set of points which make the event A true. That is, for a single rv X:

$$\boxed{\mathbb{P}(X \in A) = \int_{\{x|x\in A\}} p_X(x)\mathrm{d}x,} \tag{1.11}$$

where $\{x|x \in A\}$ denotes the set of all points x such that $x \in A$. For example, if $A = [a, b]$ (interval), we have:

$$\mathbb{P}(a \le X \le b) = \int_a^b p_X(x)\mathrm{d}x.$$

If A is the union of two disjoint (non-overlapping) intervals $[a, b]$ and $[c, d]$, i.e. $A = [a, b] \cup [c, d]$, then the probability of X taking a value in A is the sum of two integrals:

$$\mathbb{P}(X \in A) = \int_a^b p_X(x)\mathrm{d}x + \int_c^d p_X(x)\mathrm{d}x.$$

For two or more rv's we integrate the joint probability density over all such points (x, y) that meet the sought criterion:

$$\mathbb{P}(X \in A, Y \in B) = \int\int_{\{(x,y)|x\in A, y\in B\}} p_{XY}(x,y)\mathrm{d}x\mathrm{d}y,$$

where $\{(x, y)|x \in A, y \in B\}$ denotes the set of all points (x, y) such that $x \in A$ and $y \in B$.

In general, for a given set of points over which the probability needs to be calculated, we must translate what this means in terms of the upper and lower limits of integration. Let us look at some specific examples. Let (X, Y) be a 2-dimensional (bivariate) rv with joint density $p_{XY}(x, y)$. The probability that the vector (X, Y) will lie in the first quadrant of the 2D plane is:

$$\mathbb{P}(X>0,Y>0)=\int\int_{\{(x,y)|x>0,y>0\}} p_{XY}(x,y)\mathrm{d}x\mathrm{d}y$$
$$=\int_0^\infty\int_0^\infty p_{XY}(x,y)\mathrm{d}x\mathrm{d}y.$$

Suppose again that we have a random experiment involving two rv X and Y. The probability that the outcome will lie in one of the first two quadrants:

$$\mathbb{P}(X>0)=\mathbb{P}(X>0,Y\in(-\infty,\infty))=\int\int_{\{(x,y)|x>0\}} p_{XY}(x,y)\mathrm{d}x\mathrm{d}y$$
$$=\int_{-\infty}^\infty\left(\int_0^\infty p_{XY}(x,y)\mathrm{d}x\right)\mathrm{d}y.$$

1.4.28. Product of X and Y. Let X and Y be independent rv's and let $Z=XY$. The PDF of Z is:

$$\boxed{p_Z(z)=\int_{-\infty}^\infty p_X(x)p_Y(z/x)\frac{1}{|x|}\mathrm{d}x.}$$

Proof:

$$\begin{aligned}\mathbb{P}(Z\le z)=&\mathbb{P}(XY\le z)=\mathbb{P}(XY\le z,X>0)+\mathbb{P}(XY\le z,X\le 0)\\=&\mathbb{P}(Y\le z/X,X>0)+\mathbb{P}(Y\ge z/X,X\le 0)\\=&\int_0^\infty p_X(x)\int_{-\infty}^{z/x}p_Y(y)\mathrm{d}y\mathrm{d}x+\int_{-\infty}^0 p_X(x)\int_{z/x}^\infty p_Y(y)\mathrm{d}y\mathrm{d}x\end{aligned}$$

Differentiating with respect to z, we get the PDF:

$$\int_0^\infty p_X(x)p_Y(z/x)\frac{1}{x}\mathrm{d}x-\int_{-\infty}^0 p_X(x)p_Y(z/x)\frac{1}{x}\mathrm{d}x=\int_{-\infty}^\infty p_X(x)p_Y(z/x)\frac{1}{|x|}\mathrm{d}x.$$

See also Problem 7.

1.4.29. Sum of X and Y. Here is another application of the Leibniz formula (see Section 9.9). Suppose we have two rv's X,Y with joint density $p_{XY}(x,y)$. What is the density of their sum, $X + Y$? Since the density is the derivative of the CDF:

$$\begin{aligned} p_{X+Y}(z) = \frac{\mathrm{d}}{\mathrm{d}z}\mathbb{P}(X+Y<z) =& \frac{\mathrm{d}}{\mathrm{d}z}\int_{\{(x,y)|x+y<z\}} p_{XY}(x,y)\mathrm{d}x\mathrm{d}y \\ =& \frac{\mathrm{d}}{\mathrm{d}z}\int_{\{(x,y)|x<z-y\}} p_{XY}(x,y)\mathrm{d}x\mathrm{d}y \\ =& \int_{-\infty}^{\infty} \frac{\partial}{\partial z}\left(\int_{-\infty}^{z-y} p_{XY}(x,y)\mathrm{d}x\right)\mathrm{d}y \\ =& \int_{-\infty}^{\infty} p_{XY}(z-y,y)\mathrm{d}y. \end{aligned}$$

This is as far as we can go without further information about X, Y. If X and Y are independent, the joint PDF factorizes into a product, $p_{XY}(z-y,y) = p_X(z-y)\cdot p_Y(y)$, and the last operation becomes a *convolution*:

$$\boxed{p_{X+Y}(z) = \int_{-\infty}^{\infty} p_X(z-y)\cdot p_Y(y)\mathrm{d}y.}$$

Thus, the PDF of $Z = X + Y$ is the convolution of the PDFs of X and Y, whenever X and Y are statistically independent.

1.4.30. Several Variables. Suppose we have several rv's $X_1, X_2, \ldots, X_n$. Probabilistic expressions involving these rv's can be evaluated if we know the joint distribution:

$$\mathbb{P}(X_1 < b_1, \ldots, X_n < b_n) = \int_{-\infty}^{b_1}\mathrm{d}x_1 \cdots \int_{-\infty}^{b_n}\mathrm{d}x_n\, p_{X_1,\ldots,X_n}(x_1,\ldots,x_n),$$

where $p_{X_1,\ldots,X_n}(x_1,\ldots,x_n)$ is the joint PDF of $X_1,\ldots,X_n$ and $\mathbb{P}(X_1 < b_1,\ldots,X_n < b_n)$ is the joint CDF.

We can also ask about the probability of the following event:

$$\{X_1 \in B_1, X_2 \in B_2, \ldots, X_n \in B_n\}.$$

Then, using the joint PDF:

$$\mathbb{P}\{X_1 \in B_1, \ldots, X_n \in B_n\} = \int_{B_1}\mathrm{d}x_1 \cdots \int_{B_n}\mathrm{d}x_n\, p_{X_1,\ldots,X_n}(x_1,\ldots,x_n).$$

As in the single-variable case, we can write probabilities over intervals in terms of the CDFs. For example, let X, Y be two rv's and let $B_1 = (a_1, a_2)$ and $B_2 = (b_1, b_2)$. Then,

$$\begin{aligned}\mathbb{P}(X \in B_1, Y \in B_2) =&\mathbb{P}(a_1 < X < a_2, b_1 < Y < b_2)\\ =&\int_{a_1}^{a_2} \mathrm{d}x \int_{b_1}^{b_2} \mathrm{d}y\, p_{XY}(x,y)\\ =&\int_{a_1}^{a_2} \mathrm{d}x \left(\frac{\partial}{\partial x}\mathbb{P}(X < x, Y < b_2) - \frac{\partial}{\partial x}\mathbb{P}(X < x, Y < b_1) \right)\\ =&\mathbb{P}(X < a_2, Y < b_2) - \mathbb{P}(X < a_1, Y < b_2)\\ &- \mathbb{P}(X < a_2, Y < b_1) + \mathbb{P}(X < a_1, Y < b_1).\end{aligned}$$

We have made use of Eq. (1.10), i.e.

$$p_{XY}(x,y) = \frac{\partial^2}{\partial x \partial y}\mathbb{P}(X < x, Y < y),$$

and invoked the fundamental theorem of calculus (twice).

1.4.31. Additional Properties of rv's.

1.4.31.1. *Linearity of the Expectation Value.* Let X and Y be rv's and a, b constants. From the linearity of the expectation value operator:

$$\begin{aligned}\langle aX + bY\rangle =& \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}(ax+by)p_{XY}(x,y)\mathrm{d}x\mathrm{d}y\\ =&a\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x p_{XY}(x,y)\mathrm{d}x\mathrm{d}y + b\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} y p_{XY}(x,y)\mathrm{d}x\mathrm{d}y\\ =&a\int_{-\infty}^{\infty} x p_X(x)\mathrm{d}x + b\int_{-\infty}^{\infty} y p_Y(y)\mathrm{d}y\\ =&a\langle X\rangle + b\langle Y\rangle,\end{aligned}$$

where $p_{XY}(x,y)$ is the joint probability density of x and y.[7] $p_X(x)$ is the marginal density of X. Similarly for $p_Y(y)$. This can be generalized to any number of rv's, e.g. for $X = X_1 + X_2 + \cdots + X_n$ it also follows that

$$\boxed{\langle X\rangle = \langle X_1\rangle + \langle X_2\rangle + \cdots + \langle X_n\rangle.}$$

It is also trivial to show that the same result holds in the case of discrete rv's.

1.4.31.2. *Scaling Property of the Variance.* From the definition of the variance of a rv X (let $\mu_X \equiv \langle X\rangle$),

$$var(X) \equiv \langle X - \mu_X)^2\rangle = \langle X^2\rangle - 2\langle X\mu_X\rangle + (\mu_X)^2 = \langle X^2\rangle - \mu_X^2$$

---

[7] Note: while the exact form of $p_{XY}(x,y)$ may be unknown, its knowledge was not required to demonstrate linearity.

we deduce that

$$\boxed{var(aX) = a^2 var(X).}$$

1.4.31.3. *Variance of a Product of Independent Random Variables.* Let v be the velocity of a particle and t the time variable. If both are statistically independent rv's, the mean displacement factors as a product of means, $\langle vt\rangle = \langle v\rangle \cdot \langle t\rangle$, whereas its variance is

$$\begin{aligned} var(vt) =&\langle (vt)^2\rangle - \langle vt\rangle^2 \\ =&\langle v^2t^2\rangle - \langle v\rangle^2\langle t\rangle^2 \\ =&\langle v^2\rangle \cdot \langle t^2\rangle - \langle v\rangle^2\langle t\rangle^2. \end{aligned}$$

Thus, by statistically independence, we can express the mean and variance of the displacement $x = vt$ in terms of the mean and variance of v and t.

1.4.31.4. *Variance Between Pairs of Random Variables: The Covariance.* The *covariance* of X and Y is defined as (let $\mu_X \equiv \langle X\rangle$ and $\mu_Y \equiv \langle Y\rangle$):

$$\boxed{cov(X,Y) \equiv \langle (X-\mu_X)(Y-\mu_Y)\rangle = \langle XY\rangle - \mu_X \cdot \mu_Y.}$$

We note that the covariance of two independent rv's is zero since $\langle XY\rangle = \langle X\rangle \cdot \langle Y\ rangle = \mu_X \cdot \mu_Y$.

1.4.31.5. *Variance of the Sum of Two Random Variables.* Using the covariance, we may write the variance of the sum $X + Y$ as

$$\begin{aligned} var(X+Y) =&\langle (X+Y-\langle X+Y\rangle)^2\rangle \\ =&\langle (X-\mu_X)^2\rangle + \langle (Y-\mu_Y)^2\rangle + 2\langle (X-\mu_X)(Y-\mu_Y)\rangle \\ =&var(X) + var(Y) + 2cov(X,Y). \end{aligned} \tag{1.12}$$

If X and Y are statistically independent, $cov(X,Y) = 0$, and $var(X+Y) = var(X) + var(Y)$, i.e. the error in $X+Y$ is related to the errors in X and Y by adding the variances.

1.4.31.6. *Corollary: Adding Experimental Errors.* Suppose X and Y are independent rv's with standard deviations σ_X and σ_Y, respectively. Let $Z = X + Y$. Then the variances add quadratically:

$$\sigma_Z = \sqrt{\sigma_X^2 + \sigma_Y^2}.$$

This formula is often used in the analysis of laboratory experimental results. It is only valid in the case where X and Y are independent. How can you verify of X and Y are statistically independent?

1.4.31.7. *Sample Covariance.* In Formula (1.12) the covariance must be added to get the error in the sum of two rv's, $X + Y$. The covariance is zero if the two rv's are statistically independent. It is difficult to check for independence. However, it is easy to check for statistical correlation by computing the sample covariance. Suppose that the following pairs are measured experimentally $\{(x_i, y_i)\}_{i=1}^n$. This random sample is described by the empirical joint PDF:

$$\hat{p}_{XY}(x,y) = \frac{1}{n}\sum_{i=1}^{n}\delta(x-x_i)\delta(y-y_i).$$

Substitution into the definition of covariance:

$$\begin{aligned} cov(X,Y) \equiv& \langle (X-\mu_X)(Y-\mu_Y)\rangle \\ =& \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}(x-\mu_X)(y-\mu_Y)\frac{1}{n}\sum_{i=1}^{n}\delta(x-x_i)\delta(y-y_i)\mathrm{d}x\mathrm{d}y \\ =& \frac{1}{n}\sum_{i=1}^{n}(x_i-\mu_X)\cdot(y_i-\mu_Y) \end{aligned}$$

where μ_X and μ_Y are the means of X and Y, respectively. Since we have experimental data at our disposal, we take them to be sample means. This is normally adjusted by replacing $1/n$ by $1/(n-1)$ on the basis that a degree of freedom has been lost due to our use of experimental data to obtain statistical estimators for the means ($\hat{\mu}_X$ and $\hat{\mu}_Y$):

$$\boxed{cov_{n-1}(X,Y) = \frac{1}{n-1}\sum_{i=1}^{n}(x_i-\hat{\mu}_X)\cdot(y_i-\hat{\mu}_Y).}$$

This formula provides us with an explicit prescription for computing the covariance of X and Y from experimental data. One may as well directly use Formula (1.12), since it enables us to determine the amount of covariance between them, and add its contribution to the error estimate, if needed.

1.4.31.8. *Correlation Coefficient.* A concept that is related to the covariance is the correlation coefficient:

$$\boxed{\rho(X,Y) = \frac{cov(X,Y)}{\sigma_X\cdot\sigma_Y},}$$

where $\sigma_X = \sqrt{var(X)}$ and $\sigma_Y = \sqrt{var(Y)}$. ρ takes values in the range $-1 \le \rho(X,Y) \le 1$. The correlation coefficient is a measure of linear dependence between X and Y. It is more useful than the covariance in the sense that ρ is a dimensionless quantity which is normalized to the magnitude of X and Y. A value of $\rho = 1$ means that X and Y are correlated. A value of $\rho = -1$ means they are anti-correlated. A value of $\rho = 0$ means they are uncorrelated. Please note that if X and Y are independent then $\rho = 0$. However, the converse is not true. That is, $\rho = 0$ does not always imply that X and Y are independent.

The reader can easily check[8] that if $Y = aX + b$ (a, b constants) we have $cov(X,Y) = a\cdot var(X)$ and

$$\rho(X,Y) = \frac{a}{|a|} = \begin{cases} 1 & a>0 \\ -1 & a<0 \end{cases}.$$

---

[8] Start by the numerator: $cov(X,Y) = cov(X,aX+b) = \langle (X-\mu_X)(aX+b-\mu_{aX+b})\rangle$, but since $\mu_{aX+b} = a\mu_X + b$, this reduces to $cov(X,aX+b) = \langle (X-\mu_X)(aX-a\mu_X)\rangle. = a\langle (X-\mu_X)^2\rangle = a\cdot var(X)$.

Thus, the correlation coefficient is a measure of linear dependence. In this example, $\rho = 1$ if $Y = aX + b$ and $a > 0$ (X and Y are correlated), whereas $\rho = -1$ if $a < 0$ (X and Y are anti-correlated). This result is independent of the magnitude of a; it only depends on its sign. For example, $Y = 0.00001 \cdot X$ and $Y = 10000 \cdot X$ both give $\rho = 1$.

Q: Can you find examples of rv's X and Y where ρ is *not* equal to -1, 0 or 1 but some intermediate value (say 0.5)? What is the meaning of a correlation coefficient that is not equal to 0 or 1?

1.4.31.9. *Linear Correlation.* Suppose that two random variables X and Y depend on each other linearly:

$$Y = a + bX.$$

The correlation coefficient becomes:

$$\rho(X,Y) = \frac{cov(X,Y)}{\sigma_X \cdot \sigma_Y} = \frac{cov(X, a + bX)}{\sigma_X \cdot \sigma_Y} = \frac{b \cdot cov(X,X)}{\sigma_X \cdot \sigma_Y} = \frac{b \cdot \sigma_X}{\sigma_Y}$$

Therefore, the slope b is related to the value of the correlation coefficient (as well as the variances of X and Y):

$$b = \rho(X,Y)\frac{\sigma_Y}{\sigma_X}.$$

1.4.31.10. *Sample Correlation Coefficient.* Let X, Y be rv's with mean μ_X and μ_Y, respectively. Let $x_1, x_2, \ldots, x_n$ be measurements of X. Similarly for Y. The correlation coefficient can be estimated from experimental data, $\{(x_i, y_i)\}_{i=1}^n$, using the *sample correlation coefficient*:

$$\boxed{r_{X,Y} = \frac{\frac{1}{n-1}\sum_{i=1}^n (x_i - \hat{\mu}_X) \cdot (y_i - \hat{\mu}_Y)}{\sqrt{\frac{1}{n-1}\sum_{i=1}^n (x_i - \hat{\mu}_X)^2} \cdot \sqrt{\frac{1}{n-1}\sum_{i=1}^n (y_i - \hat{\mu}_Y)^2}},}$$

where n is the number of data points and $\hat{\mu}_X$ is the sample mean

$$\hat{\mu}_X = \frac{1}{n}\sum_{i=1}^n x_i,$$

and similarly for $\hat{\mu}_Y$. They are uncorrelated if $r_{X,Y} = 0$. You can also check for possible correlation between X and Y using a scatter plot. This is done by plotting the set of ordered pairs $\{(x_i, y_i)\}$ as points on the same graph.

1.4.31.11. *Uncorrelated but not Independent.* Let X and Y be rv's related by $Y = X^2$. Let μ_X be the mean of X, μ_{X^2} its second moment, etc. Clearly, these rv's are not independent of each other. However,

$$cov(X,Y) = cov(X, X^2) = \langle (X - \mu_X)(X^2 - \mu_{X^2}) \rangle = \mu_{X^3} - \mu_X \mu_{X^2}.$$

If the distribution of X is such that $\mu_{X^3} = \mu_X \mu_{X^2}$ (for example, if the mean and skewness are zero, which is the case for a zero-mean normal distribution), then $cov(X,Y) = 0$ and the rv's X and Y are uncorrelated even though they are clearly dependent on each other.

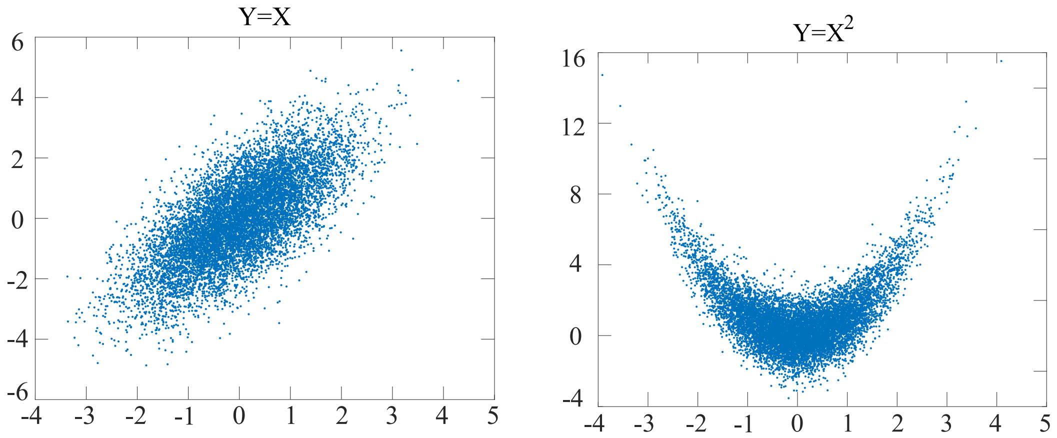


Figure 1.4. Correlations between rv's (X, Y).

This can easily be illustrated in MATLAB. Let's create two plots. One for the equation $Y = X + \eta$ (linear case), where X and η are independent standard normal rv's:

```
X=randn([1 10000]);
Y=X+randn([1 10000]);
```

and one for $Y = X^2 + \eta$ (quadratic case), where X and η are independent standard normal rv's.

```
X=randn([1 10000]);
Y=X.^2+randn([1 10000]);
```

You can think of the linear case as in the familiar form $Y = a + bX$, but for the special case of $a = 0$, $b = 1$, and noise added (η). Same for the quadratic equation, it has noise added to it, as a way to simulate the outcome of a random experiment.

In each case, a plot is generated by typing `figure;plot(X,Y,'.')` (see Fig. 1.4). The sample correlation coefficient is obtained using the `corrcoef` command, e.g. for the linear case

```
>> corrcoef(X,Y)

ans =

    1.0000    0.7025
    0.7025    1.0000
```

whereas for the quadratic case we get:

```
>> corrcoef(X,Y)

ans =

    1.0000   -0.0089
   -0.0089    1.0000
```

The diagonal elements are 1 (since X is perfectly correlated to X, as is Y correlated to Y). The off-diagonal elements are the correlation coefficients of X and Y. In the linear case, we have strong (≈ 0.7) correlation between X and Y. We would expect 1 without the additive noise, η (you can check this by reducing the amplitude of the additive noise). In the quadratic case, the correlation coefficient is nearly 0, as it should because the Gaussian rv X has zero skewness and zero mean.

1.4.32. Calculating Probabilities. If you are asked to compute the probability of a random event involving X, your first reflex should be to write down an integral of the PDF, $p_X(x)$, over the set of points that represent this event. Recall the formula (1.11) introduced previously:

$$\boxed{\mathbb{P}(X \in A) = \int_{\{x|x\in A\}} p_X(x)\mathrm{d}x,} \tag{1.13}$$

In two dimensions you do the same thing except that the joint PDF is to be used, e.g.

$$\begin{aligned}\mathbb{P}(a \leq X \leq b, c \leq Y \leq d) &= \int_{\{(x,y)|a\leq x\leq b, c\leq y\leq d\}} p_{XY}(x,y)\mathrm{d}x\mathrm{d}y \\ &= \int_a^b \int_c^d p_{XY}(x,y)\mathrm{d}x\mathrm{d}y.\end{aligned}$$

This is for the specific case where the random even is $\{a \leq X \leq b, c \leq Y \leq d\}$. For a general random event, we integrate over the set of points (x, y) such that the event is true. It is not possible to enumerate all possible events we may encounter. Some examples are:

$$\{X \in A, Y \in B\}, \quad \{X/Y < a\}, \quad \{X + Y > b\},$$
$$\{a < \cos(X) \cdot \log(Y) < b\}, \text{ etc.}$$

In each case, we integrate the joint PDF of X and Y, $p_{XY}(x, y)$, over the set of points (x, y) that obey the conditions specified in the event.

To summarize the procedure involved when calculating probabilities, there are two main steps. The first step is to write down the right hand side, but keeping in mind that the random event will need to be expressed in a form suitable for integration. The second step involves writing the integral in a form that can be solved. This sometimes involves a change of variables, if the integration region needs to be simplified.

1.4.32.1. *Single-Variable Case.* In the first step, we often invoke some algebraic manipulations in order to transform the logical statement $X \in A$ into a form that allows us to apply the information known to us. Let use revisit the example already covered in Sections 1.4.11 and 1.4.10.8. Let $Y = e^X$ and $X \sim \mathcal{N}(\mu, \sigma^2)$. You are asked to find the distribution of Y given the distribution X (a normal law in the present case). At first sight, you may think that $\mathbb{P}(Y < y)$ cannot be easily calculated because you are not given the distribution of Y. However, the distribution of X is provided. So your goal is to transform the statement $Y < y$ into one that involves X instead. In Section 1.4.10.8 we worked out the case of the log-normal distribution, $Y = e^X$ where $X \sim \mathcal{N}(\mu, \sigma^2)$.

1.4.32.2. *Two Variables Case.* Another example is $Y = U/V$ where U and V are independent standard normal variables, i.e $U \sim \mathcal{N}(0,1)$ and $V \sim \mathcal{N}(0,1)$. The CDF of Y is:

$$\mathbb{P}(Y < a) = \mathbb{P}(U/V < a) = \iint\limits_{\{(u,v)|u/v<a\}} p_U(u)p_V(v)\mathrm{d}u\mathrm{d}v$$

Effecting a change of variables $Y = U/V$, $Z = V$ (inverse: $V = Z$, $U = ZY$) under the integral sign and using the Jacobian of the transformation:

$$\mathrm{d}u\mathrm{d}v = \left|\frac{\partial(u,v)}{\partial(y,z)}\right| \mathrm{d}y\mathrm{d}z, \qquad \text{where } \frac{\partial(u,v)}{\partial(y,z)} \equiv \begin{Vmatrix} \partial_y u & \partial_z u \\ \partial_y v & \partial_z v \end{Vmatrix} = \begin{Vmatrix} z & y \\ 0 & 1 \end{Vmatrix} = z$$

where $\|\cdot\|$ denotes “matrix determinant”, whereas $|\cdot|$ denotes absolute value. Then,

$$\begin{aligned}\mathbb{P}(Y < a) = &\iint\limits_{\{(y,z)|y<a\}} p_U(yz)p_V(z)|z|\mathrm{d}z\mathrm{d}y \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty}\left\{\int_{-\infty}^{a} e^{-\frac{1}{2}y^2z^2}e^{-\frac{1}{2}z^2}|z|\mathrm{d}y\right\}\mathrm{d}z.\end{aligned}$$

Using the change of variables $w = \frac{1}{2}z^2$, $\mathrm{d}w = z\mathrm{d}z$ and replacing $\int_{-\infty}^{\infty}\mathrm{d}z$ by $2\int_0^{\infty}\mathrm{d}z$ (this replacement is allowed since its integrand is positive):

$$\begin{aligned}\mathbb{P}(Y < a) &= \frac{1}{\pi}\int_{-\infty}^{a}\left\{\int_0^{\infty} e^{-\frac{1}{2}z^2(1+y^2)}z\mathrm{d}z\right\}\mathrm{d}y \\ &= \frac{1}{\pi}\int_{-\infty}^{a}\left\{\int_0^{\infty} e^{-w(1+y^2)}\mathrm{d}w\right\}\mathrm{d}y = \int_{-\infty}^{a}\frac{1}{\pi}\frac{\mathrm{d}y}{(1+y^2)}.\end{aligned}$$

This is known as the Lorentzian (or Cauchy) distribution. The PDF of the Lorentzian distribution is obtained by differentiating with respect to a:

$$p_Y(y) = \frac{1}{\pi}\frac{1}{(1+y^2)}.$$

In another example we can ask what is the probability that a rv X takes on exactly the value x:

$$\mathbb{P}(X = x) = \lim_{\mathrm{d}x\to 0}\mathbb{P}(x < X \leq x + \mathrm{d}x) = \lim_{\mathrm{d}x\to 0}\int_x^{x+\mathrm{d}x} p(x)\mathrm{d}x = \lim_{\mathrm{d}x\to 0} p(x)\mathrm{d}x = 0$$

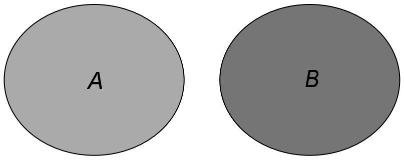


Figure 1.5. Mutually exclusive random events A and B.

provided that $p(x)$ is continuous. If $p(x)$ is discontinuous at x, this result is not necessarily zero. In this course, we will not be dealing with discontinuous probability functions.

1.4.33. Probability of Mutually Exclusive Random Events. If random events A_1, A_2 and A_n are disjoint sets, i.e. $A_i \cap A_j = \emptyset$, then the probability of any of the A_i events is a sum of probabilities:

$$\boxed{\mathbb{P}(A_1 \cup A_2 \cup \cdots \cup A_n) = \mathbb{P}(A_1) + \mathbb{P}(A_2) + \cdots + \mathbb{P}(A_n).} \tag{1.14}$$

Such a set of random events is called mutually exclusive events. The "union" $A_1 \cup A_2 \cup \cdots \cup A_n$ of random events is equivalent to a "logical OR" operation, i.e.

$$\mathbb{P}(A_1 \cup A_2 \cup \cdots \cup A_n) = \mathbb{P}(A_1 \text{ or } A_2 \text{ or } \ldots \text{ or } A_n).$$

Suppose that we measure the number of radioactive counts within a 1-second time interval. When we make the statement "12 or fewer counts were observed" (during a 1-second time interval),

$$\text{12 or fewer counts } = \text{1 count or 2 counts or ... or 12 counts.}$$

In other words, let X be a rv that represents the # of counts (in the 1-second time interval).

$$\{X \le 12\} = \{X = 1\} \cup \{X = 2\} \cup \{X = 3\} \cup \cdots \cup \{X = 12\}.$$

Decomposing the event $\{X \le 12\}$ as a union of mutually exclusive random events, i.e. $\{X = 1\} \cap \{X = 2\} = \emptyset$, etc., offers some advantages when calculating the probabilities of events. It enables us to invoke formula (1.14).

Two mutually exclusive events A and B have no overlap can be represented as shown in Fig. 1.5. What should we do if the random events are not mutually exclusive? For simplicity, consider only 2 events, A and B. Mutual exclusivity means that $A \cap B = \emptyset$. If the intersection is nonzero, then we have the situation illustrated in the Venn diagram (Fig. 1.6).

In this case, we should avoid overcounting by subtracting the intersection:

$$\boxed{\mathbb{P}(A \cup B) = \mathbb{P}(A) + \mathbb{P}(B) - \mathbb{P}(A \cap B).}$$

Let us look at the example of rolling a die. Let X be the numerical result of the die roll (# appearing on the top face). Define two random events, A and B, as follows: $A = \{X \le 3\}$

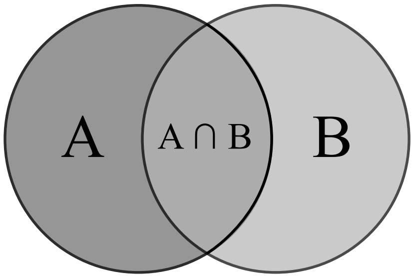


Figure 1.6. Events that are not mutually exclusive share common outcomes (as represented here by the overlap region).

and $B = \{X \text{ is odd}\}$. It is helpful to decompose these random events into a union of mutually exclusive "elementary events":

$$A = \{X \leq 3\} = \{X = 1\} \cup \{X = 2\} \cup \{X = 3\},$$

and

$$B = \{X \text{ is odd}\} = \{X = 1\} \cup \{X = 3\} \cup \{X = 5\}.$$

The union of A and B is:

$$A \cup B = \{X = 1\} \cup \{X = 2\} \cup \{X = 3\} \cup \{X = 5\}.$$

The intersection of A and B is:

$$A \cap B = \{X = 1\} \cup \{X = 3\}.$$

If the die is unbiased, i.e. $\mathbb{P}(X = x_i) = 1/6$ for $x_i \in \{1, 2, \ldots, 6\}$, then $\mathbb{P}(A \cup B) = 2/3$, $\mathbb{P}(A) = 1/2$, $\mathbb{P}(B) = 1/2$ and $\mathbb{P}(A \cap B) = 1/3$. This verifies the formula $\mathbb{P}(A \cup B) = \mathbb{P}(A) + \mathbb{P}(B) - \mathbb{P}(A \cap B)$ for this particular choice of random events.

1.4.34. Discrete Random Variables. A discrete rv X takes values in a discrete set $\mathcal{X} = \{x_i\}_{i=1}^{N}$, where N is the number of possible values X can take (cardinality of the set $\mathcal{X}$) and $x_i \in \mathcal{X}$ are the possible values. The word discrete refers to the "state space". $\mathcal{X}$, which is countable (discrete) and in the present case, contains N elements (N can also be infinite). Discrete rv's can be described using the PDF formed with Dirac delta functions:

$$p_X(x) = \sum_{i=1}^{N} p_i \delta(x - x_i), \quad p_i \geq 0, \quad \sum_i p_i = 1.$$

In this section we explicitly state the main formulas pertaining to the properties of discrete rv's by way of discrete sums and the "probability mass function" or PMF. Either description is valid.

1.4.34.1. *Properties of Discrete Random Variables.* The rv is defined by the probability distribution $\{p_i\}$ (also known as the "probability mass function" or PMF), where $p_i \geq 0$

for all i. The normalization condition is

$$\sum_{i=1}^{N} p_i = 1$$

p_i: probability that rv X takes the value x_i.

N: can be finite or infinite; in any case, the $\{p_i\}$ must sum to 1.

We note that from the definition of p_i as the probability that X takes the discrete value x_i, and the fact that the events $\{X = x_i\}$ are mutually exclusive random events, it follows that

$$\begin{aligned}\mathbb{P}(X \leq x_j) =& \mathbb{P}(\{X = x_1\} \cup \{X = x_2\} \cup \cdots \cup \{X = x_j\}) \\ =& \sum_{i=1}^{j} \mathbb{P}(\{X = x_i\}) = \sum_{i=1}^{j} p_i.\end{aligned}$$

The *mean* value of X is

$$\langle X \rangle = \sum_{i=1}^{N} p_i x_i.$$

The *n-th moment* of X is

$$\langle X^n \rangle = \sum_{i=1}^{N} p_i x_i^n.$$

The *mean* or mathematical expectation of $f(X)$ is

$$\langle f(X) \rangle \equiv \sum_{i=1}^{N} p_i f(x_i).$$

The *variance* of X is (let $\mu_X = \langle X \rangle$)

$$\sigma^2 = \mathrm{Var}(X) = \langle X - \mu_X \rangle^2 = \sum_{i=1}^{N} p_i (x_i - \mu_X)^2.$$

The variance is also equal to $\langle X^2 \rangle - (\mu_X)^2$. When calculating averages of functions of rv's, we proceed by replacing the rv X by its value x_i, multiplying the expression by p_i and summing over all i. For example,

$$\langle \exp(-X) \rangle = \sum_i p_i \exp(-x_i), \qquad \langle g(X) \rangle \equiv \sum_i p_i g(x_i).$$

This is analogous to the continuous case covered in the previous lecture where $\int p(x)$ replaces $\sum_i p_i$:

$$\langle \exp(-X) \rangle = \int_{-\infty}^{\infty} p(x) \exp(-x) \mathrm{d}x, \qquad \langle g(X) \rangle = \int_{-\infty}^{\infty} p(x) g(x) \mathrm{d}x.$$

When we deal with two discrete rv's X and Y, the joint probability can be written

$$p_{ij} \equiv \mathbb{P}(X = x_i \cap Y = y_j)$$

where $\mathbb{P}(X = x_i \cap Y = y_j)$ denotes the probability of X taking the value x_i and Y taking the value y_j. The p_{ij} are normalized to 1:

$$\sum_{i,j} p_{ij} = 1.$$

The average of a function $g(X, Y)$ is:

$$\langle g(X,Y)\rangle = \sum_{ij} p_{ij} g(x_i, y_j).$$

As before, if X and Y are statistically independent, the mean of XY equals the product of the means of X and Y:

$$\langle XY\rangle = \sum_{ij} x_i y_j \mathbb{P}(X = x_i \cap Y = y_j)$$

$$= \sum_i x_i \mathbb{P}(X = x_i) \sum_j y_j \mathbb{P}(Y = y_j) = \langle X\rangle \cdot \langle Y\rangle,$$

and similarly, we have:

$$\langle X^n Y^m\rangle = \langle X^n\rangle \cdot \langle Y^m\rangle.$$

A consequence of this result is

$$\langle f(X) g(Y)\rangle = \langle f(X)\rangle \cdot \langle g(Y)\rangle,$$

because sufficiently nice functions f, g can be expanded as a power series, enabling us to apply the result $\langle X^n Y^m\rangle = \langle X^n\rangle \cdot \langle Y^m\rangle$ to each term of the expansion.

1.4.34.2. *Poisson Distribution.* The Poisson distribution is a discrete probability distribution which is frequently used to describe counts of rare events. The main assumptions are:

- The events counted are *rare* events.
- All events are statistically independent.
- Average count rate does not change over time.

The typical application of this distribution is *radioactive counting* (for example, with a Geiger counter), where the average count $\overline{n}$ in a given time is given by the formula:

$$\overline{n} = \lambda\tau$$

where λ is average count rate and τ is time interval. For example: $\lambda = 1.5\ \mathrm{s}^{-1}$, $\tau = 10$ s gives $\overline{n} = 15$. $\overline{n}$ does not have to be an integer number.

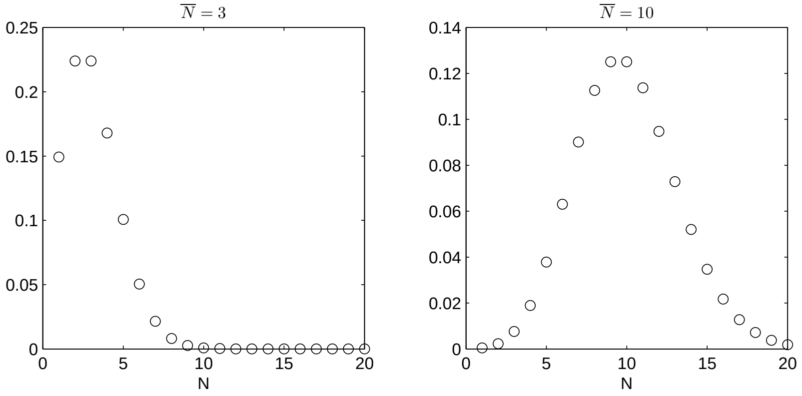


Figure 1.7. Poisson distribution (PMF) for two different parameter values.

1.4.34.3. *Probability Mass Function.* The probability distribution is completely described by a single parameter, $\overline{n}$,[9]

$$\boxed{\mathbb{P}(n;\overline{n}) = \frac{e^{-\overline{n}}\overline{n}^n}{n!}, \qquad n = 0, 1, 2, \ldots}$$

In the usual interpretation, $P(0;\overline{n})$ gives the probability of observing 0 counts in a time interval τ, $P(1;\overline{n})$ gives the probability of observing 1 count, etc. It is easy to check that this PMF is normalized to 1:

$$\sum_{n=0}^{\infty}\mathbb{P}(n;\overline{n}) = \sum_{n=0}^{\infty}\frac{e^{-\overline{n}}\overline{n}^n}{n!} = e^{-\overline{n}}\sum_{n=0}^{\infty}\frac{\overline{n}^n}{n!} = e^{-\overline{n}}e^{\overline{n}} = 1,$$

since the Taylor expansion of $\exp(x)$ is $\sum_{k=0}^{\infty} x^k/k!$. Figure 1.7 shows plots of the Poisson distribution for $\overline{n} = 3$ and $\overline{n} = 10$. Notice that the distribution looks more like a Gaussian at large $\overline{n}$.

These plots were generated in MATLAB using the commands:

```
Nbar=2;N=0:20;figure;plot(N,exp(-Nbar)*(Nbar.^N)./factorial(N),'o');
Nbar=5;N=0:20;figure;plot(N,exp(-Nbar)*(Nbar.^N)./factorial(N),'o');
Nbar=10;N=0:20;figure;plot(N,exp(-Nbar)*(Nbar.^N)./factorial(N),'o');
figure;ezplot('exp(-((x-10)^2)/(2*10))',[0,20]);
```

Two more properties of the Poisson distribution which you can easily verify are:

$$\text{average of } n = \sum \mathbb{P}(n;\overline{n})n = \overline{n}, \qquad\qquad var(n) = \sigma^2 = \overline{n} = \lambda\tau.$$

---

[9] This is in contrast to the Gaussian distribution, whose description requires two parameters: $\overline{X}$ and σ^2.

Thus, the mean and variance are both equal to $\overline{n}$. The standard deviation, $\sigma = \sqrt{\overline{n}}$, gives the error in the measurement. For the mean, the proof is trivial and left as an exercise. For the variance, the proof is easy but requires more steps.[10]

1.4.34.4. *Error Bars of a Measurement.* If the experiment yields a mean count of n, the best estimate of the error[11] in this quantity is $\sqrt{n}$. We report this measurement as

$$\boxed{n \pm \sqrt{n}.}$$

While it may seem that the error grows with n, the fractional uncertainty actually decreases with n:

$$\frac{\delta n}{n} = \frac{\sqrt{n}}{n} = \frac{1}{\sqrt{n}}$$

i.e., larger n result in smaller fractional uncertainty.

1.4.34.5. *Poisson Counts.* This example was taken from the book by Hughes & Hase and modified. A bridge cannot hold too many cars at once due to the potential for structural damage. A particular bridge is designed to hold less than 13 cars (safe level) per time interval (1 min.). In a random sample, the total number of cars recorded crossing the bridge in 10 hours was 1980.

Q: What is the average number of cars crossing per minute and its error? A: $\lambda = \frac{1980}{10\times 60} =$ 3.30 cars/min.

$$\delta\lambda = \frac{\sqrt{1980}}{10 \times 60} = 0.07 \text{ cars/min.}$$

Q: What is the probability that during a random one-minute interval 13 cars will be observed crossing? A: $\overline{n} = \lambda\tau = 3.30$, with $n = 13$

$$\mathbb{P}(n = 13; 3.3) = \frac{e^{-3.3} 3.3^{13}}{13!} = 3.3 \times 10^{-5}$$

Q: What is the probability that the bridge will fail (due to too many cars crossing)? A:

$$\begin{aligned}\mathbb{P}(13 \text{ or more cars}) =& 1 - \mathbb{P}(12 \text{ or fewer cars}) \\ =& 1 - \{\mathbb{P}(0; 3.3) + \mathbb{P}(1; 3.3) + \cdots + \mathbb{P}(12; 3.3)\} \\ =& 4.2 \times 10^{-5}.\end{aligned}$$

During 1 minute of observation, this is the probability that the bridge will fail.

---

[10] A proof can be found at: `https://proofwiki.org/wiki/Variance_of_Poisson_Distribution`

[11] Sometimes, all we have is 1 count. While this may not be the mean count, it is all that we have. The best we can do in this case is report $n \pm \sqrt{n}$.

1.4.34.6. *Poisson Distribution in the Limit of Large Means.* For large means, the Poisson distribution converges to a Gaussian distribution:

$$\boxed{\frac{e^{-\overline{n}}\overline{n}^n}{n!} \approx \frac{1}{\sqrt{2\pi\mu_X}} \exp\left(-\frac{(x-\mu_X)^2}{2\mu_X}\right)}$$

where:

$$\begin{aligned} n \text{ (discrete)} &\to x \text{ (continuous)} \\ \overline{n} &\to \mu_X \text{ (variance, mean)} \\ \sqrt{\overline{n}} &\to \sqrt{\mu_X} \text{ (standard deviation)} \end{aligned}$$

The proof makes use of Stirling's approximation

$$\log n! \approx n \log n - n + O(\log n),$$

and

$$\frac{|n-\overline{n}|}{\overline{n}} \ll 1.$$

These two conditions (Stirling approx. and $\overline{n}$ close to n) imply that our proof is valid in the limit of large means. If the mean is not large, the Stirling approximation cannot be used.

$$\begin{aligned} \frac{e^{-\overline{n}}\overline{n}^n}{n!} &= \exp\left\{-\overline{n} - \log n! + n \log \overline{n}\right\} \\ &= \exp\left\{-\overline{n} - n\log n + n + n\log\overline{n}\right\} \\ &= \exp\left\{(n-\overline{n}) + n\log(\overline{n}/n)\right\} \\ &= \exp\left\{(n-\overline{n}) + n\log\left[1 + \left(\frac{\overline{n}-n}{n}\right)\right]\right\} \\ &\approx \exp\left\{-\frac{(\overline{n}-n)^2}{2n}\right\} \approx \exp\left\{-\frac{(\overline{n}-n)^2}{2\overline{n}}\right\} \end{aligned}$$

The first step was to invoke the Stirling's approximation, $\log n! \approx n \log n - n$. The second step was to expand about mean ($\overline{n}$) for large $\overline{n}$). Then we Taylor expanded $\log(1+x) \approx x - x^2/2 + O(x^3)$. In the last step we have used the approximation $n \approx \overline{n}$ near the mean for the denominator in the argument of the exp.

The prefactor $\frac{1}{\sqrt{2\pi\overline{n}}}$ could have been recovered had we used the slightly more accurate form of the Stirling's formula:

$$n! \approx \sqrt{2\pi n}\left(\frac{n}{e}\right)^n,$$

and of course, followed by the application of $\frac{|n-\overline{n}|}{\overline{n}} \ll 1$ to justify replacing $\sqrt{2\pi n}$ by $\sqrt{2\pi\overline{n}}$. See Problem 21.

1.4.34.7. *Statistical Independence (Discrete Case).* The notion of statistical independence is the same as in the continuous case. Let X and Y be two rv's. Independence of X and Y means that the joint probability factors as a product:

$$p_{ij}^{XY} = p_i^X \cdot p_j^Y, \text{ for all } i, j \tag{1.15}$$

where p^{XY} is the joint PMF for X and Y. p_i^X is a marginal PMF:

$$p_i^X \equiv \sum_j p_{ij}^{XY}.$$

Likewise, p_j^Y is also a marginal PMF:

$$p_j^Y \equiv \sum_i p_{ij}^{XY}.$$

1.4.35. Example 1. Consider a random experiment that involves rolling a die

$$X \in \{1, 2, 3, 4, 5, 6\}$$

and tossing a coin

$$Y \in \{H, T\}.$$

You are asked to determine whether or not X is statistically independent from Y. Intuitively, this should be the case (i.e., why would a coin toss affect the outcome of rolling a die?).

For this random experiment, there are 12 possible "elementary" outcomes:

$$\begin{aligned}
(X,Y) =&(1,H), & (X,Y) =&(1,T),\\
(X,Y) =&(2,H), & (X,Y) =&(2,T),\\
(X,Y) =&(3,H), & (X,Y) =&(3,T),\\
(X,Y) =&(4,H), & (X,Y) =&(4,T),\\
(X,Y) =&(5,H), & (X,Y) =&(5,T),\\
(X,Y) =&(6,H), & (X,Y) =&(6,T).
\end{aligned}$$

To get the joint PMF we must repeat this experiment many times and record the results. Suppose that we repeat the experiment 10,000 times and count the number of times each elementary outcome occurs. Let's do this in MATLAB:

```
>> X=randi([1 2],[1 10000]);
>> Y=randi([1 6],[1 10000]);
```

We then plot a 2D histogram (see Fig. 1.8):

```
>> figure; h=histogram2(X,Y)

h =
```

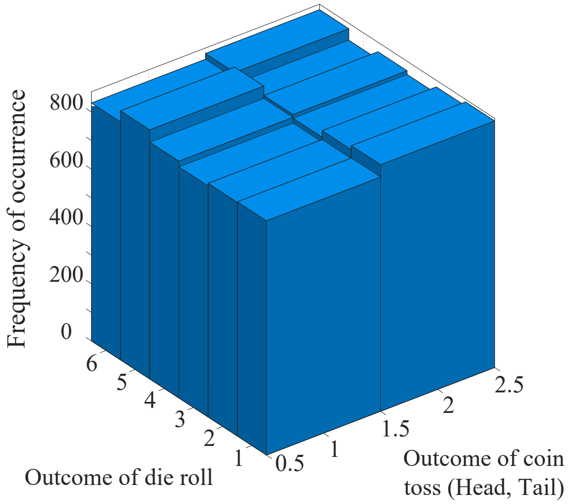


Figure 1.8. Bivariate histogram of the die & coin experiment.

```
  Histogram2 with properties:

             Data: [10000x2 double]
           Values: [2x6 double]
          NumBins: [2 6]
        XBinEdges: [0.5000 1.5000 2.5000]
        YBinEdges: [1x7 double]
         BinWidth: [1 1]
    Normalization: 'count'
        FaceColor: 'auto'
        EdgeColor: [0.1500 0.1500 0.1500]
```

The histogram is an approximation to the PMF. As you can see, this distribution is uniform. The values used to plot the histogram are:

```
>> h.Values

ans =

   818   816   807   827   870   831
   861   847   824   837   811   851
```

Dividing by the number of experiments performed (10,000):

```
>> h.Values/10000
```

X\Y	heads	tails	sum
1	1/12	1/12	1/6
2	1/12	1/12	1/6
3	1/12	1/12	1/6
4	1/12	1/12	1/6
5	1/12	1/12	1/6
6	1/12	1/12	1/6
sum	1/2	1/2	

Table 1.5. Joint PDF for an experiment that involves rolling a die ($X \in \{1,2,3,4,5,6\}$) and tossing a coin ($Y \in \{H,T\}$).

```
ans =

    0.0818    0.0816    0.0807    0.0827    0.0870    0.0831
    0.0861    0.0847    0.0824    0.0837    0.0811    0.0851
```

gives an approximation to the joint PMF. Each entry is approximately equal to 1/12. A PMF with entries equal to 1/12 can be represented as a matrix (see Table 1.5). The marginal PMFs for X and Y are obtained by summing along rows and columns, respectively. You can check that for the data shown in Table 1.5), Eq. (1.15) holds for all i, j. Therefore, X and Y are statistically independent.

We also know that statistical independence implies the variables are uncorrelated. Let's check this by computing the correlation coefficient:

```
>> corrcoef(X,Y)

ans =

    1.0000   -0.0115
   -0.0115    1.0000
```

The MATLAB command `corrcoef` computes the matrix of correlation coefficients, $\begin{bmatrix} \rho(X,X) & \rho(X,Y) \\ \rho(Y,X) & \rho(Y,Y) \end{bmatrix}$. The diagonal elements should be 1 (since X is fully correlated with X; same for Y) whereas the off-diagonal elements should be zero. Indeed, the off-diagonal elements are two orders of magnitude smaller than 1, indicating the lack of correlation between X and Y.

A counter-example illustrating statistical dependence would be the joint PMF shown in Table 1.6, which differs from Table 1.5 only in the second row. Namely, when the result from rolling the die is 2, the coin toss always yields "tails". (Don't try too hard to imagine how this can possibly happen in the lab; it is perhaps easier to imagine that a magician is doing the experiment for you.) Because $p^{XY}_{2,1} = 0 \neq p^X_2 \cdot p^Y_1 = \frac{1}{6} \cdot \frac{1}{2}$, we are unable to prove statistical independence of X and Y.

X\Y	heads	tails	sum
1	1/12	1/12	1/6
2	0/12	1/6	1/6
3	1/12	1/12	1/6
4	1/12	1/12	1/6
5	1/12	1/12	1/6
6	1/12	1/12	1/6
sum	1/2	1/2	

Table 1.6. Joint PDF for an experiment that involves rolling a die ($X \in \{1, 2, 3, 4, 5, 6\}$) and tossing a coin ($Y \in \{H, T\}$). This joint PMF is the same as that of Table 1.5 except for the second row.

1.4.36. Example 2. The joint distribution of the bivariate rv (X, Y) is given by

$$p_{XY}(x_i, y_j) = \begin{cases} k\dfrac{|x_i|}{2^{y_j}} & x_i = -1, 1; y_j = 1, 2, 3, \ldots \text{ (to infinity)} \\ 0 & \text{otherwise} \end{cases}$$

(a) k is a constant. Find the value of k.

$$\sum_i \sum_j p_{ij} = k2 \sum_j \frac{1}{2^{y_j}} = k2 \cdot 1 = 2k. \qquad k = 1/2.$$

(b) Find the marginal probability distributions of X and Y.

$$p_X(x_i) = \sum_j p_{ij} = \sum_j \frac{1}{2}|x_i| \frac{1}{2^{y_j}} = \frac{1}{2}|x_i|. \qquad x_i = -1, 1.$$

$$p_Y(y_j) = \sum_i p_{ij} = \frac{1}{2^{y_j}}. \qquad y_j = 1, 2, 3, \ldots$$

(c) Are X and Y statistically independent?

Forming the product of marginal distributions,

$$p_X(x_i)p_Y(y_j) = \frac{1}{2}|x_i| \cdot \frac{1}{2^{y_j}} = p_{XY}(x_i, y_j)$$

Hence X and Y are independent.

1.4.36.1. *Bernoulli(p) pmf.*

$$p_X(x) = \begin{cases} p & \text{if } x = 1, \\ q := 1 - p & \text{if } x = 0, \\ 0 & \text{otherwise} \end{cases};$$

1.4.36.2. *binomial(n, p) pmf.*

$$p_X(x) = \begin{cases} b(n,p;x) & \text{if } x = 0,1,\dots,n \\ 0 & \text{otherwise;} \end{cases};$$

If X has the Bernoulli(p) pmf, then we say that X has the Bernoulli(p) distribution and write

$$X \sim \text{Bernoulli}(p),$$

with similar remarks for the binomial(n, p) and Poisson(λ) distributions. Of course, the distribution function of a discrete r.v. with pmf p_X satisfies

$$\mathbb{P}(X < x) = \sum_{y \le x} p_X(y) := \sum_{\mathbb{Z} \ni y \le x} p_X(y),$$

and, for $a, b \in \mathbb{Z}$ with $a < b$, we have

$$\mathbb{P}(a < X \le b) = \mathbb{P}(X \le b) - \mathbb{P}(X \le a) = \sum_{y=a+1}^{b} p_X(y).$$

1.4.37. Cross-Correlation in Image Analysis. The concept of covariance leads to the cross-correlation analysis. Cross-correlation is a type of covariance that involves comparing two signals (or images) together through pixel-by-pixel multiplication of a window (or ROI) that is translated across different regions of a target signal (or image). If the two signals (or images) are of the same size, a single value is obtained. If the sliding window is smaller than the target signal (or image), the output is a function of the translation coordinate(s).

The 2D cross-correlation of a $M \times N$ matrix, X, and a $P \times Q$ matrix, H, is a matrix C, of size $M + P - 1$ by $N + Q - 1$. Its elements are given by:

$$C(x, y) = \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} X(m, n)\overline{H}(m - x, n - y), \qquad \begin{cases} -(P-1) \le x \le M - 1, \\ -(Q-1) \le y \le N - 1, \end{cases}$$

where the bar denotes complex conjugation. Likewise, a 1D signal can also be compared to another signal, for purposes of comparison or pattern recognition. The true cross-correlation sequence of two random samples $\{x_n\}$ and $\{y_n\}$ is

$$R_{xy}(m) = \langle x_{n+m} y_n^* \rangle = \langle x_n y_{n-m}^* \rangle,$$

where $-\infty < n < \infty$ and asterisk denotes complex conjugation. The raw cross-correlation is computed as:

$$\hat{R}_{xy}(m) = \begin{cases} \sum_{n=0}^{N-m-1} x_{n+m} y_n^*, & m \ge 0, \\ \hat{R}_{xy}^*(-m), & m < 0. \end{cases}$$

In MATLAB these two commands are implemented as `xcorr2` and `xcorr`, respectively. For more information including examples, see the MATLAB documentation:
`https://www.mathworks.com/help/signal/ref/xcorr2.html`
`https://www.mathworks.com/help/matlab/ref/xcorr.html`

1.5. Conditional Probability and Conditional Expectation

1.5.1. Conditional densities. The conditional density of X given Y is defined as

$$p_{X|Y}(x|y) = \frac{p_{X,Y}(x,y)}{p_Y(y)},$$

where $p_{X,Y}(x,y)$ is the joint PDF of X and Y, $p_Y(y)$ is the marginal PDF of Y. This is a consequence of the formula for conditional probability,

$$\mathbb{P}(A|B) = \frac{\mathbb{P}(A \cap B)}{\mathbb{P}(B)}$$

with $A = \{X = x\}$ and $B = \{Y = y\}$, i.e.

$$\begin{aligned}&\mathbb{P}(x < X \leq x + \mathrm{d}x | y < Y \leq y + \mathrm{d}y)\mathrm{d}x \\ &\qquad = \frac{\mathbb{P}(x < X \leq x + \mathrm{d}x, y < Y \leq y + \mathrm{d}y)\mathrm{d}x\mathrm{d}y}{\mathbb{P}(y < Y \leq y + \mathrm{d}y)\mathrm{d}y}.\end{aligned}$$

An interpretation of $p_{X|Y}(x|y)$ is obtained by integrating it:

$$\mathbb{P}(a < X \leq b | Y = y) = \int_a^b p_{X|Y}(x|y)\mathrm{d}x$$

(i.e. the probability that $X \in [a, b]$ given that $Y = y$). However, the left hand side $\{Y = y\}$ is an event with probability zero, which is ill-defined. We instead use a limit to circumvent this difficulty:

$$\mathbb{P}(a < X \leq b | Y = y) = \lim_{\epsilon \to 0} \mathbb{P}(a < X \leq b || Y - y| < \epsilon).$$

The conditional expectation of X given $Y = y$ is defined as

$$\langle X | Y = y \rangle = \int_{-\infty}^{\infty} x p_{X|Y}(x|y)\mathrm{d}x.$$

A consequence of this definition is:

$$\begin{aligned}\langle Y \rangle &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} y p_{X,Y}(x,y)\mathrm{d}x\mathrm{d}y \\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} y \left[p_{Y|X}(y|x)p_X(x)\right]\mathrm{d}x\mathrm{d}y \\ &= \int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty} y p_{Y|X}(y|x)\mathrm{d}y\right] p_X(x)\mathrm{d}x \\ &= \int_{-\infty}^{\infty} \langle Y | X = x \rangle p_X(x)\mathrm{d}x.\end{aligned}$$

An analogous concept of “conditional probability mass” exists for the case of discrete rv’s. See Problems 38 and 39 for more on conditional densities.

1.5.2. Conditional Expectation. We may also calculate expectation values under some condition. This is the same idea as calculating the normal expectation value, except that we use the conditional density instead of the regular density. For (a) the condition involves a random event H. If X is a rv, H is a random event and $p_{X|H}(x)$ is the conditional density of X under the condition H, the expectation value of X under the condition H is:

$$\langle X|H\rangle \equiv \int x p_{X|H}(x)\mathrm{d}x,$$

where the integral is over all possible values of X (i.e., the "range" of X). As an example, the event H could be $H = \{Y = 10\}$, or it could be $H = \{Y = y\}$ (where the value y remains unspecified). You can check that $\langle X|H\rangle$ is still linear in X. For (b) the condition is a rv, e.g., $\langle X|Y\rangle$. The conditional expectation $\langle X|Y\rangle$ is obtained by calculating $\langle X|Y = y\rangle$. The result will be a function of y. Then replace y by the rv Y. Notice that the end result for $\langle X|Y\rangle$ is itself a rv. In other words, to get $\langle X|Y\rangle$ we use $\langle X|Y = y\rangle$ together with $y = Y(\omega)$. The meaning of $\langle X|Y\rangle$ is "the function of Y that best approximates X".

From these definitions many properties follow. For example, it is easy to check that

$$\langle\langle Y|X\rangle\rangle = \int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty} y\, p_{Y|X}(y|x)\,\mathrm{d}y\right] p_X(x)\,\mathrm{d}x = \int_{-\infty}^{\infty} y\, p_Y(y)\,\mathrm{d}y = \langle Y\rangle.$$

We used the definitions of conditional probability $p_{Y|X}(y|x)p_X(x) = p_{XY}(x, y)$ and marginal density $p_Y(y) = \int_{-\infty}^{\infty} p_{XY}(x, y)\mathrm{d}x$. More properties of conditional expectations can be found at this site (click on *Proof* to obtain the proofs of various results):

`https://www.randomservices.org/random/expect/Conditional.html`

In Problem 40 you are asked to calculate expectation values under some condition.

1.6. Signal Averaging Reduces Relative Error

An important concept in experimental science is that of "signal averaging". This is done to reduce the noise error, or equivalently, to reduce the size of the error bars relative to the measurement. Suppose X is a rv and we perform n measurements of X. We obtain the data set $\{x_i = X(\omega_i)\}_{i=1}^{n}$. Another way to view this experiment is to consider the simultaneous measurement of n independent rv's $X_1, \ldots, X_n$, each of which has the same distribution as X: each has mean μ_X and variance ($var(X_i) < \infty$). We form the average:

$$\overline{X_{av}}(\omega) = \frac{X_1(\omega) + X_2(\omega) + \cdots + X_n(\omega)}{n},$$

where a single value of ω is used, as we assumed simultaneous measurement of $X_1, \ldots, X_n$. The variance of this sum is

$$var(\overline{X_{av}}) = \frac{\sum_{i=1}^{n} var(X_i)}{n^2} \propto \frac{1}{n},$$

where we used the property $var(aX) = a^2 var(X)$. The noise is the square root of the variance $\sigma = \sqrt{var(\overline{X_{av}})}$. Thus, signal averaging reduces the noise from random errors.

We have just derived the formula for standard error: the mean of $\overline{X_{av}}(\omega) = \frac{X_1(\omega)+X_2(\omega)+\cdots+X_n(\omega)}{n}$ is μ_X (where $\mu_X = \langle X \rangle$) and its standard deviation is $\sqrt{var(X)/n} = \sigma_X/\sqrt{n}$. We recognize this as the standard error.

If the X_i are iidrv the signal-to-noise ratio (SNR) is defined as:

$$\mathrm{SNR} = \frac{\text{signal}}{\text{noise}} = \frac{\overline{X_{av}}}{\sqrt{var(\overline{X_{av}})}} \propto \sqrt{n}$$

Thus, SNR improves with signal averaging.

1.7. Some Theorems on Random Variables

1.7.1. Normal Linear Transform Theorem. The normal linear transform theorem is:

$$\boxed{\alpha + \beta \mathcal{N}_1(\mu, \sigma^2) = \mathcal{N}_2(\alpha + \beta\mu, \beta^2\sigma^2).}$$

(We denoted $\mathcal{N}$ with subscripts 1 and 2 to emphasize that they are different rv's, i.e., the rv on the right hand side is created from the rv on the left hand side.)

Proof: Let $Y = \alpha + \beta X$, where $X \sim \mathcal{N}_1(\mu, \sigma^2)$. Write

$$\begin{aligned}\mathbb{P}(Y < a) = \mathbb{P}(\alpha + \beta X < a) = \mathbb{P}(X < (a-\alpha)/\beta)& \\ = \int_{-\infty}^{(a-\alpha)/\beta} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2} \mathrm{d}x.&\end{aligned}$$

and make a substitution of variables $y = \alpha + \beta x$, $\mathrm{d}y = \beta \mathrm{d}x$ to get an integral of the form $\int_{-\infty}^{a} p_Y(y)\mathrm{d}y$:

$$= \int_{-\infty}^{a} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-((y-\alpha)/\beta-\mu)^2/2\sigma^2} (\mathrm{d}y/\beta) = \int_{-\infty}^{a} \frac{1}{\sqrt{2\pi\beta^2\sigma^2}} e^{-(y-\alpha-\beta\mu)^2/2\beta^2\sigma^2} \mathrm{d}y,$$

which is the CDF of a normal rv with mean $\alpha + \beta\mu$ and variance $\beta^2\sigma^2$. In the special case $\mu = 0$, $\sigma^2 = 1$ we have:

$$\alpha + \beta \mathcal{N}_1(0, 1) = \mathcal{N}_2(\alpha, \beta^2).$$

1.7.2. Normal Sum Theorem. The normal sum theorem is:

$$\boxed{\mathcal{N}_3(\mu_1 + \mu_2, \sigma_1^2 + \sigma_2^2) = \mathcal{N}_1(\mu_1, \sigma_1^2) + \mathcal{N}_2(\mu_2, \sigma_2^2),}$$

where on the right-hand-side is the sum of two statistically independent rv's. In other words, let $X \sim \mathcal{N}_1(\mu_1, \sigma_1^2)$ and $Y \sim \mathcal{N}_2(\mu_2, \sigma_2^2)$ be independent rv's. (We denoted $\mathcal{N}$ with subscripts 1, 2 and 3 to emphasize that they are different rv's.) We are asking what is the distribution of the new rv $U = X + Y$. The proof of this involves handling a 2D integral of the joint PDF of X and Y:

$$\mathbb{P}(X+Y<a)=\frac{1}{2\pi\sigma_1\sigma_2}\iint\limits_{\{(x,y)|x+y<a\}} e^{-\frac{(x-\mu_1)^2}{2\sigma_1^2}}e^{-\frac{(y-\mu_2)^2}{2\sigma_2^2}}\mathrm{d}x\mathrm{d}y.$$

With some effort, you should be able to simplify this double-integral and show that it is the CDF of the rv $X+Y$ (use the change of variables $V=X+Y$, $Z=Y$).

1.7.3. Sum of Independent Gaussians. Suppose that $X_1,\ldots,X_n$ are iidrv and normal, say, $\mathcal{N}(0,1)$. The distribution of their sum is also normal. This can be proven by induction, using the result from Section 1.7.2.

1.7.4. Sum of Two Independent Cauchy's. Let X,Y be independent Cauchy rv's. What is the distribution of their sum $X+Y$? We start with the CDF:

$$\mathbb{P}(X+Y<a)=\iint\limits_{\{(x,y)|x+y<a\}}\frac{1}{\pi^2}\frac{1}{(1+x^2)}\frac{1}{(1+y^2)}\mathrm{d}x\mathrm{d}y.$$

Let us effect a change of variables: $u=x+y$ and $v=y$. The inverse is $y=v$ and $x=u-v$. The area element is:

$$\mathrm{d}x\mathrm{d}y=\left|\frac{\partial(x,y)}{\partial(u,v)}\right|\mathrm{d}u\mathrm{d}v=\left|\det\begin{pmatrix}1&1\\0&1\end{pmatrix}\right|\mathrm{d}u\mathrm{d}v=\mathrm{d}u\mathrm{d}v.$$

In the new coordinates, the integral is:

$$\mathbb{P}(X+Y<a)=\frac{1}{\pi^2}\int_{-\infty}^{a}\mathrm{d}u\int_{-\infty}^{\infty}\mathrm{d}v\frac{1}{(1+(u-v)^2)}\frac{1}{(1+v^2)}.$$

To solve the integral over v go to `www.wolframalpha.com` and type:

```
integrate (1/(1+(u-v)^2))*(1/(1+v^2)) from v=-infinity to infinity
```

The result is:

$$\int_{-\infty}^{\infty}\mathrm{d}v\frac{1}{(1+(u-v)^2)}\frac{1}{(1+v^2)}=\frac{2\pi}{4+u^2}.$$

This gives the CDF in integral form. Differentiating with respect to a gives the PDF:

$$p_{X+Y}(a)=\frac{1}{\pi}\frac{2}{(4+a^2)}=\frac{1}{\pi}\frac{1}{2(1+(a/2)^2)}.$$

The general Cauchy distribution has PDF $p(x)=\left[\pi\gamma\left(1+\left(\frac{x-x_0}{\gamma}\right)^2\right)\right]^{-1}$, where x_0 is the center and γ is the scale parameter (related to the width). Thus, adding two Cauchy rv's centered at 0 with "scale parameter" of $\gamma=1$ results also in a Cauchy distribution centered at 0, but with $\gamma=2$ (i.e. it is twice as broad as the $\gamma=1$ case).

1.7.5. Central Limit Theorem. One of the most important theorems in probability theory is the central limit theorem (CLT). The CLT describes many important physical phenomena observed in nature that arise from the sum of many independent random effects (e.g. microscopic forces). Loosely speaking, the central limit theorem states that regardless of the distribution of these random effects, the limiting distribution is Gaussian.

Let $(X_1, \ldots, X_n)$ be a sequence of iidrv (independent identically distributed rv), each having mean μ_X and variance σ^2. Then,

$$\lim_{n\to\infty} \text{rv}\left\{\frac{1}{n}\sum_{i=1}^{n}(X_i - \mu_X)\right\} \xrightarrow{d} \frac{1}{\sqrt{n}}\mathcal{N}(0, \sigma^2).$$

This is equivalent to saying that the arithmetic average $\frac{1}{n}\sum_{i=1}^{n} X_i$ converges[12] (in distribution) to a *normal law* with mean μ_X and variance $\dfrac{\sigma^2}{n}$:

$$\boxed{\lim_{n\to\infty} \text{rv}\left\{\frac{1}{n}\sum_{i=1}^{n} X_i\right\} \xrightarrow{d} \mathcal{N}\left(\mu_X, \frac{\sigma^2}{n}\right).}$$

The quantities $\{X_i\}$ are rv's. Their sum is also a rv; the CLT states that the sum will be Gaussian-distributed.

Note: that the arithmetic average should also have the mean μ_X comes as no surprise. But also that the variance $\frac{\sigma^2}{n}$ scales as $1/n$ should come as no surprise if you recall the definition of standard error, which states that the error in the mean scales as $1/\sqrt{n}$.

The central limit theorem is very important in the physical sciences because many physical measurements yield Gaussian distributions as a result of the effects of many small additive forces. For example, the Brownian motion of a particle is the result of many small collisions with solvent molecules, yielding a Gaussian distribution for the net displacement.

The CLT is illustrated in Fig. 1.9. The histogram on the left represents the probability distribution of a single rv, X_1. The histogram in the center is the distribution of the average of two such iidrv $\frac{1}{2}(X_1 + X_2)$. The histogram on the right is the distribution for the average of 10 iidrv, $\frac{1}{10}(X_1 + X_2 + \cdots + X_{10})$. As can be seen, while each rv has a uniform (flat) distribution, as the histogram on the left shows, the more rv's we average, the closer the distribution of the average approaches a normal (bell-shaped) distribution.

1.7.5.1. *Random Walk in One Dimension.* The random walk, which is an application of the CLT, is important in the physical sciences. Brownian motion is a limit of the random walk.

Let X_i be the rv which denotes the displacement at the i-th step

$$X_i \in \{-\sigma, +\sigma\}$$

---

[12] Convergence in distribution means that the distribution functions converge pointwise:

$$\lim_{n\to\infty} \mathbb{P}(\overline{X}_n \le x) = F_n(x),$$

where $F_n(x)$ denotes the CDF of the normal random variable with mean μ and variance σ^2/n and $\overline{X}_n = \frac{1}{n}(X_1 + \cdots + X_n)$.

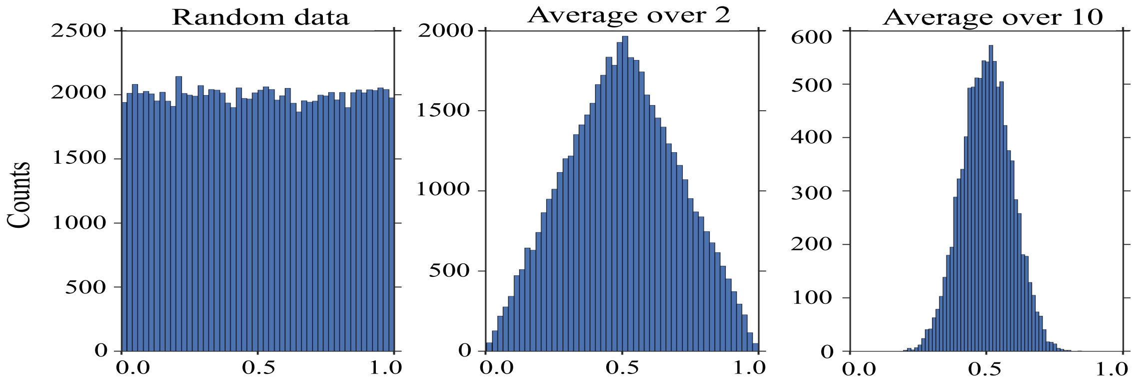


Figure 1.9. Illustration of the central limit theorem.

and each outcome occurs with equal probabilities, i.e.

$$p_\sigma = \frac{1}{2} \qquad \text{and} \qquad p_{-\sigma} = \frac{1}{2}.$$

These displacements at different points in time are assumed to be statistically independent. After n such steps the net displacement is

$$S_n = X_1 + \cdots + X_n,$$

where $\overline{X_i} = \frac{1}{2}\sigma + \frac{1}{2}(-\sigma) = 0$. Therefore, $\overline{S_n} = 0$. Also, $\text{var}X_i = \frac{1}{2}(\sigma^2) + \frac{1}{2}(-\sigma)^2 = \sigma^2$. Then,

$$\text{var}X_i = \overline{X_i^2} - \overline{X_i}^2 = \sigma^2.$$

By statistical independence of the X_i's:

$$\overline{S_n^2} = \sum_{i=1}^{n} \text{var}X_i = n\sigma^2,$$

The total duration of the random walk is $t = n\Delta t$. We have

$$\overline{S_n^2} = \left(\frac{\sigma^2}{\Delta t}\right) t = 2D\,t.$$

The quantity $D = \frac{\sigma^2}{2\Delta t}$ is called the *diffusion constant* (or diffusion coefficient). D has units of length square divided by time (e.g. m^2/s).

By the central limit theorem, we have that

$$\boxed{\lim_{n\to\infty} S_n = X_1 + \cdots + X_n \sim \mathcal{N}(0, n\sigma^2)}$$

$\lim S_n \sim \mathcal{N}(0, n\sigma^2)$ means that its PDF is

$$p_{S_n}(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left[-\frac{x^2}{4Dt}\right].$$

This PDF is also called transition probability density.[13] It is the probability of finding the particle at (x, t) under the condition that it was at position $x = 0$ at time $t = 0$.

The average position of the random walker after the n-th step is zero: $\overline{S_n} = 0$. This means that if we repeat the random walk experiments, say 10,000 times, the average position after n steps will be zero. It *does not* mean that the random walker automatically returns to the origin. It is merely a statement about the random walk when the walk is repeated many times.

On the other hand, the result $\overline{S_n^2} = 2D\,t$ about the mean square displacement being proportional to t (or root mean square displacement, x, being proportional to $\sqrt{t}$) should be contrasted to the case of ballistic motion for which $x = vt$ (displacement proportional to t). The different powers of t reflect the fact that in diffusional motion, there is a lot of back-and-forth, leading to a shorter displacement over time.

1.7.5.2. *Random Walk in Three Dimensions.* In three dimensions, the displacement is a 3-components vector $R = (X, Y, Z)$. If the components X, Y, Z are statistically independent of each other, the joint probability density is a product:

$$p_{XYZ}(x, y, z, t) = p_X(x, t) p_Y(y, t) p_Z(z, t),$$

where $p_X(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{x^2}{4Dt}\right]$, etc. (for each component). Applying the result of the previous section for each direction (component), we obtain the joint probability density for the 3D random walk:

$$\boxed{p_{XYZ}(x, y, z, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)}$$

where $r^2 = x^2 + y^2 + z^2$, $\vec{r} = (x, y, z)$.

In 3D the mean square displacement (MSD) is[14]

$$\langle r^2 \rangle = \langle x^2 + y^2 + z^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 2Dt + 2Dt + 2Dt = 6Dt.$$

In the general case of d dimensions, $\vec{r} = (x_1, \dots, x_d)$, the MSD is:

$$\langle r(t)^2 \rangle = \langle x_1^2 + \cdots + x_d^2 \rangle = 2dDt.$$

---

[13] A transition probability density is written $p(x, t|y, s)$ to the denote the probability of finding a particle at position x at time t given that it was initially at position y at some earlier time s.

[14]

$$\langle r(t)^2 \rangle \equiv \frac{1}{(4\pi Dt)^{3/2}} \iiint_{\mathbb{R}^3} r^2 \exp\left(-\frac{r^2}{4Dt}\right) \mathrm{d}^3 r$$

.

1.8. Importance Sampling

1.8.1. Law of Large Numbers (LLN). Let $X_1, \ldots, X_n$ be a sequence of iiddv each with mean μ. We form the sample mean:

$$\overline{X}_n = \frac{1}{n}\sum_{i=1}^{n} X_i = \frac{1}{n}(X_1 + \cdots + X_n).$$

Then, for any $\epsilon > 0$,

$$\boxed{\lim_{n\to\infty} \mathbb{P}(|\overline{X}_n - \mu| > \epsilon) = 0.}$$

This is the *weak law of large numbers* (WLLN). For a proof of the WLLN, see Problem 17. $\overline{X}_n$ is the *sample mean.* The *strong law of large numbers* is[15]

$$\boxed{\mathbb{P}\left(\lim_{n\to\infty} |\overline{X}_n - \mu| > \epsilon\right) = 0.}$$

Both weak and strong LLN are statements about how the sample mean converges to the real mean. However, there is an important difference: the weak LLN tells us how sequences of probabilities ($\mathbb{P}$) converge whereas the strong LLN tells us how the sequence of rv $\overline{X}_n$ behaves in the limit. The CLT, on the other hand, is a much stronger[16] statement: the sample mean (arithmetic average) rv converges (in distribution) to a normal law. The central limit theorem (CLT) should not be confused with the LLN.

1.8.1.1. *WLLN In Words.* The statement $\lim_{n\to\infty} \mathbb{P}(|\overline{X}_n - \mu| > \epsilon) = 0$ for any $\epsilon > 0$ simply means that if we take any sequence of iidrv's $X_1, \ldots, X_n$, their arithmetic average tends to their mathematical expectation as $n \to \infty$. Thus, we can approximate mathematical expectations (which may be difficult to compute, especially if the distribution is unknown), using arithmetic averages formed using experimental data. The larger n is, the better the approximation of the mathematical expectation.

Since X_i are rv's, the WLLN formulation also applies to functions of rv's, $Y_i = f(X_i)$, since the latter are also rv's. If desired, f could be almost any formula. For example, suppose that X_i is the acceleration of a particle, a_i (i.e., $X_i \equiv a_i$). The force is mass times acceleration: $F(X_i) = ma = mX_i$. The WLLN allows us to compute not only the average acceleration, $\langle X_i \rangle$, but the average force, $\langle F(X_i) \rangle$, by simply renaming $Y_i = f(X_i)$ and applying it to the sequence $\{Y_i\}$.

1.8.2. Expectation With Respect To Probability Measure. The mathematical expectation of X was defined as:

$$\langle X \rangle = \int_{\mathbb{R}} xp(x)\mathrm{d}x,$$

---

[15] The proof of the strong law requires the Borel-Cantelli lemma, which we have not covered.

[16] This is a stronger statement because it is a statement about the entire distribution law of a rv, not just its mean and variance.

where $p(x)$ is the PDF of X and the integral is taken over the range of X (here, $\mathbb{R}$). $p(x)\mathrm{d}x$ is the probability measure. It will be useful to use the notation $\langle X\rangle_p$ to emphasize that the PDF used to calculate the mathematical expectation is p. This way, there is no ambiguity as to which probability measure is used. For example, if the PDF of Y is $q(y)$, then we write:

$$\langle Y\rangle_q = \int yq(y)\mathrm{d}y.$$

(Note: y is a dummy integration variable; the choice of symbol is unimportant.) The WLLN states that if Y is distributed according to $q(y)$, then its mathematical expectation can be approximated by the arithmetic average:

$$\langle Y\rangle_q \approx \frac{1}{n}\sum_{i=1}^{n} Y_i,$$

where the Y_i's are sampled according to the distribution q. If instead the PDF of Y had been some other function f, we would have written $\langle Y\rangle_f$ for $\int yf(y)\mathrm{d}y$. The two numerical values $\langle Y\rangle_f$ and $\langle Y\rangle_q$ can, of course, be different, since f and q may be different functions.

As far as the WLLN is concerned, it is meant to enable us to approximate mathematical expectations of rv's (or functions of rv's) by arithmetic averages constructed using experimental data. We present several examples below to illustrate applications of the WLLN. The WLLN is best explained by working out specific examples.

1.8.3. Numerical Integration by Monte-Carlo Method. Monte-Carlo methods can be used to estimate the numerical value of integrals. For example, suppose we want to compute the integral:

$$I = \int_a^b h(x)\mathrm{d}x$$

which is the same as

$$I = \int_a^b \frac{h(x)(b-a)}{(b-a)}\mathrm{d}x = \int_a^b u(x)p(x)\mathrm{d}x = \langle u(X)\rangle_p$$

where $\langle\cdot\rangle_p$ denotes the mathematical expectation with respect to the PDF $p(x)$ and

$$u(x) = h(x)(b-a), \qquad p(x) = \frac{1}{(b-a)}.$$

Thus, $p(x)$ is the PDF of a uniformly distributed rv. This integral can be evaluated by generating random numbers $X_1,\ldots,X_n$ that are iidrv and uniformly distributed on the interval $[a,b]$. By the WLLN, the following estimator converges to I:

$$\hat{I} = \frac{1}{n}\sum_{i=1}^{n} u(X_i) \to \langle u(X)\rangle_p = \int_a^b u(x)p(x)\mathrm{d}x = I.$$

This gives us a way to evaluate integrals by generating random numbers. For multidimensional integrals, this method has important advantages. Namely, the generation of random numbers followed by estimation of I is less computationally intensive than the direct numerical integration (by quadratures) of the multi-dimensional integral.

There is no special reason to pick the uniform distribution. In fact, any distribution $p(x)$ can be used. In some cases, special choices of $p(x)$ may be advantageous. For example, sampling the domain $[a, b]$ may be a waste of time if most of the points within that interval correspond to regions where $h(x)$ is zero or nearly zero. In that case, we instead want to sample regions of the domain where $|h(x)| > 0$ is concentrated.

In other words, let

$$I = \int_a^b h(x)\mathrm{d}x = \int_a^b \frac{h(x)}{p(x)} p(x)\mathrm{d}x = \langle u(X) \rangle_p, \qquad u(x) = \frac{h(x)}{p(x)}$$

and choose $p(x)$ such that the "peaks" of p correspond to the peaks of h. The numerical value of I can be estimated by sampling iidrv $X_1, \ldots, X_n$ according to $p(x)$ and computing the sum:

$$I \approx \frac{1}{n} \sum_{i=1}^{n} u(X_i) = \frac{1}{n} \sum_{i=1}^{n} \frac{h(X_i)}{p(X_i)}, \qquad X_i \sim p(x).$$

1.8.4. Change of Distribution. Suppose that X is a rv with PDF $p(x)$ and we want to calculate the average of a function, $f(X)$ of X. Let $q(x) > 0$ be another PDF on the same probability space as p. Then,

$$\langle f(X) \rangle_p = \int f(x)p(x)\mathrm{d}x = \int \frac{f(x)p(x)}{q(x)} q(x)\mathrm{d}x = \langle \left(\frac{f(X)p(X)}{q(X)} \right) \rangle_q .$$

Here, $\langle f(X) \rangle_p$ denotes the mathematical expectation of f calculated using the PDF $p(x)$ for X, whereas $\langle \left(\frac{f(X)p(X)}{q(X)} \right) \rangle_q$ is the expectation of fp/q calculated by associating the PDF $q(x)$ to X instead.

In the first case, $X_1, \ldots, X_n$ random numbers are sampled from the distribution $p(x)$ and the integral is estimated as:

$$\langle f(X) \rangle_p \approx \frac{1}{n} \sum_{i=1}^{n} f(X_i).$$

Convergence is assured by the LLN. In the second case, $X_1, \ldots, X_n$ are sampled from the distribution $q(x)$ and the integral is estimated as

$$\langle \left(\frac{f(X)p(X)}{q(X)} \right) \rangle_q \approx \frac{1}{n} \sum_{i=1}^{n} \frac{f(X_i)p(X_i)}{q(X_i)}.$$

The correction factor p/q is called the likelihood ratio. This method, of course, requires us to be able to compute the ratio p/q for any value of X that we may sample. The idea is to choose an importance distribution q that leads to faster convergence than the nominal distribution p. We generally want to choose q such that its spikes correspond to those of

fp; in fact, it can be shown that q should be proportional to fp. Choosing q can be done using an "educated guess" or by random sampling of the function.

1.8.5. Calculation of Probabilities. Since probabilities are expectation values of indicator functions, the WLLN can also be used to speed up the calculation of probabilities. This is especially useful for rare events. For example, suppose we want to calculate the probability of an event $\{X \in A\}$, where the PDF for X is $p(x)$. From experimental measurements $X_1, \ldots, X_n$, this would normally be approximated by

$$\mathbb{P}(X \in A) = \langle \mathbf{1}_{X\in A}\rangle_p = \int_{\mathbb{R}} \mathbf{1}_A(x)p(x)\mathrm{d}x \approx \frac{1}{n}\sum_{i=1}^{n} \mathbf{1}_A(X_i) = \frac{\#\text{ draws in A}}{n}$$

where $\mathbf{1}_A(x)$ is the indicator function of A, i.e. it is a function that equals 1 when $x \in A$ and 0 otherwise. However, if $p(x)$ is such that this event rarely happens, we are going to need n very large or else the result will be zero.

On the other hand, the WLLN enables us to reweigh the integral, if we can find a better distribution $q(x)$ that samples values that are closer to the set A:

$$\langle \mathbf{1}_{X\in A}\rangle_p = \langle [\frac{\mathbf{1}_A(X)p(X)}{q(X)}]\rangle_q \approx \frac{1}{n}\sum_{i=1}^{n} \frac{\mathbf{1}_A(X_i)p(X_i)}{q(X_i)}. \qquad X_i \sim q(x)$$

If the event is rare, the ratio p/q will be small (yielding the correct probability for the rare event), whereas the summation will count several non-zero terms, giving a more accurate answer (for the same n).

A special case of $\mathbb{P}(X \in A)$ is the estimation of the CDF, $\mathbb{P}(X < x)$, which can be expressed as $\langle \mathbf{1}_{\{X<x\}}\rangle_p$, and which equals to $\langle \left[\frac{\mathbf{1}_{\{X<x\}}p(X)}{q(X)}\right]\rangle_q$. And if $q(x)$ is a better distribution than $p(x)$, we can use the latter formula, together with the WLLN, to approximate the CDF by a summation.

1.8.6. Generalization to d-Dimensions. All of the above formulas are valid in d-dimensions. $x \in \mathbb{R}$ and $X \in \mathbb{R}$ are replaced by $\mathbf{x} \in \mathbb{R}^d$ and $\mathbf{X} \in \mathbb{R}^d$, respectively. Likewise, $\mathrm{d}x$ stands for $\mathrm{d}^d\mathbf{x}$, the d-dimensional volume element in the d-dimensional integral.

1.9. Comparing Distributions

Given some random samples $x_1, \ldots, x_n$ and $y_1, \ldots, y_n$ of two rv's X and Y, respectively. It is natural to compare them to see if there is a difference between them. We have already mentioned that one may compare sample means, sample variances and sample covariance. However, these statistical quantifiers are the lowest order moments (first, second) of the distributions. They do not provide a complete comparison. Two rv's are identical if and only if their distributions match. To compare distributions, we must use distance metrics. In this section we discuss a number of popular methods: the Kolmogorov-Smirnov test, the cross entropy, the Bhattacharyya distance, Wasserstein metric and the Kullback-Leibler divergence.

In mathematics a metric on a set X is a function $d : X \times X \to [0, \infty)$ that obeys the following conditions for all $x, y, z \in X$: 1) $d(x, y) = 0$ if and only if $x = y$. 2) $d(x, y) = d(y, x)$ (symmetry). 3) $d(x, y) \leq d(x, z) + d(z, y)$ (triangle inequality).

1.9.1. Kolmogorov-Smirnov test.

1.9.2. Cross entropy.

1.9.3. Bhattacharyya distance.

1.9.4. Wasserstein metric.

1.9.5. Kullback-Leibler divergence and the Relative Entropy.

1.9.5.1. *Entropy.* Suppose we have a rv X taking values x in the set $\mathcal{X}$ each with probability $p(x)$. The Shannon entropy

$$H[X] = -\sum_{x \in \mathcal{X}} \mathbb{P}(X = x) \log \mathbb{P}(X = x) \qquad \text{(discrete rv } X\text{)}$$

or

$$H[X] = -\int p(x) \log p(x) \mathrm{d}x \qquad \text{(continuous rv } X\text{)}$$

quantifies the "lack" of information about the system described by $p(x)$. For example, if we have a system that can be found in 6 possible states with probabilities $(1, 0, 0, 0, 0, 0)$, the entropy is lowest ($H = 0$). On the other hand, if the probability distribution is $(1/6, 1/6, 1/6, 1/6, 1/6, 1/6)$ (uniform distribution) the entropy is maximal. The uniform distribution shows the system can be found in any of its 6 states with equal probability; therefore we do not know anything about its state. In the case of the first distribution we know exactly which state the system is in (the first state). If entropy quantifies the lack of information, the negative of the entropy quantifies information.

There are other measures of entropy. The Renyi entropy measure is

$$H_\alpha^R[X] = \frac{1}{1-\alpha} \log \sum_{x \in \mathcal{X}} \mathbb{P}(X = x)^\alpha.$$

The Tsallis entropy measure is

$$H_\alpha^T[X] = c \frac{\sum_{x \in \mathcal{X}} \mathbb{P}(X = x)^\alpha - 1}{1 - \alpha}.$$

Here, $\alpha > 0$ is a positive parameter and c is a positive constant depending on the particular units used. Both of these families include the Shannon measure as a special case in the limit $\alpha \to 1$, where $H_1^R(p) = H_1^T(p) = H(p)$. We may interchangeably write $H(p)$ for $H[X]$

and vice versa, since X is defined by its distribution p. From this, we see that

$$H(p) = -\frac{1}{n} \log p(x^n)$$

where $p(x^n) = \prod_{i=1}^n p(x_i)$. This expression for $H(p)$ is called the empirical entropy of the empirical probability distribution.

1.9.5.2. *Empirical entropy.* The above definitions presume that we know the distributions. Suppose that instead we have data $x_1, x_2, \ldots, x_n$ all taking values in the discrete set $\mathcal{X}$. The empirical PMF is:

$$p(x) = \frac{1}{n} \sum_{i=1}^{n} \delta_x(x_i),$$

where $\delta_x(x_i)$ is the Kronecker delta function and $x \in \mathcal{X}$. Using the definition of entropy:

$$H(p) = -\sum_{x\in\mathcal{X}} p(x) \log p(x) = -\sum_{x\in\mathcal{X}} \frac{1}{n} \sum_{i=1}^{n} \delta_x(x_i) \log p(x) = -\frac{1}{n} \sum_{i=1}^{n} \log p(x_i).$$

In the last step we have interchanged the order of the two sums and used

$$\sum_{x\in\mathcal{X}} \delta_x(x_i) \log p(x) = \log p(x_i).$$

1.9.5.3. *KL Divergence.* Suppose that we have two PDFs $q(x)$ and $p(x)$ defined on the same probability space (i.e. the range of values is the same $x \in \mathcal{X}$, and the set of all possible random events is identical) with PDFs $q(x)$ and $p(x)$. Here we assume that the range is $\mathcal{X} = (-\infty, \infty)$. The relative entropy between q and p is defined by:

$$D_{KL}[p(x) : q(x)] = \int_{-\infty}^{\infty} p(x) \log \left(\frac{p(x)}{q(x)} \right) \mathrm{d}x.$$

This can easily be generalized to discrete rv's by taking

$$p(x) = \sum_{i=1}^{N} p_i \delta(x - x_i), \qquad q(x) = \sum_{i=1}^{N} q_i \delta(x - x_i),$$

where N is the number of possible values $x \in \mathcal{X}$ the rv can take. This gives:

$$D_{KL}[p : q] = \sum_{x\in\mathcal{X}} p(x) \log \left(\frac{p(x)}{q(x)} \right) = \sum_{i=1}^{N} p_i \log \left(\frac{p_i}{q_i} \right).$$

We note that D_{KL} is not symmetric, i.e. $D_{KL}[p : q] \neq D_{KL}[q : p]$, and nor does it satisfy the triangle inequality. Therefore, it is not technically a metric. It is possible to make it symmetric by taking the sum $D_{KL}[p : q] + D_{KL}[q : p]$ in order to obtain a metric.

1.9.5.4. *Relationship to cross-entropy.* Cross-entropy is closely related to relative entropy or KL-divergence that computes distance between two probability distributions. For example, in between two discrete PMFs, the relation between them is:

$$H(p,q) = -\sum_{x\in\mathcal{X}} p(x)\log q(x) \qquad \text{cross entropy}$$

$$H(p) = -\sum_{x\in\mathcal{X}} p(x)\log p(x) \qquad \text{entropy}$$

$$D_{KL}[p:q] = \sum_{x\in\mathcal{X}} p(x)\log\left(\frac{p(x)}{q(x)}\right) \qquad \text{relative entropy}$$

$$H(p,q) = H(p) + D_{KL}[p:q]$$

Expressing the KL divergence in the form

$$D_{KL}[p:q] = \sum_{x\in\mathcal{X}} p(x)\log p(x) - \sum_{x\in\mathcal{X}} p(x)\log q(x)$$

yields the interpretation of the KL divergence to be something like the following: if P is the "true" distribution, then the KL divergence is the amount of information "lost" when expressing it via Q.

1.9.6. Density Estimation. So far we have worked dealt with *parametric statistics* meaning that we assumed knowledge of the PDF in order to compute statistics involving rv's. For example, concepts such as mean and variance were defined in terms of PDFs. The PDF is either given to us, or it is estimated from the data by fitting its parameters (e.g. mean, variance) to the histogram. This procedure has limited capabilities, as it requires choosing a model for the PDF. *Non-parametric statistics* makes no assumptions about the form of the PDF. The density function (PDF) is instead derived from the data. Recall that (rescaled) histograms are a discrete approximation to the PDF. In this section, we will show that non-parametric estimates of the density can be constructed using a sum of kernel functions.

1.9.6.1. *Kernels.* Kernels are best described informally as "bump functions". An example is the Gaussian function, also known as *radial basis function*

$$K_x(y) = K(x,y) = e^{-\frac{\|x-y\|^2}{2\sigma^2}},$$

which is a fundamental solution to the heat equation describing the response to a point source of heat in thermodynamics. Another example is the polynomial kernel:

$$K_x(y) = K(x,y) = (x\cdot y + 1)^d.$$

Kernels in statistics must be non-negative, real-valued integrable functions $K_x : \mathbb{R} \to \mathcal{X}$ satisfying symmetry, $K_x(-y) = K_x(y)$ and normalization, $\int_{-\infty}^{\infty} K_x(y)\mathrm{d}y = 1$.

A *reproducing kernel* K_x operates on a Hilbert space H of functions that are defined on a set X. A function $K : X \times X \to \mathbb{R}$ defined by the inner product on H:

$$K(x, y) = \langle K_x, K_y \rangle_H$$

that has the property of taking a function f and evaluating it at x:

$$\langle f, K_x \rangle_H = f(x),$$

is called *reproducing* because it maps a function f to its value $f(x)$. An example is the Dirac measure $\delta_x(y)$ and the Hilbert space $L^2(\mathbb{R})$:

$$\langle f, \delta_x \rangle_{L^2} = \int_{-\infty}^{\infty} f(y) \cdot \overline{\delta_x(y)} \mathrm{d}y = \int_{-\infty}^{\infty} f(y)\delta(x - y)\mathrm{d}y = f(x).$$

1.9.6.2. *Kernel Density Estimation.* Kernel density estimation (KDE) is method for estimating the probability density function of a rv. It can also be viewed as a data smoothing technique where inferences about the population are made (PDF), based on a finite data sample (histogram).

Let $(x_1, x_2, \ldots, x_n)$ be independent and identically distributed samples drawn from some univariate distribution with an unknown density f at any given point x. We are interested in estimating the shape of this function f. Its kernel density estimator is

$$\widehat{f}_h(x) = \frac{1}{n} \sum_{i=1}^{n} K_h(x - x_i) = \frac{1}{nh} \sum_{i=1}^{n} K\Big(\frac{x - x_i}{h}\Big)$$

where K is the kernel — a non-negative function — and $h > 0$ is a smoothing parameter called the bandwidth. We note that $K_x(y)$ in the previous section is now denoted $K(y - x)$. A kernel with subscript h is called the scaled kernel and defined as $K_h(x) = (1/h) \cdot K(x/h)$. The KDE can be though of as a weighted average, where the weight is:

$$w_i = \frac{1}{h} K\Big(\frac{x - x_i}{h}\Big).$$

The choice of bandwidth h matters in practice. Wider bandwidths smooth out the data more (low variance). Narrower bandwidths result in noisier data (high variance). Obviously, if we pick too low a bandwidth, the density estimation has a generally greater bias because the moving average (trendline) is less responsive to changes in the data points.

Suppose that we measure a signal Y_i that is the sum of the underlying signal $f(x_i)$ and some additive noise ξ_i:

$$Y_i = f(x_i) + \xi_i$$

where one usually assumes that

$$\xi_i \sim \mathcal{N}(0, \sigma^2).$$

Here, x_i represents some internal variables that are not directly measured. We denote them as x_i rather than X_i, to emphasize that those variables have already been “fixed” at the time of the measurement, i.e.

$$f(x_i) = \langle f(X_i) | X_i = x_i \rangle.$$

Taking the conditional expectation given $X_i = x_i$ we find:

$$\langle Y_i | X_i = x_i \rangle = \langle f(X_i) | X_i = x_i \rangle.$$

We will obtain in the next section an expression for $\langle Y_i | X_i = x_i \rangle$.

1.9.6.3. *Kernel Regression.* The problem of kernel regression can be summarized as follows. We want to estimate the conditional expectation $\langle Y | X = x \rangle$, which is a function of x. First note that:

$$\langle Y | X = x \rangle = \int y p_Y(y|x) \mathrm{d}y = \int y \frac{p_{XY}(x,y)}{p_X(x)} \mathrm{d}y.$$

However, this requires knowledge of the densities. We use the following kernel density estimates:

$$\hat{p}_{XY}(x,y) = \frac{1}{n} \sum_{i=1}^{n} K_h(x - x_i) K_h(y - y_i), \quad \hat{p}_X(x) = \frac{1}{n} \sum_{i=1}^{n} K_h(x - x_i),$$

where the hat denotes estimate. We get the following estimate:

$$\begin{aligned}
\hat{\mathbb{E}}[Y|X = x] = &\int \frac{y \sum_{i=1}^{n} K_h(x - x_i) K_h(y - y_i)}{\sum_{j=1}^{n} K_h(x - x_j)} \mathrm{d}y, \\
= &\frac{\sum_{i=1}^{n} K_h(x - x_i) \int y K_h(y - y_i) \mathrm{d}y}{\sum_{j=1}^{n} K_h(x - x_j)}, \\
= &\frac{\sum_{i=1}^{n} K_h(x - x_i) y_i}{\sum_{j=1}^{n} K_h(x - x_j)},
\end{aligned}$$

We have used the reproducing property of kernels:

$$\int y K_h(y - y_i) \mathrm{d}y = y_i.$$

1.10. Problems

Problem 1. The height of a person is measured over time, every month from birth to The data set consists of the person's age in months and her height in centimeters. The summary statistics for the data are provided below:

$x =$ age, in months

$y =$ height, in centimeters

$\overline{x} = 44 \qquad s_x = 8.5 \qquad \overline{y} = 82 \qquad s_y = 4.1$

Also, the correlation coefficient between x and y is $r = 0.860$

(a) What is the slope of the LSRL? (Round to the nearest hundredth.)
(b) What is the y-intercept of the LSRL? (Round to the nearest hundredth.)
(c) Find the equation of the least-squares regression line (with y as the response variable)
(d) What percentage of the variation in predicted height can be explained for by the LSRL

Problem 2. Suppose that we have an amplifier that takes a voltage and amplifies it by a factor of 10×, i.e. $f(x) = 10x$. Suppose that we feed this amplifier the following input voltages:

$$X = \{2.53, 2.55, 2.45, 2.49, 2.50, 2.52, 2.47, 2.48, 2.56, 2.49\}$$

(a) What is the sample variance at the *output* of the amplifier?

(b) Suppose that we have two rv's, X and Y and they are statistically independent. Furthermore, suppose that $var(X)$=2.7 and $var(Y)$=2.5. Compute the value of $var(X + Y)$ and $var(X - Y)$.

(c) Given that $var(X)$=2.7, $var(Y)$=2.5 and $\rho(X, Y)$=0.9 (correlation coefficient), what is $var(X + Y)$ and $var(X - Y)$?

(d) If X, Y and Z are statistically independent and $var(X)$=1.7, $var(Y)$=2.3 and $var(Z)$=1.4. What is $var(0.3X + 0.7Y + 0.5Z)$?

Solution. (a) First, calculate the sample variance of X and then multiply by 100. Then multiply each X_i by 10 and then calculate the sample variance of the multiplied values. The sample variance of the X's is 0.001249. Multiply this by 100 to get 0.1249. Multiplying each X by 10 and taking the sample variance we get 0.1249, which is the same as the first method. From this we confirmed the validity of the formula $var(aX) = a^2 var(X)$.

(b) By statistical independence we have

$$var(X + Y) = var(X) + var(Y) = 2.7 + 2.5 = 5.2.$$

Then from

$$var(aX + bY) = a^2 var(X) + b^2 var(Y),$$

with $a = 1$ and $b = -1$ we have

$$var(X - Y) = (1)^2 var(X) + (-1)^2 var(Y) = var(X) + var(Y) = 2.7 + 2.5 = 5.2.$$

From this, we conclude that when X and Y are statistically independent, $var(X + Y) = var(X - Y) = var(X) + var(Y)$.

(c) From the definition of the correlation coefficient

$$\rho(X, Y) = \frac{cov(X, Y)}{\sqrt{var(X) var(Y)}}$$

we have $cov(X, Y) = \rho(X, Y)\sqrt{var(X) var(Y)}$. Then, inserting this into:

$$var(X + Y) = var(X) + var(Y) + 2cov(X, Y)$$

we get:

$$var(X+Y) = var(X) + var(Y) + 2\rho(X,Y)\sqrt{var(X)var(Y)}$$

from which we can obtain a numerical value:

$$var(X+Y) = 2.7 + 2.5 + 2(0.9)[(2.7)(2.5)]^{1/2} = 9.877.$$

For $var(X-Y)$ we have:

$$var(X-Y) = var(X) + var(-Y) + 2\rho(X,-Y)\sqrt{var(X)var(-Y)}$$

and since $var(-Y) = (-1)^2 var(Y) = var(Y)$, we have:

$$var(X-Y) = var(X) + var(Y) + 2\rho(X,-Y)\sqrt{var(X)var(Y)}$$

Now, using the property $cov(aX,bY) = ab \cdot cov(X,Y)$, we see that

$$\rho(aX,bY) = \frac{cov(aX,bY)}{\sqrt{var(aX)var(bY)}} = \frac{ab \cdot cov(X,Y)}{|a||b|\sqrt{var(X)var(Y)}} = \frac{ab}{|a||b|}\rho(X,Y).$$

For $a = 1$ and $b = -1$,

$$\rho(1\cdot X, -1\cdot Y) = \frac{(1)\cdot(-1)}{|1||-1|}\rho(X,Y) = -\rho(X,Y).$$

Hence,

$$var(X-Y) = var(X) + var(Y) - 2\rho(X,Y)\sqrt{var(X)var(Y)}$$

and then we have

$$var(X-Y) = 2.7 + 2.5 - 2(0.9)[(2.7)(2.5)]^{1/2} = 0.5235.$$

We conclude that $var(X+Y)$ is not equal to $var(X-Y)$ when X and Y are correlated to some extent.

(d) If X, Y and Z are statistically independent, then we can write:

$$var(aX + bY + cZ) = a^2 var(X) + b^2 var(Y) + c^2 var(Z),$$

where a, b, c are constants. Hence,

$$\begin{aligned} var(0.3X + 0.7Y + 0.5Z) &= (0.3)^2 var(X) + (0.7)^2 var(Y) + (0.5)^2 var(Z) \\ &= (0.3)^2 1.7 + (0.7)^2 2.3 + (0.5)^2 1.4 = 1.630. \end{aligned}$$

■

Problem 3. Suppose that X is a rv with distribution $p_X(x)$ and $Y = g(X)$ is another rv related to X via a continuous differentiable function g. Prove that the density of Y can be written as:

$$p_Y(y) = \int_{-\infty}^{\infty} p_X(x)\delta(y - g(x))\mathrm{d}x.$$

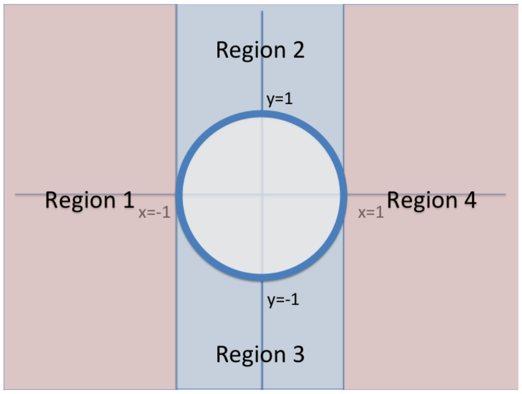


Figure 1.10. Partition of the region $x^2 + y^2 > 1$ into 4 regions.

Solution. Starting with the CDF:

$$\mathbb{P}(Y < a) = \mathbb{P}(g(X) < a) = \int_{\{x:g(x)<a\}} p_X(x)\mathrm{d}x = \int_{-\infty}^{\infty} \mathbf{1}_{g(x)<a}(x)p_X(x)\mathrm{d}x.$$

Using the fact that the Dirac delta function is the derivative of the Heaviside function:

$$\delta(x) = \frac{\mathrm{d}}{\mathrm{d}x}\theta(x), \qquad \theta(x) := \mathbf{1}_{x>0}(x)$$

And if the origin is shifted to x_0, we may change variables to $x = \tilde{x} - x_0$:

$$\delta(\tilde{x} - x_0) = \frac{\mathrm{d}}{\mathrm{d}\tilde{x}}\theta(\tilde{x} - x_0), \qquad \theta(\tilde{x} - x_0) := \mathbf{1}_{\tilde{x}>x_0}(\tilde{x})$$

Taking the derivative with respect to a we get the PDF, $p_Y(a)$:

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}}{\mathrm{d}a}\mathbf{1}_{a>g(x)}(x)p_X(x)\mathrm{d}x = \int_{-\infty}^{\infty} \delta(a - g(x))p_X(x)\mathrm{d}x.$$

■

Problem 4. Find the probability distribution function of the rv $Z = X^2 + Y^2$ in terms of the distribution of X and Y.

Solution. The probability that the vector (X, Y) lies outside the unit circle $\{(x, y)|x^2 + y^2 = 1\}$ is:

$$\mathbb{P}(X^2 + Y^2 > 1) = \iint_{\{(x,y)|x^2+y^2>1\}} p_{XY}(x, y)\mathrm{d}x\mathrm{d}y.$$

This can be calculated explicitly by splitting the integration domain ($\mathbb{R}^2 - \{\text{unit disc}\}$) into 4 regions (Fig. 1.10).

$$\mathbb{P}(X^2+Y^2>1) = \underbrace{\int_{-\infty}^{\infty}\left(\int_{-\infty}^{-1} p_{XY}(x,y)\mathrm{d}x\right)\mathrm{d}y}_{\text{Region 1}} + \underbrace{\int_{-\infty}^{\infty}\left(\int_{1}^{\infty} p_{XY}(x,y)\mathrm{d}x\right)\mathrm{d}y}_{\text{Region 4}}$$
$$+ \underbrace{\int_{-1}^{1}\left(\left\{\int_{-\infty}^{-\sqrt{1-x^2}} + \int_{\sqrt{1-x^2}}^{\infty}\right\} p_{XY}(x,y)\mathrm{d}y\right)\mathrm{d}x}_{\text{Regions 2 and 3}}.$$

Another way to calculate this would be to convert $p_{XY}(x,y)$ to polar coordinates $p_{R,\Theta}(r,\theta)$ and integrate from $r=1$ to ∞ while letting θ range from 0 to 2π. ■

Problem 5. Find the probability distribution function of the rv $Z=\sqrt{X^2+Y^2}$ in terms of the distribution of X and Y.

Solution. Suppose that $X, Y \sim \mathcal{N}(0,\sigma^2)$ (zero-mean Gaussians) are independent rv's. Consider the transformation to polar coordinates:

$$R=\sqrt{X^2+Y^2}, \quad \Theta = \tan^{-1}(Y/X).$$

The inverse transformation is:

$$x = r\cos\theta, \quad y = r\sin\theta.$$

What is the distribution of Θ and R? Let us do R. The CDF of R is found by writing:

$$\mathbb{P}(R<r) = \iint\limits_{\{(x,y)|\sqrt{x^2+y^2}<r\}} \frac{1}{2\pi\sigma^2} e^{-(x^2+y^2)/(2\sigma^2)}\mathrm{d}x\mathrm{d}y.$$

It will be convenient to transform to polar coordinates. The Jacobian of the transformation yields the new area element:

$$\mathrm{d}x\mathrm{d}y = \left|\frac{\partial(x,y)}{\partial(r,\theta)}\right| \mathrm{d}r\mathrm{d}\theta,$$

where

$$\frac{\partial(x,y)}{\partial(r,\theta)} = \left\|\begin{matrix}\partial_r x & \partial_\theta x\\ \partial_r y & \partial_\theta y\end{matrix}\right\| = \left\|\begin{matrix}\cos\theta & -r\sin\theta\\ \sin\theta & r\cos\theta\end{matrix}\right\| = r.$$

Then,

$$\mathbb{P}(R<r) = \frac{1}{2\pi\sigma^2}\int_0^{2\pi}\mathrm{d}\theta\int_0^r \mathrm{d}r e^{-r^2/(2\sigma^2)}\cdot r = \frac{1}{\sigma^2}\int_0^r \mathrm{d}r e^{-r^2/(2\sigma^2)}\cdot r.$$

The corresponding PDF is obtained by differentiating with respect to r:

$$\boxed{p_R(r) = \frac{r}{\sigma^2}e^{-r^2/(2\sigma^2)}.}$$

We have recovered the Rayleigh distribution, by constructing the rv $R=\sqrt{X^2+Y^2}$, where $X, Y \sim \mathcal{N}(0,\sigma^2)$.

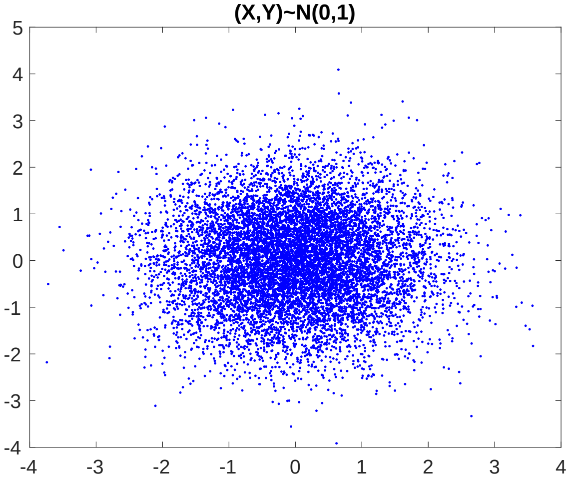


Figure 1.11. Scatter plot of the ordered pairs $\{(X_i, Y_i)\}_{i=1}^{10{,}000}$, where $X_i, Y_i \sim \mathcal{N}(0,1)$ are all independent.

The derivation of the distribution for Θ is trivial. Recall that $\Theta = \tan^{-1}(Y/X)$. Then,

$$\mathbb{P}(\Theta < \theta) = \iint\limits_{\{(x,y)|\tan^{-1}(y/x)<\theta\}} \frac{1}{2\pi\sigma^2} e^{-(x^2+y^2)/(2\sigma^2)} \mathrm{d}x\mathrm{d}y.$$

Transformation to polar coordinates gives:

$$\mathbb{P}(\Theta < \theta) = \int_0^\theta \mathrm{d}\theta \int_0^\infty \mathrm{d}r \frac{1}{2\pi\sigma^2} e^{-r^2/(2\sigma^2)} r.$$

The integral over r can be solved with the substitution $w = r^2/(2\sigma^2)$, $\mathrm{d}w = r\mathrm{d}r/\sigma^2$. Thus, our CDF is:

$$\mathbb{P}(\Theta < \theta) = \frac{1}{2\pi} \int_0^\theta \mathrm{d}\theta = \frac{\theta}{2\pi},$$

where $\theta \in [0, 2\pi]$. The PDF is that of a uniform distribution:

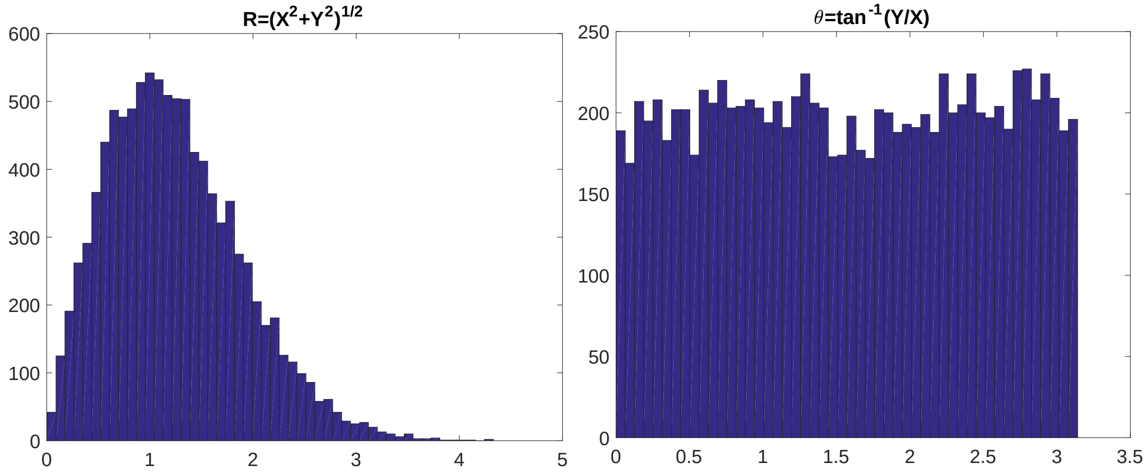
$$\boxed{p_\Theta(\theta) = \frac{1}{2\pi},}$$

with $\theta \in [0, 2\pi]$. Thus, R is Rayleigh whereas Θ is uniform. This can be seen in Fig. 1.11, which is a scatter plot of the pairs (X, Y), where $X, Y \sim \mathcal{N}(0, 1)$. This plot was generated in MATLAB as follows:

```
>> X=randn([1 10000]); Y=randn([1 10000]);
>> figure;plot(X,Y,'.b');title('(X,Y)~N(0,1)');
>> set(gca,'fontsize',16);
```

The distributions of R and Θ can be plotted by taking the pairs (X, Y) and generating R, Θ. Histograms of R and Θ are shown in Fig. 1.12. It can be seen that R is Rayleigh and Θ is uniform. These plots were generated in MATLAB using the following commands:

```
>> R=sqrt(X.^2+Y.^2); theta=atan(Y./X);
>> figure;hist(R,50);
>> set(gca,'fontsize',16);
>> title('R=(X^2+Y^2)^{1/2}');
>> figure;hist(theta+pi/2,50);set(gca,'fontsize',16);
>> title('\theta=tan^{-1}(Y/X)');
```



(a) R **(b)** Θ

Figure 1.12. Histograms of R and Θ, as generated from a sequence of rv's $\{(X_i, Y_i)\}_{i=1}^{10{,}000}$, where $X_i, Y_i \sim \mathcal{N}(0, 1)$ are all independent.

$\blacksquare$

Problem 6. The median of a finite list of numbers is the "middle" number, when those numbers are listed in order from smallest to greatest. (A set of an even number of observations has no distinct middle value and the median is usually defined to be the arithmetic mean of the two middle values.)

(a) Prove that given a random sample $x_1, \ldots, x_n$ (take n as odd, so there is a middle value) of a rv X, the median is the value x_{50} that is the middle data point in the ordered list of the random sample.

(b) Explain the relationship between median and mean. When would you use one vs the other?

Solution. (a) The median is defined as the value x_{50} satisfying:

$$\int_{-\infty}^{x_{50}} p(x)\mathrm{d}x = \frac{1}{2}.$$

Substituting the empirical distribution

$$p(x) = \frac{1}{n}\sum_{i=1}^{n} \delta(x - x_i),$$

into the definition of median:

$$\frac{1}{2} = \int_{-\infty}^{x_{50}} \frac{1}{n}\sum_{i=1}^{n} \delta(x - x_i)\mathrm{d}x = \frac{1}{n}(n/2),$$

i.e. for this integral to equal 1/2 it must evaluate to $(n/2)/n = 1/2$. In other words, half the terms in the summation contribute. Which terms? The integral is over the range $(-\infty, x_{50}]$, i.e. begins at $-\infty$ and ends at x_{50}. Integration will therefore pick out all the terms labeled x_i that are found in the interval $(-\infty, x_{50}]$. Each term is a Dirac delta function that integrates to 1. Thus, it is a counter of sorts. Once we have found the midway point of the ordered list, the corresponding value x_{50} is called the median.

(b) The median, like the mean, attempts to produce some kind of average of a random sample. The media ignores the extreme and outlier values since it only picks the central value. The mean is affected by outliers. ■

Problem 7. We have learned that given two independent rv's X and Y, we may form a new rv Z that is the sum of X and Y, i.e. $Z = X + Y$, and that the probability density of Z is the convolution of the densities of X and Y, i.e.

$$p_{X+Y}(a) = \int_{-\infty}^{\infty} p_X(a - y)p_Y(y)\mathrm{d}y$$

or in terms of CDFs:

$$\begin{aligned}
\mathbb{P}(X + Y \leq a) &= \iint\limits_{\{(x,y):x+y\leq a\}} p_X(x)p_Y(y)\mathrm{d}x\mathrm{d}y \\
&= \int_{-\infty}^{\infty} \left(\int_{-\infty}^{a-y} p_X(x)\mathrm{d}x \right) p_Y(y)\mathrm{d}y \\
&= \int_{-\infty}^{\infty} \mathbb{P}(X \leq a - y)p_Y(y)\mathrm{d}y
\end{aligned}$$

Please note: limits of integration $(-\infty, \infty)$ should be replaced by the domain of definition of the rv if different from $(-\infty, \infty)$.

(a) Suppose that X and Y are independent and let $X \sim Uni(0, 1)$, $Y \sim Uni(0, 1)$ (uniformly distributed over the interval [0,1]), i.e. PDF is $p_X(x) = 1$ for $0 \leq x \leq 1$ and same for $p_Y(y)$. What is the PDF of $X + Y$?

(b) Show that if $X \sim \mathcal{N}(\mu_1, \sigma_1^2)$ and $Y \sim \mathcal{N}(\mu_2, \sigma_2^2)$ then $X + Y \sim \mathcal{N}(\mu_1 + \mu_2, \sigma_1^2 + \sigma_2^2)$.

(c) Suppose that you play 2 lotteries. In the first lottery you either win \$1000 with probability 1/2 or lose (with probability 1/2) and get nothing. In the second lottery you are guaranteed of winning *something*; however the payout is less: the payout follows a Rayleigh distribution with mode equal to \$100. (The Rayleigh PDF is $p_Y(y) = (y/\sigma^2)e^{-x^2/(2\sigma^2)}$, where σ is the mode, the mean is $\sigma\sqrt{\pi/2}$.). You can assume that X and Y are independent. What is the PDF describing the total payout from both lotteries? Plot the PDF. What is the average amount you'd expect to win?

(d) Consider Newton's law, $F = ma$, where m is mass and a is acceleration. Given the distributions of m and a as $\mathcal{N}(10, 1)$ and $\mathcal{N}(10, 0.1)$, respectively. What is the distribution of F?

(e) Find the mode of the following PDF, which approximates the thumb length X in inches in a particular country:

$$p(x) = \begin{cases} \frac{\pi}{4}\sin\left(\frac{\pi(x-2)}{2}\right), & 2 \le x \le 4 \\ 0, & \text{elsewhere} \end{cases}$$

Solution. (a) The convolution is

$$p_{X+Y}(a) = \int_0^1 p_X(a-y)p_Y(y)\mathrm{d}y = \int_0^1 p_X(a-y)\mathrm{d}y = \int_0^1 \mathbf{1}_{[0,1]}(a-y)\mathrm{d}y,$$

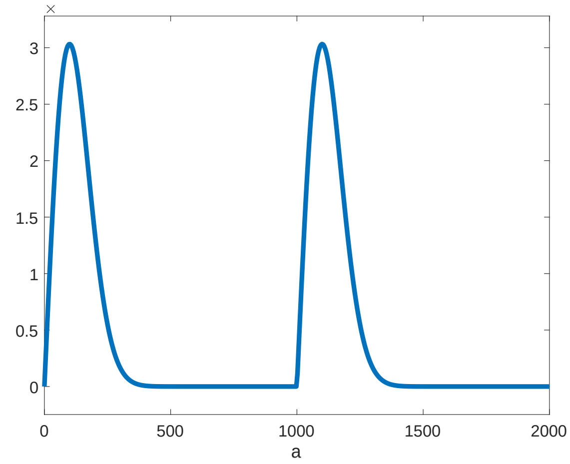
where $\mathbf{1}_A(y)$ is the indicator function over the set A. The latter results in an integral equal to zero unless $a - y \in [0, 1]$, or $-y \in [0, 1] - a$ or $y \in a + [-1, 0]$. The overlap between $a + [-1, 0]$ and the limits of integration $[0, 1]$ can be split into 2 regions: $a \in [0, 1]$ and $a \in [1, 2]$. In the first region the overlap progressively increases; in the second region it decreases. Performing the integral we obtain the tent function:

$$p_{X+Y}(a) = \int_0^1 \mathbf{1}_{[0,1]}(a-y)\mathrm{d}y = \begin{cases} \int_0^a \mathrm{d}y = a & 0 \le a \le 1 \\ \int_{a-1}^1 \mathrm{d}y = 2-a & 1 < a \le 2 \\ 0 & \text{otherwise} \end{cases}$$

(c) Let $Z = X + Y$ and $p_X(x) = p_0\delta(x - x_l) + p_1\delta(x - x_w)$, with $x_l = \$0$ and $x_w = \$10^3$. $p_Y(y)$ is given to us with $\sigma = \$100$. The PDF of Z is the convolution ($a > 0$):

$$\begin{aligned} p_{X+Y}(a) &= \int_0^\infty p_X(a-y)p_Y(y)\mathrm{d}y \\ &= \int_0^\infty [p_0\delta(a-y) + p_1\delta(a-y-x_w)]\frac{y}{\sigma^2}e^{-y^2/(2\sigma^2)}\mathrm{d}y \\ &= p_0\frac{a}{\sigma^2}e^{-a^2/(2\sigma^2)} + p_1\frac{(a-x_w)}{\sigma^2}e^{-(a-x_w)^2/(2\sigma^2)}\mathbf{1}_{[x_w,\infty)}(a), \end{aligned}$$

where $\sigma = \$100$, $x_w = \$10^3$, $p_1 = 1/2$ and $p_0 = 1/2$.



The mean value:

$$\begin{aligned}\langle Z\rangle =&\frac{p_0}{\sigma^2}\int_0^\infty a^2 e^{-a^2/(2\sigma^2)}\mathrm{d}a+\frac{p_1}{\sigma^2}\int_0^\infty (a-x_w)ae^{-(a-x_w)^2/(2\sigma^2)}\mathbf{1}_{[x_w,\infty)}(a)\mathrm{d}a\\ =&p_0\sigma\sqrt{\frac{\pi}{2}}+\frac{p_1}{\sigma^2}\int_0^\infty a'(a'+x_w)e^{-(a')^2/(2\sigma^2)}\mathrm{d}a'\\ =&p_0\sigma\sqrt{\frac{\pi}{2}}+\frac{p_1}{\sigma^2}(5\times 10^5)(20+\sqrt{2\pi})\approx \$562.50\end{aligned}$$

which is right about somewhere between the two peaks, as we would expect the average to be, based on the center-of-mass of this PDF. (We have used `wolframalpha.com` to obtain a numerical value for this integral in the last line.)

(d) Let $Z = XY$. The PDF of Z is:

$$p_Z(z)=\int_{-\infty}^{\infty} p_X(x)p_Y(z/x)\frac{1}{|x|}\mathrm{d}x \qquad (*)$$

Plugging in the distributions for X and Y: $\mathcal{N}(10,1)$ and $\mathcal{N}(10,0.1)$, we have:

$$p_Z(z)=\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi(0.1^2)}}\int_{-\infty}^{\infty} e^{-(x-10)^2/2}e^{-(z/x-10)^2/2(0.1^2)}\frac{1}{|x|}\mathrm{d}x$$

A proof is:

$$\begin{aligned}\mathbb{P}(Z\le z)=&\mathbb{P}(XY\le z)=\mathbb{P}(XY\le z, X>0)+\mathbb{P}(XY\le z, X\le 0)\\ =&\mathbb{P}(Y\le z/X, X>0)+\mathbb{P}(Y\ge z/X, X\le 0)\\ =&\int_0^\infty p_X(x)\int_{-\infty}^{z/x} p_Y(y)\mathrm{d}y\mathrm{d}x+\int_{-\infty}^0 p_X(x)\int_{z/x}^{\infty} p_Y(y)\mathrm{d}y\mathrm{d}x\end{aligned}$$

Differentiating with respect to z, we get the PDF:

$$\begin{aligned} p_Z(z) &= \int_0^{\infty} p_X(x)p_Y(z/x)\frac{1}{x}\mathrm{d}x - \int_{-\infty}^{0} p_X(x)p_Y(z/x)\frac{1}{x}\mathrm{d}x \\ &= \int_{-\infty}^{\infty} p_X(x)p_Y(z/x)\frac{1}{|x|}\mathrm{d}x \end{aligned}$$

(e) The mode here can be found by setting the derivative to zero: $p'(x) = 0$. In the nonzero region $2 \le x \le 4$ the derivative of $\frac{\pi}{4}\sin\left(\frac{\pi(x-2)}{2}\right)$ is $p'(x) = \frac{\pi^2}{8}\cos\left(\frac{\pi(x-2)}{2}\right)$. Setting the derivative equal to zero we must solve $\cos\left(\frac{\pi(x-2)}{2}\right) = 0$. Taking the inverse cosine, $\frac{\pi(x-2)}{2} = \frac{\pi}{2} + k\pi$, $k \in \mathbb{Z}$, or $x - 2 = 1 + 2k$ and $x = 3 + 2k$. The solution in the interval $2 \le x \le 4$ is $x = 3$. ■

Problem 8. The Poisson's law with parameter a ($a > 0$) is defined by:

$$\mathbb{P}[k \ events] = e^{-a}\frac{a^k}{k!},$$

where $k = 0, 1, 2, \ldots$. With $a = \lambda\tau$, where λ is the average number of events per units time and τ is the length of the interval $(t, t+\tau)$, the probability of k events in τ is

$$\mathbb{P}(k; t, t+\tau) = e^{-\lambda\tau}\frac{(\lambda\tau)^k}{k!}.$$

This equation assumes that λ is independent of t. If λ depends on t, the product $\lambda\tau$ gets replaced by the integral $\int_t^{t+\tau}\lambda(\xi)\mathrm{d}\xi$, and the probability of k events in the interval $(t, t+\tau)$ is

$$\mathbb{P}(k; t, t+\tau) = \exp\left[-\int_t^{t+\tau}\lambda(\xi)\mathrm{d}\xi\right]\frac{1}{k!}\left[\int_t^{t+\tau}\lambda(\xi)\mathrm{d}\xi\right]^k.$$

The parameter λ is called the rate parameter. $\lambda(t)$ is the rate function. Suppose that a company manufactures superconducting wire. Upon close examination of the product on the assembly line, you find that the defect density along the length of the wire is not uniform. For wire strips of length D, the defect density $\lambda(x)$ along the wire length x varies as

$$\lambda(x) = \lambda_0 + \frac{1}{2}(\lambda_1 - \lambda_0)\left(1 + \cos(\frac{2\pi x}{D})\right), \quad \lambda_1 > \lambda_0$$

for $0 \le x \le D$ due to greater wire contamination at the edges $x = 0$ and $x = D$.

(i) What is the meaning of $\lambda(x)$ in this case?

(ii) What is the average number of defects for a wire strip of length D?

(iii) Find an expression for the probability of k defects on a wire strip of length D?

Solution. (i) Bearing in mind that $\lambda(x)$ is a defect density, i.e., the average number of defects per unit length at x, we conclude that $\lambda(x)\Delta x$ is the average number of defects in the tape from x to $x + \Delta x$.

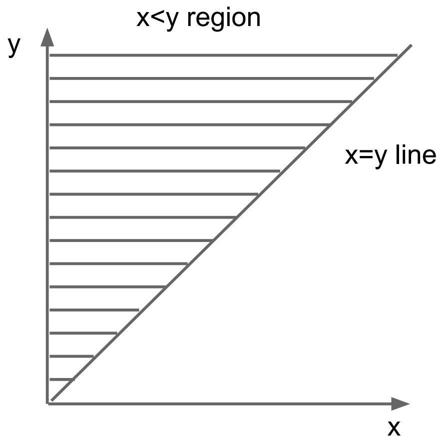


Figure 1.13. Integration in the $x < y$ region.

(ii) Given the definition of $\lambda(x)$ we conclude that the average number of defects along the whole wire is merely the integral of $\lambda(x)$, i.e.,

$$\int_0^D \lambda(x)\mathrm{d}x = \int_0^D \left[\lambda_0 + \frac{1}{2}(\lambda_1 - \lambda_0)\left(1 + \cos\frac{2\pi x}{D}\right)\right]\mathrm{d}x = \frac{\lambda_0 + \lambda_1}{2}D = \Omega.$$

(iii) Assuming the Poisson law holds, use the equation with x and Δx (distances) replacing t and τ (times). Thus,

$$\mathbb{P}(k; x, x + \Delta x) = \exp(-\int_x^{x+\Delta x} \lambda(\zeta)\mathrm{d}\zeta)\frac{1}{k!}(\int_x^{x+\Delta x} \lambda(\zeta)\mathrm{d}\zeta)^k.$$

In particular, with $x = 0$ and $x + \Delta x = D$, we obtain

$$\mathbb{P}(k; 0, D) = \Omega^k \frac{e^{-\Omega}}{k!}$$

■

Problem 9. Let X and Y be independent rv's having the exponential distribution with parameters λ and μ respectively. (Recall that if rv X has exponential distribution with parameter $\lambda > 0$, its CDF is $\mathbb{P}(X < x) \equiv 1 - e^{-\lambda x}$, $x \geq 0$, whose density is $\mathrm{d}\mathbb{P}(X < x)/\mathrm{d}x = \lambda e^{-\lambda x}$.) Let $U = \min\{X, Y\}$, $V = \max\{X, Y\}$ and $W = V - U$. Find the probability $\mathbb{P}(U = X) = \mathbb{P}(X \leq Y)$. Show that U and W are statistically independent.

Solution. First you should realize that the logical statements $U = X$ and $X \leq Y$ mean the same thing. Indeed, $U = \min\{X, Y\}$ less than or equal to X implies that both $X \leq X$ (if $\min\{X, Y\} = X$) and $Y \leq X$ (if $\min\{X, Y\} = Y$). The former ($X \leq X$) is a trivial statement which is true at all times. Thus, it can be ignored. The only non-trivial statement left is $Y \leq X$, hence the equivalence of the two statements $U = X$ and $X \leq Y$. If the two statements are equivalent, then their probabilities are also equal: $\mathbb{P}(U = X) = \mathbb{P}(X \leq Y)$.

$\mathbb{P}(U = X) = \mathbb{P}(X \le Y)$ can be computed since it is in terms of X and Y whose distributions are known. Since $\mathbb{P}(X \le Y)$ involves both X and Y we must integrate the joint PDF of X and Y over the set of all points (x, y) such that $x < y$ is satisfied:

$$\mathbb{P}(X \le Y) = \int_{\{(x,y)|x<y\}} p_{XY}(x, y)\,\mathrm{d}x\mathrm{d}y.$$

Let's integrate along horizontal strips, as shown in Fig. 1.13. Thus,

$$\mathbb{P}(X \le Y) = \int_0^y \mathrm{d}x \int_0^\infty \mathrm{d}y\, p_{XY}(x, y) = \int_0^y \mathrm{d}x \int_0^\infty \mathrm{d}y\, p_X(x)p_Y(y),$$

where in the second equality we invoked the statistical independence of X and Y and wrote the integrand as a product of densities in X and Y. Now, we invoke the shorthand notation $\mathbb{P}(X \le y) = \int_0^y p_X(x)\mathrm{d}x$ and use the fact that $p_Y(y) = \mu e^{-\mu y}$ and rewrite this as:

$$\mathbb{P}(X \le Y) = \int_0^\infty \mathbb{P}(X \le y)\mu e^{-\mu y}\mathrm{d}y = \int_0^\infty (1 - e^{-\lambda y})\mu e^{-\mu y}\mathrm{d}y = \frac{\lambda}{\mu + \lambda}.$$

For $w > 0$, $\mathbb{P}(U \le u, W > w) = \mathbb{P}(U \le u, W > w, X \le Y) + \mathbb{P}(U \le u, W > w, X > Y)$.[17] Thus, there are two terms to calculate. For the first one:

$$\begin{aligned}\mathbb{P}(U \le u, W > w, X \le Y) =& \mathbb{P}(X \le u, Y > X + w)\\ =& \iint\limits_{\{(x,y)|x\le u, y>x+w\}} p_{XY}(x, y)\,\mathrm{d}x\mathrm{d}y\\ =& \int_0^u \mathrm{d}x\,\lambda e^{-\lambda x} \underbrace{\int_{x+w}^\infty \mathrm{d}y\,\mu e^{-\mu y}}_{-e^{-\mu y}]_{x+w}^{\infty}}\\ =& \int_0^u \lambda e^{-\lambda x} e^{-\mu(x+w)}\mathrm{d}x\\ =& \frac{\lambda}{\lambda+\mu} e^{-\mu w}(1 - e^{-(\lambda+\mu)u})\end{aligned}$$

and similarly, $\mathbb{P}(U \le u, W > w, X > Y) = \frac{\mu}{\lambda+\mu} e^{-\lambda w}(1 - e^{-(\lambda+\mu)u})$. Hence, for $0 \le u \le u + w < \infty$, we have an expression which factorizes into the product of a function of u with a function of w. Hence U and W are independent:

$$\mathbb{P}(U \le u, W > w) = (1 - e^{-(\lambda+\mu)u}) \left(\frac{\lambda}{\lambda+\mu} e^{-\mu w} + \frac{\mu}{\lambda+\mu} e^{-\lambda w}\right).$$

■

Problem 10. A coin is flipped n times. The outcome is a rv X, which can take the value *heads* or *tails* (X = *heads* or X = *tails*). For n measurements, there are n such rv's

---

[17] Since the two events $\{U \le u, W > w, X \le Y\}$ and $\{U \le u, W > w, X > Y\}$ are mutually exclusive whereas the event $\{X \le Y\} \cup \{X > Y\}$ is always true. Recall that two events A and B are mutually exclusive if there is no overlap: $A \cap B = \emptyset$.

(and corresponding results): $X_1, X_2, \ldots, X_n$. The coin is possibly biased. Therefore, the probabilities of each outcome are not necessarily 1/2. Instead they are given in term of a parameter $-1/2 \leq \theta \leq 1/2$ quantifying the bias:

$$\mathbb{P}(X = heads) = 1/2 + \theta, \qquad \mathbb{P}(X = tails) = 1/2 - \theta.$$

(a) Explain how the numerical value of the bias parameter, θ, can be determined experimentally (empirically) by flipping the coin several times, i.e. find an explicit formula for $\hat{\theta}_n$, the estimator of θ, in terms of $X_1, \ldots, X_n$. Show that, under specific circumstances, $\hat{\theta}_n$ converges to θ in probability, i.e. show that $\mathbb{P}(|\hat{\theta}_n - \theta| > \epsilon) \to 0$, as $n \to \infty$ for any $\epsilon > 0$.

(b) Denote the number of times where you get heads as the result by H (and H is a rv, because its value may differ each time this experiment is done). Write down an explicit expression for H in terms of the experimental data. Find the mathematical expectation of H.

(c) Find the variance of H. For which value(s) of θ is the variance a minimum? A maximum?

(d) Calculate the "signal-to-noise ratio" of H. Explicitly give the dependence of SNR on n.

(e) For a fixed value of n, find the conditions for which the SNR is 1) infinite and 2) undetermined/undefined. Give a physical explanation of those two different situations.

(f) Find the limiting (n large) distribution of H.

Solution. (a) The probability $\mathbb{P}(X = heads)$ can be determined by counting the number of heads, i.e. let f_H be the empirical probability

$$f_H = \frac{1}{n}\sum_{i=1}^{n} \mathbf{1}_{\{X_i = heads\}},$$

where $\mathbf{1}_{\{X_i = heads\}}$ equals 1 if $X_i = heads$ and 0 otherwise. Taking the mathematical expectation we get

$$\langle f_H \rangle = \frac{1}{n}\sum_{i=1}^{n} \langle \mathbf{1}_{\{X_i = heads\}} \rangle,$$

where

$$\langle \mathbf{1}_{\{X_i = heads\}} \rangle = \sum_{\{x_i : x_i = heads\}} \mathbb{P}(X_i = heads) = \mathbb{P}(X_i = heads)$$

Therefore (the X_i are iidrv, with the same distribution as X),

$$\langle f_H \rangle = \mathbb{P}(X = heads).$$

By the law of large numbers (LLN), f_H converges to $\mathbb{P}(X_i = heads)$ as n increases. Now, since $\mathbb{P}(X = heads) = 1/2 + \theta$, which is also equal to $\langle f_H \rangle$, we take our estimator $\hat{\theta}$ to be:

$$\hat{\theta}_n = \left(\frac{1}{n} \sum_{i=1}^{n} \mathbf{1}_{\{X_i = heads\}} \right) - \frac{1}{2},$$

which implies that $\hat{\theta}_n$ converges to $\mathbb{P}(X = heads) - \frac{1}{2}$, as n increases. However, $\mathbb{P}(X = heads) - \frac{1}{2}$ is also equal to θ, by the LLN. Thus, $\hat{\theta}_n \to \theta$.

(b)

$$H = \sum_{i=1}^{n} \mathbf{1}_{\{X_i = heads\}}$$

where $\mathbf{1}_{X_i = heads}$ equals 1 when $X_i = heads$ and 0 when $X_i = tails$. Taking expectation value:

$$\langle H \rangle = \sum_{i=1}^{n} \langle \mathbf{1}_{\{X_i = heads\}} \rangle = \sum_{i=1}^{n} \mathbb{P}(\{X_i = heads\}) = \sum_{i=1}^{n} (1/2 + \theta) = n(1/2 + \theta).$$

(c) Variance:

$$\begin{aligned} var(H) = \sum_{i=1}^{n} var(\mathbf{1}_{\{X_i = heads\}}) &= \sum_{i=1}^{n} \langle (\mathbf{1}_{\{X_i = heads\}})^2 \rangle - \langle \mathbf{1}_{\{X_i = heads\}} \rangle^2 \\ &= n(1/2 + \theta) - n(1/2 + \theta)^2. \end{aligned}$$

since $(\mathbf{1}_{\{X_i = heads\}})^2 = \mathbf{1}_{\{X_i = heads\}}$. The variance reaches a maximum when $\theta = 0$ and a minimum when $\theta = \pm 1/2$.

(d) Find the dependence of SNR on n:

$$\text{SNR} = \frac{n(1/2 + \theta)}{\sqrt{n}\sqrt{1/4 - \theta^2)}} \propto \sqrt{n}.$$

(e) SNR is undetermined when $\theta = -1/2$ (probability of heads=0). 1) SNR is infinite when $\theta = 1/2$ (probability of heads=1).

(f) By the CLT, the limiting distribution is Gaussian. The mean is $n(1/2 + \theta)$ and variance is $n(1/2 + \theta) - n(1/2 + \theta)^2$. ■

Problem 11. Consider a die which is unbiased. (a) You roll the die once. What is the probability of getting a "1" vs a "4"?

(b) You roll the die twice. What is the probability of getting a total of "2" (i.e. "1" on both trials) versus the probability of getting a total of "7" ("Total" means you add the two results together.)

(c) You roll the die 10,000 times and record the results. What is the probability distribution of the mean (i.e. the mean of all the results), its first moment and variance?

Solution. (a) 1/6 and 1/6

(b) 2: 1/6 times 1/6 = 1/36

7: 6 times 1/6 times 1/6 = 1/6

(c) by the CLT the distribution converges to the normal law, $\mathcal{N}(3.5, \sigma^2/10000)$, where the value of σ^2 is:

$$\sigma^2 = \sum_{i=1}^{6}(x_i - \mu)^2 p_i = 2.917$$

■

Problem 12. What power of t (time) does the root-mean-square displacement in a 1D random walk depend on? How does this differ from the case of ballistic motion. Explain.

Solution. For random walk the root mean square displacement is proportional to $\sqrt{t}$ whereas for ballistic motion it depends on t. The $\sqrt{t}$ dependence can be explained by the large number of "back-and-forth" steps in the random walk. ■

Problem 13. Consider the normal (Gaussian) distribution with parameters μ and σ^2, i.e. let $X \sim \mathcal{N}(\mu, \sigma^2)$. Show all calculations.

(a) Calculate moments of all orders ($n = 0, 1, 2, 3, \dots$) for X.

(b) Calculate the central moments of all orders for X.

(c) Define a new function $K(t) = \log\langle e^{tX}\rangle$, and Taylor expand $K(t)$ in powers of t:

$$K(t) = \sum_{n=1}^{\infty} \kappa_n \frac{t^n}{n!}.$$

Find a general expression for the coefficients κ_n.

(d) Define a new function $M(t) = \exp(K(t))$. Show how the moments can be obtained from $M(t)$ in terms of the κ_n's.

(e) Show how the density of X, $p(x)$, can be constructed from a knowledge of the statistical moment, or from the central moments, or from the κ_n's.

(f) Explain why the method in (e) of reconstructing $p(x)$ is important from an experimental science standpoint.

Solution. (a) The moments of odd orders are all zero because the integral of an odd function (n-th moment of X, where n is odd) times an even function (Gaussian PDF) vanishes because the integrand is odd. On the other hand, the moment $\langle X^n\rangle$, where n is even are non-zero. They are calculated as follows:

$$\langle X^n\rangle = \int_{\mathbb{R}} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2} \cdot x^n \,\mathrm{d}x,$$

where we use

$$\int_0^{\infty} e^{-ax^2} x^n \mathrm{d}x = \frac{(n-1)!!}{2^{n/2+1} a^{n/2}} \sqrt{\frac{\pi}{a}}$$

for n even. The result is:

$$\langle X^n \rangle = \sigma^n (n-1)!!.$$

The first few moments are:

order	moment	central moment
$n=1$	μ	0
$n=2$	$\mu^2+\sigma^2$	σ^2
$n=3$	$\mu^3+3\mu\sigma^2$	0
$n=4$	$\mu^4+6\mu^2\sigma^2+3\sigma^4$	$3\sigma^4$
$n=5$	$\mu^5+10\mu^3\sigma^2+15\mu\sigma^4$	0

see `https://en.wikipedia.org/wiki/Normal_distribution#Moments`

(b) See solution to (a).

(c) Expand $e^{tX} = \sum_{i=0}^{\infty} \frac{t^i X^i}{i!}$ and take the average, $\langle e^{tX} \rangle = \sum_{i=0}^{\infty} \frac{t^i \langle X^i \rangle}{i!}$. On the other hand, take the exponential of $K(t)$,

$$e^{K(t)} = e^{\sum_{n=1}^{\infty} \kappa_n \frac{t^n}{n!}} = 1 + \sum_{n=1}^{\infty} \kappa_n \frac{t^n}{n!} + \frac{1}{2}\left(\sum_{n=1}^{\infty} \kappa_n \frac{t^n}{n!}\right)^2 + \frac{1}{3!}\left(\sum_{n=1}^{\infty} \kappa_n \frac{t^n}{n!}\right)^3 + \dots.$$

We can now identify the like powers of t (let $\mu_r = \langle X^r \rangle$):

$$\begin{aligned}
t^1 &: \mu_1 = \kappa_1 & \mu_1 &= \kappa_1 \\
t^2 &: \mu_2/2 = \kappa_2/2 + \kappa_1^2/2 & \mu_2 &= \kappa_2 + \kappa_1^2 \\
t^3 &: \mu_3/6 = \kappa_3/6 + \kappa_1\kappa_2/2 + \kappa_1^3/6 & \mu_3 &= \kappa_3 + 3\kappa_1\kappa_2 + \kappa_1^3 \\
&\vdots & &\vdots
\end{aligned}$$

This can be "inverted" to give:

$\kappa_1 = \mu_1$

$\kappa_2 = \mu_2 - \mu_1^2$

$\kappa_3 = \mu_3 - 3\mu_2\mu_1 + 2\mu_1^3$

$\vdots$

(d) $M(t) = \langle e^{tX} \rangle = \langle \sum_{i=0}^{\infty} t^i X^i / i! \rangle = \sum_{i=0}^{\infty} t^i \langle X^i \rangle / i!$. The moments are obtained by differentiation with respect to t and setting $t=0$:

$$\mu_r \equiv \langle X^r \rangle = \frac{\mathrm{d}^r}{\mathrm{d}t^r} M(t)\bigg|_{t=0}.$$

(e) Consider the quantity $\langle e^{tX}\rangle$,

$$M(t) = \sum_{r=0}^{\infty} \frac{t^r \mu_r}{r!} = \langle e^{tX}\rangle \equiv \int_{-\infty}^{\infty} e^{tx} p(x)\mathrm{d}x.$$

We can solve for $p(x)$ by invoking the inversion formula:

$$\frac{1}{2\pi i}\lim_{T\to\infty}\int_{\gamma-iT}^{\gamma+iT} e^{-st}M(s)\mathrm{d}s = \frac{1}{2\pi i}\lim_{T\to\infty}\int_{\gamma-iT}^{\gamma+iT} e^{-st}\left[\int_{-\infty}^{\infty} e^{sx}p(x)\mathrm{d}x\right]\mathrm{d}s.$$

$$= \frac{1}{2\pi}\lim_{T\to\infty}\int_{-\infty}^{\infty}\int_{-T}^{T} e^{\gamma(x-t)}e^{i(x-t)\tau}p(x)\mathrm{d}x\mathrm{d}\tau.$$

Then integrating over τ and invoking $\delta(x-a) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i(x-a)t}\mathrm{d}t$:

$$= \int_{-\infty}^{\infty} e^{\gamma(x-t)}\delta(x-t)p(x)\mathrm{d}x = p(t).$$

(f) This is important because if we know all the moments, we can reconstruct $p(x)$. The moments can be estimated from experimental data. ■

Problem 14. The scores in a chemistry class from 2016 were as follows (out of 100):

40.311 33.386 44.142 65.631 41.066 47.051 42.322 50.752 30.730 28.777 50.885 45.143 29.997 34.107 31.045 39.684 25.157 38.825 41.838 35.716 26.620 44.827 50.506 63.251 32.622 59.843 56.967 50.783 51.961 39.746 50.895 36.447 26.660 49.376 29.302 37.166 33.532 33.627 34.030 34.816 52.107 58.384 50.539 37.568 39.806 54.394 42.399 40.042 47.231 21.915

(a) If the course policy is to assign 'A' grades to the top 10-percentile of the class and 'F' to the rest, how many students obtained an F?

(b) Draw a histogram of the exam results.

(c) Calculate the mean, standard deviation and median of the exam and indicate those quantities on the histogram. (Explain how those quantities are calculated from the data.)

(d) In units of standard deviation (σ), how far is the 10-percentile from the mean?

(e) Reconstruct the PDF of this rv X (score), using the numerical data.

(f) Suppose that the 2017 scores were:

59.378 102.006 54.660 39.713 61.877 46.731 17.570 45.646 71.654 19.959 58.948 57.506 78.838 31.859 20.175 31.766 39.408 41.096 31.092 52.754 53.712 67.778 66.991 37.362 57.768 72.032 48.005 78.559 46.742 84.157 66.175 90.976 72.627 40.335 19.464 60.673 51.911 34.235 35.143 39.269 48.814 83.537 50.505 40.340 47.480 58.682 72.354 56.195 74.103 50.013

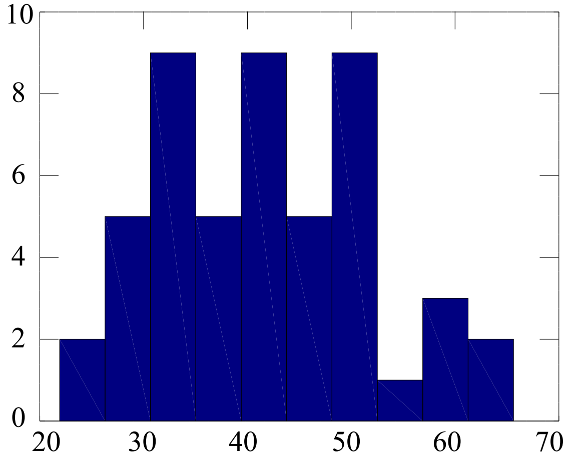


Figure 1.14. Histogram.

Plot histogram and calculate distribution parameters. Are these scores significantly different from those of 2016? (Why/why not?)

Solution. (a) The top 10-percentile is called the 90th percentile, and is the value of x_{90} such that

$$\int_{-\infty}^{x_{90}} p(x)\mathrm{d}x = 0.90.$$

Numerically, there is a function in MATLAB called `prctile` that will compute this for us. I get 55.68 for the above data. This means that all scores below this get an 'F'; we count 45 of those.

(b) See Figure 1.14.

(c) Mean = 41.679 (use formula for sample mean), std = 10.372 (use formula for sample standard deviation), median = 40.177 (order the numbers and pick the middle one).

(d) In MATLAB, we simply type `(prctile(d,90)-mean(d))/std(d)` and obtain 1.3500.

(e) From the raw data we can calculate the moments of the distribution:

r	raw moment	central moment
1	41.679	9.4502×10^{-15}
2	1842.5	105.43
3	8.5908×10^{4}	325.47
4	4.1974×10^{6}	2.6805×10^{4}
5	2.1355×10^{8}	2.0898×10^{5}

and using the inversion formula, we can obtain $p(x)$.

(f) The mean/std are 53.371 ± 19.136. Compare this to 41.679 ± 10.372. These two numbers are not significantly different because their error bars overlap considerably. ■

Problem 15. Prove, using the law of large numbers, that the histogram of a rv X converges to its PDF, $p(x)$.

Solution. Let X have CDF $F(x)$. Let $X_1, X_2, \dots, X_n$ be a random sample of F. Define the indicator function $\mathbf{1}_{(-\infty,x]}(y)$ to be equal to 1 if $y \le x$ and zero otherwise. Then,

$$\langle \mathbf{1}_{(-\infty,x]}(X_i) \rangle = \int_{-\infty}^{x} p(x_i)\mathrm{d}x_i = \mathbb{P}(X_i \le x) = F(x).$$

For each n, the histogram of the random sample is:

$$F_n(x) = \frac{1}{n}\sum_{i=1}^{n} \mathbf{1}_{(-\infty,x]}(X_i)$$

Its expectation value is:

$$\langle F_n(x) \rangle = \frac{1}{n}\sum_{i=1}^{n} \langle \mathbf{1}_{(-\infty,x]}(X_i) \rangle = F(x).$$

It then follows from the law of large numbers that $F_n(x)$ converges to $F(x)$. If the CDFs converge, the PDFs also converge. ■

Problem 16. Prove, using the law of large numbers, that the empirical distribution of random variable X, $\hat{p}(x)$ converges to its PDF, $p(x)$.

Solution. The solution is identical to that of Problem 15. The empirical distribution $\hat{p}(x) = \frac{1}{n}\sum_{i=1}^{n} \delta(x - x_i)$ has the empirical CDF:

$$\mathbb{P}(X \le x) = \int_{-\infty}^{x} \hat{p}(x)\mathrm{d}x = \frac{1}{n}\#\{i : x_i \le x\},$$

where $\#\{i : x_i \le x\}$ denotes the number of data points x_i satisfying the condition $x_i \le x$. Let's denote the random variables as X_i and x_i, their corresponding values. Since n data points are used to construct this CDF let us denote it as $F_n(x)$. Its expectation value is

$$\langle F_n(x) \rangle = \frac{1}{n}\langle \#\{i : X_i \le x\} \rangle = \frac{1}{n}\langle \sum_{i=1}^{n} \mathbf{1}_{(-\infty,x]}(X_i) \rangle = F(x),$$

where $F(x)$ is the CDF of $p(x)$ and $\#\{i : X_i \le x\} = \sum_{i=1}^{n} \mathbf{1}_{(-\infty,x]}(X_i)$. It then follows from the law of large numbers that $F_n(x)$ converges to $F(x)$. Since the CDFs converge, the PDFs also converge, as the PDF is obtained from the CDF by differentiation. ■

Problem 17. Consider the weak law of large numbers (WLLN): Let X_1, $X_2, \dots$ be iidrv with mean μ and variance $\sigma^2 < \infty$. Then, $(1/n)\sum_{i=1}^{n} X_i$ converges to μ in probability.

(a) Prove the WLLN.

(b) Illustrate it using a numerical example, i.e. choose $\epsilon > 0$, generate random sequences $X_1, \dots, X_n$, compute the sample mean $\overline{X}_n$, record this value as m_1. Generate a second random sequence, and obtain the sample mean as m_2. Repeat this process many times (r times) and plot a histogram of the sample means $(m_1, m_2, \dots, m_r)$. Then increase n and repeat this process. You should now have several histograms as function of n. Then plot the probability $\mathbb{P}(|\overline{X}_n - \mu| \geq \epsilon)$ as a function of n and show that it converges to 0 as n increases. Since we are dealing with experimental data, the probability should be calculated empirically:

$$\mathbb{P}(|\overline{X}_n - \mu| \geq \epsilon) = \frac{1}{r}\sum_{j=1}^{r} \mathbf{1}_{|m_j - \mu| \geq \epsilon}$$

where $\mathbf{1}_{|m_j - \mu| \geq \epsilon}$ is an "indicator function", i.e. equals 1 when $|m_j - \mu| \geq \epsilon$ and equals 0 otherwise.

Solution. (a) Weak law: let $\overline{X}_n = (1/n)(X_1 + X_2 + \cdots + X_n)$, $var(\overline{X}_n) = (1/n^2)n \cdot var(X_1) = \sigma^2/n$, and $\overline{x}_n = \frac{x_1 + \cdots + x_n}{n}$. Then,

$$\begin{aligned}
\mathbb{P}(|\overline{X}_n - \mu| \geq \epsilon) &= \int_{\{(x_1,\dots,x_n) \mid |\overline{x}_n - \mu| \geq \epsilon\}} p_1(x_1) \cdot \dots \cdot p_n(x_n) \mathrm{d}x_1 \dots \mathrm{d}x_n \\
&\leq \int_{\{|\overline{x}_n - \mu| \geq \epsilon\}} \frac{(\overline{x}_n - \mu)^2}{\epsilon^2} p_1(x_1) \cdot \dots \cdot p_n(x_n) \mathrm{d}x_1 \dots \mathrm{d}x_n \\
&\leq \int_{\mathbb{R}^n} \frac{(\overline{x}_n - \mu)^2}{\epsilon^2} p_1(x_1) \cdot \dots \cdot p_n(x_n) \mathrm{d}x_1 \dots \mathrm{d}x_n \\
&= \frac{var(\overline{X}_n)}{\epsilon^2} = \frac{\sigma^2}{n\epsilon^2} \to 0 \text{ as } n \to \infty.
\end{aligned}$$

This completes the proof of the WLLN. The first inequality is justified because $|\overline{x}_n - \mu| \geq \epsilon$, and therefore, $1 \leq \frac{|\overline{x}_n - \mu|}{\epsilon}$, and consequently (squaring both sides), $1 \leq \frac{|\overline{x}_n - \mu|^2}{\epsilon^2}$. The second equality is justified because the integral is everywhere non-negative. Therefore, extending the region of integration from the restricted set $\{(x_1, \dots, x_n) : |\overline{x}_n - \mu| \geq \epsilon\}$ to the whole space $\mathbb{R}^n$ leads to an upper bound. This proof assumes the existence of the variance σ^2 of X_i.

(b) There are many possible solutions here. Here is mine. I used this code in MATLAB to generate the random numbers and required plots:

```
m=10000; r=10000;
X=10*randn([m,r])+100;
for j=1:r,
    Xn(j)=(1/j)*squeeze(sum(X(1:j,j),1));
end;
figure;plot(Xn);
figure;hist(X(100,1:100),20);
figure;hist(X(10000,1:10000),50);
```

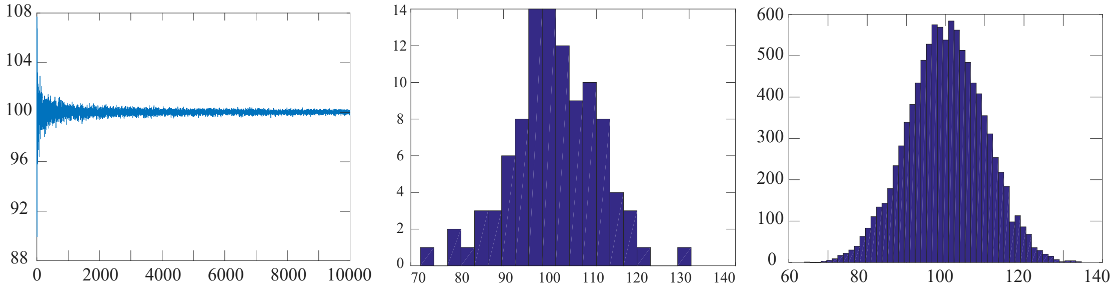


Figure 1.15. Law of large numbers illustrated.

Here we generated random variables $\sim \mathcal{N}(100, 100)$. The first plot (Fig. 1.15) illustrates the LLN because the arithmetic averages are shown to converge to the true mean (100) as the number of terms in the sum increases. The histograms show that with only a few terms, we do not get a nice Gaussian, whereas using 10,000 terms, we get a nice bell curve. (If you chose a distribution other than normal, these histograms should reflect the chosen distribution.) $\blacksquare$

Problem 18. Derive the probability distribution of a biased random walk (i.e. let $p_\sigma = 1/2 + \delta$ and $p_{-\sigma} = 1/2 - \delta$ for some bias $0 \le \delta \le 1/2$).

Solution. By the CLT, the distribution will be Gaussian, of course. The mean step size is $\mu_i = \langle X_i \rangle = \sigma(p_\sigma - p_{-\sigma}) = \sigma(1/2 + \delta - 1/2 + \delta) = 2\sigma\delta$. So the total displacement

$$X_{tot} = X_1 + X_2 + \cdots + X_n$$

has expectation value

$$\langle X_{tot} \rangle = 2\sigma\delta n,$$

instead of 0. (i.e. it "drifts" linearly with time at constant speed $2\sigma\delta$.)

The variance is $var(X_i) = \langle X_i - \mu_i \rangle^2 = p_\sigma(\sigma - 2\sigma\delta)^2 + p_{-\sigma}(-\sigma - 2\sigma\delta)^2 = (1/2 + \delta)\sigma^2(1 - 2\delta)^2 + (1/2 - \delta)\sigma^2(1 + 2\delta)^2 = \sigma^2(1/2 + \delta)(1 - 4\delta + 4\delta^2) + \sigma^2(1/2 - \delta)(1 + 4\delta + 4\delta^2) = \sigma^2[1 - 4\delta^2]$. The total variance is:

$$var(X_{tot}) = var(X_1) + \cdots + var(X_n) = \sigma^2[1 - 4\delta^2]n,$$

as opposed to $\sigma^2 n$. Thus, the variance is reduced. When $\delta = \pm 1/2$ (meaning steps are always to the left, or always to the right), then the variance is zero because the path is no longer random, but instead becomes deterministic. $\blacksquare$

Problem 19. Prove that in 3D the mean square displacement is $6Dt$, and in the general case of d dimensions, it is equal to $2dDt$ (a direct calculation of the d-dimensional integral requires the spherical volume element in d-dim, which includes some Gamma functions).

Solution. In 3D the mean square displacement is

$$\begin{aligned}\langle r(t)^2\rangle \equiv&\frac{1}{(4\pi Dt)^{3/2}}\int_{\mathbb{R}^3} r^2\exp\left(-\frac{r^2}{4Dt}\right)\mathrm{d}^3r\\ =&\frac{1}{(4\pi Dt)^{3/2}}\int_{\mathbb{R}^3} r^2\exp\left(-\frac{r^2}{4Dt}\right)r^2\mathrm{d}r\mathrm{d}(\cos\theta)\mathrm{d}\phi\\ =&\frac{4\pi}{(4\pi Dt)^{3/2}}\int_0^\infty r^4\exp\left(-\frac{r^2}{4Dt}\right)\mathrm{d}r\end{aligned}$$

To integrate this we use the famous result $\int_{-\infty}^{\infty} e^{-ax^2}\mathrm{d}x = \sqrt{\pi/a}$, differentiate wrt a twice: $\int_{-\infty}^{\infty} x^4 e^{-ax^2}\mathrm{d}x = \frac{3}{4}\sqrt{\pi}a^{-5/2}$.

$$\frac{4\pi}{(4\pi Dt)^{3/2}}\int_0^\infty r^4\exp\left(-\frac{r^2}{4Dt}\right)\mathrm{d}r = \frac{4\pi}{(4\pi Dt)^{3/2}}\frac{3}{8}\sqrt{\pi}(4Dt)^{5/2} = 6Dt.$$

In the general case of d dimensions, the mean square displacement is:

$$\langle r(t)^2\rangle = \langle x_1^2+\cdots+x_d^2\rangle = 2dDt.$$

There is no d-dimensional integral needed here, as each $\overline{x_1^2}$ contributes $2Dt$, and there are d such terms, for a total of $2dDt$. ■

Problem 20. Prove that for the Poisson distribution the mean and variance are both equal to the parameter of the distribution.

Solution. Proofs can be found here:
`http://filestore.aqa.org.uk/subjects/AQA-MS03-W-2-SM.PDF`
`https://proofwiki.org/wiki/Variance_of_Poisson_Distribution` ■

Problem 21. Prove that Poisson distribution converges to a Gaussian in the limit of large n. However, obtain the coefficient of the exponential as well (the prefactor), making use of the slightly more accurate Stirling's formula.

Solution. The calculation we did previously was:

$$\begin{aligned}\frac{e^{-\overline{n}}\overline{n}^n}{n!} &= \exp\{-\overline{n}-\log n! + n\log\overline{n}\}\\ &= \exp\{-\overline{n} - n\log n + n + n\log\overline{n}\}\\ &= \exp\{(n-\overline{n}) + n\log(\overline{n}/n)\}\\ &= \exp\left\{(n-\overline{n}) + n\log\left[1+\left(\frac{\overline{n}-n}{n}\right)\right]\right\}\\ &\approx \exp\left\{-\frac{(\overline{n}-n)^2}{2n}\right\} \approx \exp\left\{-\frac{(\overline{n}-n)^2}{2\overline{n}}\right\}\end{aligned}$$

The prefactor $\frac{1}{\sqrt{2\pi\overline{n}}}$ is recovered by using

$$n! \approx \sqrt{2\pi n}\left(\frac{n}{e}\right)^n.$$

Now, replace $\frac{e^{-\overline{n}}\overline{n}^n}{n!}$ by $\frac{1}{\sqrt{2\pi n}}\frac{e^{-\overline{n}}\overline{n}^n}{\left(\frac{n}{e}\right)^n} = \frac{1}{\sqrt{2\pi n}}e^{-\overline{n}}\overline{n}^n e^{-n\log n+n}$. This gives the desired result with the correct prefactor. ■

Problem 22. Let $X \sim \mathcal{N}(0,1)$. Generate iid random numbers on a computer (say, 10,000 numbers). Those are the different realizations of X, i.e. $x_1, x_2, \ldots, x_{10{,}000}$. Next, consider another random variable, Y.

(a) Let $Y = X + 1$, so that we now have 10,000 pairs of points: (x_1, y_1), (x_2, y_2), …, $(x_{10{,}000}, y_{10{,}000})$. Plot these 10,000 pairs $\{(x_i, y_i)\}$ as dots on scatter plot. Fit a straight line. What slope do you get? From the data, calculate the sample correlation coefficient. Is Y correlated to X? Why?

(b) Let X be as previously defined. Let Z be distributed identically to X, but independent of X. Generate random numbers on a computer to obtain pairs $\{(x_i, z_i)\}$ of random numbers. Define a new random variable $Y = X + Z$. Is Y correlated to X? Why? (Plot XY pairs on a scatter plot, fit a straight line, calculate $r_{X,Y}$.)

(c) Let X be as defined previously. Let $Y \sim \mathcal{N}(0,1)$. Generate random numbers for X and Y, and plot the resulting pairs $\{(x_i, y_i)\}$ on a scatter plot. Are X and Y correlated? Why?

Solution. (a) Y is correlated to X ($r = 1$). On a scatter plot, we should see a perfect straight line (no deviation from it).

(b) $cov(X,Y) = cov(X, X+Z) = cov(X,X) + cov(X,Z) = var(X) = 1$, hence $r = 1$. Here on a scatter plot there will be random deviations from a straight line due to Z. However, fitting a straight line will still give a slope of 1.

(c) Totally uncorrelated, since X and Y are independent. (Scatter plot looks random.) ■

Problem 23. Choose a distribution we have *not* used in class. Fix (choose) the parameters of the distribution. Let X be a random variable distributed accordingly. Calculate the mean and variance of X analytically (i.e. using the distribution function). Use a computer to generate random numbers according to the distribution of X. (How do you generate such random numbers?) Plot the histogram of X, compare to the PDF or PMF of X (plot both on the same graph). Calculate numerically the mean and variance of X (using the random numbers you generated). Compare to the true values of mean and variance obtained from the PDF or PMF.

Problem 24. Let X be the result of rolling a die. Generate n random numbers on a computer and obtain the random sample $X_1, X_2, \ldots, X_n$. Take the arithmetic average: $\overline{X}_n \equiv \frac{1}{n}\sum_{i=1}^{n} X_i$. Plot $\overline{X}_n$ versus n. What do you conclude? What theorem does this exercise illustrate?

Solution. This illustrates the law of large numbers. See the article for the plot:
`https://en.wikipedia.org/wiki/Law_of_large_numbers` ■

Problem 25. Let Y be a Poisson rv with parameter λ. Prove that Y can be written as the sum

$$Y = X_1 + X_2 + \cdots + X_n,$$

where X_i are independent identically distributed rv's, also with the Poisson distribution. What should be the lambda parameter of the X_i?

Solution. Let's do the case of two rv's. Let $Z = X + Y$ where X and Y are Poisson, with parameters λ and μ, respectively. Then the PMF of Z is:

$$\mathbb{P}(Z = z) = \sum_{x=0}^{z} \frac{e^{-\lambda}\lambda^x}{x!}\frac{e^{-\mu}\mu^{z-x}}{(z-x)!} = \frac{e^{-(\lambda+\mu)}}{z!}\sum_{x=0}^{z}\binom{z}{x}\lambda^x\mu^{z-x}$$

Thus, Z is also Poisson, but with mean $\lambda+\mu$. This can be extended to n Poisson variables. Their sum will also be Poisson. If $Y = X_1 + \cdots + X_n$ has parameter λ, then each X_i must have parameter λ/n. ■

Problem 26. Let $X_1, \ldots, X_n$ be a sequence of independent random variables with CDF's F_n (X_i has CDF F_i, $i = 1, \ldots, n$). Let X be a random variable with CDF F. The sequence X_n is said to *converge in distribution* if the CDF's converge pointwise, i.e.,

$$\lim_{n\to\infty} F_n(x) = F(x),$$

at all points x for which F is continuous.

(a) Show that convergence of the CDF's also implies the PDF's. i.e. let f_i be the PDF of independent rv's X_i ($i = 1, \ldots, n$) and f be the PDF of X. Prove that convergence of the CDF's implies:

$$\lim_{n\to\infty} f_n(x) = f(x)$$

for all x.

(b) Prove that the sequence of independent rv's $X_i \sim \mathcal{N}(1/n, 1)$ converges *in distribution* to a standard normal random variable.

Solution. Since

$$\frac{1}{\sqrt{2\pi}}\exp\left(-\frac{1}{2}\left[x - \frac{1}{n}\right]^2\right) \to \exp\left(-\frac{x^2}{2}\right),$$

it follows that X_n converges in distribution to $X\ \mathcal{N}(0, 1)$. ■

Problem 27. Let $X_n \sim \mathcal{N}(0, 1/n)$ and let $X = 0$. Prove that for any $\epsilon > 0$,

$$\mathbb{P}(|X_n| > \epsilon) \to 0$$

as $n \to \infty$. This is an example of *convergence in probability*, i.e. $\mathbb{P}(|X_n| > \epsilon) \to 0$ implies that X_n converges in probability to X (=0), since $\mathbb{P}(|X_n| > \epsilon) = \mathbb{P}(|X_n - X| > \epsilon)$.

Solution. First we note that $\mathbb{P}(|X_n| > \epsilon) = \mathbb{P}(|X_n|^2 > \epsilon^2)$. The latter is the integral:

$$\int\limits_{\{x_n^2>\epsilon^2\}} p(x_n)\mathrm{d}x_n \leq \int\limits_{\{x_n^2>\epsilon^2\}} \frac{x_n^2}{\epsilon^2}p(x_n)\mathrm{d}x_n \leq \int_{\mathbb{R}} \frac{x_n^2}{\epsilon^2}p(x_n)\mathrm{d}x_n$$

$$= \frac{\langle X_n^2\rangle}{\epsilon^2} = \frac{var(X_n)}{\epsilon^2} = \frac{1}{n\epsilon^2} \to 0$$

■

Problem 28. Let X_i be iidrv with uniform distribution over the interval [0,1]. Take the sum $S_n = X_1 + X_2 + \cdots + X_n$. Find the distribution of X_n analytically (i.e. find its CDF and PDF). Show numerically (i.e. by generating random numbers on a computer) the histogram of S_n from $n = 1, 2, \ldots, 10$. What do you conclude?

Solution. This is straightforward and will be left as an exercise (simply generate random numbers in MATLAB to construct S_n, and plot using the `hist` function). S_1 has the uniform distribution. S_2 has the "tent" distribution. etc. whereas S_n for large n looks more and more Gaussian as n increases, thanks to the CLT. Convergence to a Gaussian is very fast and does not require n to be very large. ■

Problem 29. Suppose that X has a PDF, $p(x) = \frac{1}{2}\sin(x)$, where $x \in [0, \pi]$, and equals zero elsewhere. Calculate its mean and variance. Calculate its skewness and kurtosis. Compare skewness and kurtosis to those of a normal distribution (with same mean and variance).

Solution. We will do the first two moments (others are obtained similarly):

$$\langle X\rangle = \int_0^{\pi} \frac{1}{2}\sin(x)x\mathrm{d}x = \frac{\pi}{2}.$$

$$\langle X - \frac{\pi}{2}\rangle^2 = \int_0^{\pi} \frac{1}{2}\sin(x)(x - \frac{\pi}{2})^2\mathrm{d}x = \frac{1}{4}(\pi^2 - 8).$$

Those results can be obtained from WolframAlpha by typing:

```
integrate x*(1/2)*sin(x) from 0 to Pi
integrate ((x-Pi/2)^2)*(1/2)*sin(x) from 0 to Pi
```

■

Problem 30. Let $X \sim \mathcal{N}(0, 1)$. What is the distribution of $Y = X^3 + 5$?

Solution.

$$\mathbb{P}(Y < y) = \mathbb{P}(X^3 + 5 < y) = \mathbb{P}(X \leq \sqrt[3]{y-5}) = \int_{-\infty}^{\sqrt[3]{y-5}} \frac{1}{\sqrt{2\pi}}e^{-x^2/2}\mathrm{d}x.$$

It is also ok to calculate its PDF by differentiating the above CDF with respect to y, making use of the Leibniz formula. ■

Problem 31. Calculate the mean and the variance of a random variable X distributed according to the PDF:

$$p(x) = \frac{\gamma}{(x-\mu)^2+\gamma^2}.$$

Solution. For the mean we have an integral of the type (set $\gamma = 1$, $\mu = 0$ without loss of generality, since I analyze the "tail" of the function here):

$$\int_{-\infty}^{\infty} \frac{1}{x^2+1} x \mathrm{d}x$$

When x is large, this integral behaves like $\int 1/x \sim \log(x)$, which diverges with x. Thus, the mean does not exist. For the variance, we have an integral of the type

$$\int_{-\infty}^{\infty} \frac{1}{x^2+1} x^2 \mathrm{d}x \sim \int \mathrm{d}x \sim x \to \infty$$

which also diverges. Thus, it has no variance. ■

Problem 32. The probability of k successes in n trials is ($k = 0, 1, \dots, n$, $0 \le p \le 1$):

$$\mathbb{P}(k \text{ successes}) = \binom{n}{k} p^k (1-p)^{n-k}.$$

B is a random variable distributed as such. Prove that B has mean np and variance $np(1-p)$.

Solution. See `https://en.wikipedia.org/wiki/Binomial_distribution` ■

Problem 33. Suppose that you have a string instrument (e.g., electric guitar) whose strings, when plucked, behave like oscillators. The potential energy of the string is modeled by an anharmonic oscillator which consists of the sum of quadratic and quartic terms:

$$V(x) = ax^2 + bx^4. \qquad a, b \text{ non-negative constants}$$

The potential V is transferred to kinetic energy, which is then measured by the guitar's pick-up coils and sent to the amplifier. The noise statistics of V are important for the design of the guitar amplifier circuits.

If the position x (x: extension of the center of the string from its equilibrium position) is measured experimentally using an interferometer whose instrument noise is known to be normally distributed with mean μ and variance σ^2, what would you expect the noise statistics of V to look like? (i.e. find the probability distribution of V) Note: you can assume there are no temporal correlations in the noise.

(a) When $b = 0$ and a is nonzero (no anharmonicity).

(b) When $a = 0$ and b is nonzero (anharmonic part only).

Solution. (a) When $V = ax^2$, the probability of $V < v$, $\mathbb{P}(V < v)$, is:

$$\mathbb{P}(ax^2 \quad < \quad v) \quad = \quad \mathbb{P}(-\sqrt{\tfrac{v}{a}} \quad < \quad x \quad < \quad \sqrt{\tfrac{v}{a}}) \quad = \quad \frac{1}{\sqrt{2\pi\sigma^2}} \int\limits_{-\sqrt{\frac{v}{a}}}^{\sqrt{\frac{v}{a}}} e^{-(x-\mu)^2/2\sigma^2} \mathrm{d}x.$$

Differentiating with respect to v gives the PDF, $p_V(v) = \frac{\mathrm{d}\mathbb{P}(V<v)}{\mathrm{d}v}$:

$$\frac{e^{-(\sqrt{v/a}-\mu)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}} \cdot \frac{\mathrm{d}}{\mathrm{d}v}\sqrt{v/a} - (\text{lower limit}) = \frac{e^{-(\sqrt{v/a}-\mu)^2/2\sigma^2} + e^{-(\sqrt{v/a}+\mu)^2/2\sigma^2}}{\sqrt{8av\pi\sigma^2}}$$

(b) When $V = bx^4$ the probability of $V < v$, $\mathbb{P}(V < v)$, is (imaginary roots are discarded, because probabilities are non-negative quantities):

$$\mathbb{P}(bx^4 \quad < \quad v) \quad = \quad \mathbb{P}(-(v/b)^{\frac{1}{4}} \quad < \quad x \quad < \quad (v/b)^{\frac{1}{4}}) \quad = \quad \frac{1}{\sqrt{2\pi\sigma^2}} \int\limits_{-(v/b)^{1/4}}^{(v/b)^{1/4}} e^{-(x-\mu)^2/2\sigma^2} \mathrm{d}x.$$

The PDF is obtained by differentiation, $p_V(v) = \frac{\mathrm{d}\mathbb{P}(V<v)}{\mathrm{d}v}$:

$$\begin{aligned} &\frac{e^{-((v/b)^{1/4}-\mu)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}} \cdot \frac{\mathrm{d}}{\mathrm{d}v}(v/b)^{1/4} - (\text{lower limit}) \\ &\qquad\qquad = \frac{1}{v^{3/4}} \frac{e^{-((v/b)^{1/4}-\mu)^2/2\sigma^2} + e^{-((v/b)^{1/4}+\mu)^2/2\sigma^2}}{\sqrt{32\pi\sigma^2}\, b^{1/4}} \end{aligned}$$

■

Problem 34. The joint density of X and Y is

$$p_{XY}(x, y) = \begin{cases} 2 & \text{if } 0 \le x \le y \le 1; \\ 0 & \text{otherwise.} \end{cases}$$

Another rv Z is independent from X and Y and has the same distribution as X. (a) Find the covariance matrix of the vector (X, Y, Z). (b) Calculate the first two moments of a new rv that is the sum of all 3, i.e. $X + Y + Z$. (c) Compute $cov(X, Y + Z)$. (d) Compute the covariance matrix of the vector $(X, X + Z, Y + Z)$.

Solution. (a) Let $\mathbf{v} = (X, Y, Z)$. Then, since Z is independent of X and Y, we can immediately put 0's in a few places:

$$cov(\mathbf{v}, \mathbf{v}) = \begin{bmatrix} cov(X,X) & cov(X,Y) & cov(X,Z) \\ cov(Y,X) & cov(Y,Y) & cov(Y,Z) \\ cov(Z,X) & cov(Z,Y) & cov(Z,Z) \end{bmatrix}$$
$$= \begin{bmatrix} var(X) & cov(X,Y) & 0 \\ cov(Y,X) & var(Y) & 0 \\ 0 & 0 & var(Z) \end{bmatrix}$$

For $var(X)$ and $var(Y)$, we need the marginal PDFs:

$$p_X(x) = \int_{\{y\in[0,1]|y>x\}} p_{XY}(x,y)\mathrm{d}y = \int_x^1 2\mathrm{d}y = 2\ y|_{y=x}^{y=1} = 2(1-x).$$
$$p_Y(y) = \int_{\{x\in[0,1]|x<y\}} p_{XY}(x,y)\mathrm{d}x = \int_0^y 2\mathrm{d}x = 2\ x|_{x=0}^{x=y} = 2y.$$

where $0 \le x, y \le 1$. Using the marginal PDFs,

$$\langle X\rangle = \int_0^1 xp_X(x)\mathrm{d}x = \int_0^1 x2(1-x)\mathrm{d}x = \frac{1}{3},$$
$$var(X) = \int_0^1 (x-\frac{1}{3})^2 p_X(x)\mathrm{d}x = \frac{1}{18}.$$
$$\langle Y\rangle = \int_0^1 yp_Y(y)\mathrm{d}y = \int_0^1 y2y\mathrm{d}x = \frac{2}{3},$$
$$var(Y) = \int_0^1 (y-\frac{2}{3})^2 p_Y(y)\mathrm{d}y = \frac{1}{18}.$$

Finally, for $cov(X,Y)$ we use the joint PDF:

$$cov(X,Y) = \langle (X-\langle X\rangle)(Y-\langle Y\rangle)\rangle = \int_0^1 \mathrm{d}x \int_x^1 (x-\frac{1}{3})(y-\frac{2}{3})2\,\mathrm{d}y$$
$$= \int_0^1 \frac{1}{9}(1-3x)^2(1-x)\mathrm{d}x = \frac{1}{36}.$$

The covariance matrix is:

$$cov(\mathbf{v}, \mathbf{v}) = \begin{bmatrix} \frac{1}{18} & \frac{1}{36} & 0 \\ \frac{1}{36} & \frac{1}{18} & 0 \\ 0 & 0 & \frac{1}{18} \end{bmatrix}.$$

(b) First moment:

$$m_1 = \langle X+Y+Z\rangle = \langle X\rangle + \langle Y\rangle + \langle Z\rangle = 2\langle X\rangle + \langle Y\rangle = \frac{2}{3} + \frac{2}{3} = \frac{4}{3}.$$

Second moment:

$$m_2 = \langle X+Y+Z\rangle^2 = \langle X^2\rangle + \langle Y^2\rangle + \langle Z^2\rangle + 2\langle XY\rangle + 2\ \langle YZ\rangle + 2\langle XZ\rangle.$$

Since Z is independent of X and Y and has the same distribution as X:

$$m_2 = 2\langle X^2\rangle + \langle Y^2\rangle + 2\langle XY\rangle + 2\langle Y\rangle\langle Z\rangle + 2\langle X\rangle\langle Z\rangle.$$

where

$$\langle X^2\rangle = \int_0^1 x^2 2(1-x)\mathrm{d}x = \frac{1}{6}$$

$$\langle Y^2\rangle = \int_0^1 y^2 2y \mathrm{d}x = \frac{1}{2}$$

$$\langle XY\rangle = \int_0^1 \mathrm{d}x \int_x^1 xy2\,\mathrm{d}y = \int_0^1 (x-x^3)\mathrm{d}x = \frac{1}{4}.$$

Therefore,

$$m_2 = 2\cdot\frac{1}{6} + \frac{1}{2} + 2\cdot\frac{1}{4} + 2\cdot\frac{2}{3}\cdot\frac{1}{3} + 2\cdot\frac{1}{3}\cdot\frac{1}{3} = 2.$$

(c) By linearity, and independence of Z from X:

$$cov(X, Y+Z) = cov(X,Y) + cov(X,Z) = cov(X,Y) = \frac{1}{36}.$$

(d) Let $\mathbf{v} = (X, X+Z, Y+Z)$. The covariance matrix is:

$$cov(\mathbf{v},\mathbf{v}) = \begin{bmatrix} var(X) & cov(X, X+Z) & cov(X, Y+Z) \\ cov(X+Z, X) & var(X+Z) & cov(X+Z, Y+Z) \\ cov(Y+Z, X) & cov(Y+Z, X+Z) & var(Y+Z) \end{bmatrix}$$

$$= \begin{bmatrix} var(X) & cov(X,X)+cov(X,Z) & cov(X,Y)+cov(X,Z) \\ cov(X,X)+cov(Z,X) & var(X+Z) & cov(X,Y)+cov(X,Z)+cov(Y,Z)+cov(Z,Z) \\ cov(Y,X)+cov(Z,X) & cov(X,Y)+cov(X,Z)+cov(Y,Z)+cov(Z,Z) & var(Y+Z) \end{bmatrix}$$

Since Z is independent of X and Y, this simplifies to:

$$= \begin{bmatrix} var(X) & var(X) & cov(X,Y) \\ var(X) & var(X) & cov(X,Y)+var(Z) \\ cov(Y,X) & cov(X,Y)+var(Z) & var(Y) \end{bmatrix} = \begin{bmatrix} \frac{1}{18} & \frac{1}{18} & \frac{1}{36} \\ \frac{1}{18} & \frac{1}{18} & \frac{1}{36}+\frac{1}{18} \\ \frac{1}{36} & \frac{1}{36}+\frac{1}{18} & \frac{1}{18} \end{bmatrix}$$

$$= \begin{bmatrix} \frac{1}{18} & \frac{1}{18} & \frac{1}{36} \\ \frac{1}{18} & \frac{1}{18} & \frac{3}{36} \\ \frac{1}{36} & \frac{3}{36} & \frac{1}{18} \end{bmatrix}$$

Problem 35. The covariance matrix of the vector (X,Y,Z) is

$$\begin{bmatrix} cov(X,X) & cov(X,Y) & cov(X,Z) \\ cov(Y,X) & cov(Y,Y) & cov(Y,Z) \\ cov(Z,X) & cov(Z,Y) & cov(Z,Z) \end{bmatrix} = \begin{bmatrix} 2 & 0 & 1 \\ 0 & 4 & -1 \\ 1 & -1 & 4 \end{bmatrix}.$$

(a) Calculate the variance of the rv $X+Y+Z$. (b) Compute $cov(X, Y+Z)$. (c) Compute the covariance matrix of the random vector $(X, X+Z, Y+Z)$.

Solution. (a)

$$var(X+Y+Z) = cov(X+Y+Z, X+Y+Z) = 2+4+4+1+1-1-1 = 10.$$

(b)

$$cov(X, Y+Z) = cov(X,Y) + cov(X,Z) = 0+1 = 1.$$

(c) Let $\mathbf{v} = (X, X+Z, Y+Z)$. Then,

$$\begin{aligned}
cov(\mathbf{v},\mathbf{v}) &= \begin{bmatrix} cov(X,X) & cov(X,X+Z) & cov(X,Y+Z) \\ cov(X+Z,X) & cov(X+Z,X+Z) & cov(X+Z,Y+Z) \\ cov(Y+Z,X) & cov(Y+Z,X+Z) & cov(Y+Z,Y+Z) \end{bmatrix} \\
&= \begin{bmatrix} cov(X,X) & cov(X,X)+cov(X,Z) & cov(X,Y)+cov(X,Z) \\ cov(Z,X)+cov(X,X) & cov(X,X)+2cov(X,Z)+cov(Z,Z) & cov(X,Y)+cov(X,Z)+cov(Z,Y)+cov(Z,Z) \\ cov(Y,X)+cov(Z,X) & cov(Y,X)+cov(Y,Z)+cov(Z,X)+cov(Z,Z) & cov(Y,Y)+2cov(Y,Z)+cov(Z,Z) \end{bmatrix} \\
&= \begin{bmatrix} 2 & 2+1 & 0+1 \\ 1+2 & 2+2(1)+4 & 0+1+(-1)+4 \\ 1+0 & 0+(-1)+1+4 & 4+2(-1)+4 \end{bmatrix} = \begin{bmatrix} 2 & 3 & 1 \\ 3 & 8 & 4 \\ 1 & 4 & 6 \end{bmatrix}
\end{aligned}$$

■

Problem 36. Distribution of the sum of two random variables. (a) Prove that the sum of two discrete and independent rv's (e.g. $X+Y$, where X and Y are independent) has distribution function (PMF) given by the convolution of two PMFs (one for X, one for Y), i..e,

$$\mathbb{P}(X+Y=k) = \sum_{l=0}^{k} \mathbb{P}(X=l)\mathbb{P}(Y=k-l).$$

Let X and Y be two independent rv's. X is Poisson with parameter 2. Y is Poisson with parameter 3. (b) Find the expectation and the variance of the sum $X+Y$. (c) Find the probability mass function (PMF) of the rv $X+Y$.

Solution. (a) Let $Z = X+Y$ (X and Y are independent), then

$$\begin{aligned}
\mathbb{P}(X+Y=k) &= \sum_{x+y=k} \mathbb{P}(X=x, Y=y) \\
&= \sum_{x=0}^{k} \mathbb{P}(X=x, Y=k-x) \\
&= \sum_{x=0}^{k} \mathbb{P}(X=x)\mathbb{P}(Y=k-x)
\end{aligned}$$

(b) For Z Poisson with parameter λ, $\langle Z\rangle = var(Z) = \lambda$. Thus, $\langle X\rangle = 2$, $\langle Y\rangle = 3$ and $\langle X+Y\rangle = \langle X\rangle + \langle Y\rangle_8 = 2+3 = 5$. Next, we have $var(X) = 2$, $var(Y) = 3$ and since X

and Y are independent, we have $var(X+Y) = var(X) + var(Y) = 2+3 = 5$. Then,

$$\begin{aligned}\mathbb{P}(X+Y=k) =& \sum_{x=0}^{k} \frac{e^{-\lambda}\lambda^x}{x!}\frac{e^{-\mu}\mu^{k-x}}{(k-x)!} \\ =& \frac{e^{-(\lambda+\mu)}}{k!}\sum_{x=0}^{k}\binom{k}{x}\lambda^x\mu^{k-x} \\ =& \frac{e^{-(\lambda+\mu)}(\lambda+\mu)^k}{k!}\end{aligned}$$

and the sum of two Poisson rv's is also Poisson with additive parameters $\lambda+\mu$. Therefore, $X+Y$ is Poisson with parameter 2+3=5. The distribution is $\mathbb{P}(X+Y=k) = e^{-5}e^k/k!$ for $k = 0, 1, 2, \ldots$. ■

Problem 37. $X_1, X_2, \ldots, X_n$ are independent rv's, such that X_j is Poisson with parameter 2, $j = 1, 2, \ldots, n$. Find the expectation, the variance and standard deviation of the variable:

$$\overline{X} = \frac{X_1 + X_2 + \cdots + X_n}{n}.$$

Solution. If Z is Poisson with parameter λ, $\langle Z\rangle = var(Z) = \lambda$. Here, X_j is Poisson with parameter 2. We have $\langle\overline{X}\rangle = \langle\frac{1}{n}\sum_{j=1}^n X_j\rangle = \sum_{j=1}^n \frac{1}{n}\langle X_j\rangle = \frac{1}{n}n\cdot 2 = 2$. Since $X_1, \ldots, X_n$ are independent we have $var(\overline{X}) = \frac{1}{n^2}var(X_1+X_2+\cdots+X_n) = \frac{1}{n^2}(var(X_1)+\cdots+var(X_n))$ $= \frac{1}{n^2}n\cdot 2 = \frac{2}{n}$ and $\sigma_{\overline{X}} = \sqrt{\frac{2}{n}}$. ■

Problem 38. Let $X \sim \mathcal{N}(0,1)$ and $Y \sim \mathcal{N}(0,4)$ be independent rv's. What is the conditional density of $Z = X+Y$ given $X = 3$ (i.e. under the condition $X = 3$).

Solution. Recall that the sum of two independent Gaussians is also Gaussian with additive means and variances. Since $Z = X+Y$ we have that Z given $X = 3$ has the same distribution as $3+Y$ given $X = 3$. Since Y is independent from X and $3+Y \sim \mathcal{N}(3,4)$ this yields that the rv $Z|X=3 \sim \mathcal{N}(3,4)$. Thus, $p_{Z|X=3}(z) = \frac{1}{2\sqrt{2\pi}}\exp(-\frac{1}{8}(z-3)^2)$. ■

Problem 39. $X_1, X_2, \ldots, X_{10}$ are iidrv's with $X_j \sim \mathcal{N}(0,4)$, $j = 1, \ldots, 10$. Find the conditional density of X_1 under the condition $X_1 + X_2 + \cdots + X_{10} = 3$.

Solution. We have $Y = X_2 + X_3 + \cdots + X_{10} \sim \mathcal{N}(0, 9\cdot 4) = \mathcal{N}(0,36)$. Using the definition of conditional probability

$$p_{X_1|X_1+Y=3}(x_1) = \frac{p_{X_1,X_1+Y}(x_1,3)}{p_{X_1+Y}(3)} = \frac{p_{X_1,Y}(x_1,3-x_1)}{p_{X_1+Y}(3)}.$$

Since X_1 and Y are independent, we have

$$\begin{aligned}p_{X_1,Y}(x_1,3-x_1) &= p_{X_1}(x_1)p_Y(3-x_1) \\ =& \frac{1}{2\sqrt{2\pi}}\exp(-\frac{1}{8}(x_1)^2)\frac{1}{6\sqrt{2\pi}}\exp(-\frac{1}{72}(3-x_1)^2).\end{aligned}$$

We also have $X_1 + Y \sim \mathcal{N}(0, 10 \cdot 4)$ and $p_{X_1+y}(3) = \frac{1}{\sqrt{80\pi}} \exp(-\frac{1}{80}3^2)$. Finally we find that $p_{X_1|X_1+Y=3}(x_1) = \frac{1}{\sqrt{2\pi \cdot 18/5}} \exp(-\frac{1}{2 \cdot 18/5}(x_1 - 0.3)^2)$. ■

Problem 40. Exercise on conditional expectations: (a) By applying the above definitions, check the trivial case $\langle X|X\rangle = X$. Here, X is a random variable, i.e., $\langle X|X\rangle(\omega) = X(\omega)$. (b) Check also that $\langle Y|X\rangle = \langle Y\rangle$ when X and Y are independent. Here, $\langle Y\rangle$ is the random variable taking the constant value $\langle Y\rangle$ for any ω, i.e. $\langle Y|X\rangle(\omega) = \langle Y\rangle(\omega)$.

Let $X \sim \mathcal{N}(0, 1)$ and $Y \sim \mathcal{N}(0, 4)$ be independent rv's. Let $Z = X + Y$. (c) Compute $\langle Z|X = 3\rangle$ (expectation value calculated using the conditional density of Z under the condition $X = 3$). (d) Calculate $\langle Z|X\rangle$.

Solution. (a) First let's check that $\langle X|X\rangle = X$. First we start with $\langle X|X = x'\rangle$, whose definition is $\langle X|X = x'\rangle = \int x p_{X,X=x'}(x)\mathrm{d}x$. Notice that $p_{X,X=x'}(x) = \delta(x - x')$ is the only possible PDF (i.e. the probability that $X = x$ given that $X = x'$ can only be non-zero iff $x = x'$). Hence, $\langle X|X = x'\rangle = x'$. Replace x' by X and get $\langle X|X\rangle = X$.

(b) To prove $\langle Y|X\rangle = \langle Y\rangle$, we write $p_{Y|X=x}(y) = \frac{p_{Y,X}(y,x)}{p_X(x)} = \frac{p_Y(y)p_X(x)}{p_X(x)} = p_Y(y)$ since X and Y are independent. Then, $\langle Y|X = x\rangle = \int y p_{Y|X=x}(y)\mathrm{d}y = \int y p_Y(y)\mathrm{d}y = \langle Y\rangle$. Therefore, $\langle Y|X\rangle = \langle Y\rangle$.

(c) From Problem 38 we have already calculated the conditional density of Z. Using that density, we get that $\langle Z|X = 3\rangle = 3$. (d) Conditional expectation is linear: $\langle Z|X\rangle = \langle X + Y|X\rangle = \langle X|X\rangle + \langle Y|X\rangle = X + \langle Y\rangle = X$. ■

Problem 41. Let $X_1, \dots, X_{10}$ be iidrv with $X_j \sim \mathcal{N}(0, 4)$, $j = 1, \dots, 10$. Let $S = X_1 + \dots + X_{10}$. (a) Calculate $\langle X_1|S = 3\rangle$. (b) Calculate $\langle X_1|S\rangle$.

Solution. (a) Using the conditional distribution obtained in Problem 6, we get $\langle X_1|S = 3\rangle = 0.3$. Another solution: by symmetry, for $j = 1, 2, \dots, 10$ we get $\langle X_1|S = 3\rangle = \langle X_j|S = 3\rangle$. Hence $10\langle X_1|S = 3\rangle = \sum_{j=1}^{10}\langle X_1|S = 3\rangle = \sum_{j=1}^{10}\langle X_j|S = 3\rangle = \langle \sum_{j=1}^{10} X_j|S = 0\rangle = \langle S|S = 3\rangle = 3$. Hence $\langle X_1|S = 3\rangle = 0.3$. (b) In a similar way as in (a), using symmetry we get $\langle X_1|S\rangle = S/10$. ■

Problem 42. Choose a space craft pilot in the nearest galaxy at random and call N the number of accidents during a year for this pilot. The number of accidents N depends on another random variable, P, which quantifies the pilot's skills. The number of accidents given some skillset $P = p$ has $Binomial(4, p)$ distribution, i.e., $N|P = p \sim Binomial(4, p)$. The parameter P among the population of pilots has $P \sim U([0, 1])$ (uniform distribution). (a) Find the marginal distribution of N. (b) Find $\langle N|P\rangle$. (c) Find $\langle N\rangle$.

Solution. (a) The marginal distribution of N reads as

$$\mathbb{P}(N = n) = \int_0^1 \mathbb{P}(N = n|P = p)p_P(p)\mathrm{d}p = \int_0^1 \binom{4}{n} p^n(1 - p)^{4-n}\mathrm{d}p$$

for $n = 0, 1, 2, 3, 4$ (this may be calculated explicitly but it is a bit time consuming). (b) $N|P = p \sim Binomial(4, p)$ we have $\langle N|P = p\rangle = 4p$ thus $\langle N|P\rangle = 4P$. (c) We have $\langle N\rangle = \langle\langle N|P\rangle\rangle = \langle 4P\rangle = 4\langle P\rangle = 4\int_0^1 p \cdot 1\mathrm{d}p = 4\frac{1}{2}\, p^2\big|_{p=0}^{p=1} = 2$. ■

Problem 43. Let X be a random variable with the following distribution function (PMF):

$$\mathbb{P}(X = 1) = 0.2$$
$$\mathbb{P}(X = 2) = 0.3$$
$$\mathbb{P}(X = 3) = 0.3$$
$$\mathbb{P}(X = 4) = 0.2$$

Find $\langle X\rangle$, $\langle X^2\rangle$, the variance and skewness.

Solution. The mean is:

$$\langle X\rangle = 1 * 0.2 + 2 * 0.3 + 3 * 0.3 + 4 * 0.2 = 2.5$$

Second moment:

$$\langle X^2\rangle = 1 * 0.2 + 4 * 0.3 + 9 * 0.3 + 16 * 0.2 = 7.3$$

Variance:

$$\sigma^2 = var(X) = \langle X^2\rangle - \langle X\rangle^2 = 7.3 - (2.5)^2 = 1.05$$

Skewness:

$$\frac{\langle (X - \langle X\rangle)^3\rangle}{\sigma^3}$$
$$= \frac{0.2 * (1 - 2.5)^3 + 0.3 * (2 - 2.5)^3 + 0.3 * (3 - 2.5)^3 + 0.2 * (4 - 2.5)^3}{(1.05)^{3/2}} = 0$$

■

Problem 44. A random variable X has binomial distribution $B(3, 0.4)$. See
`https://en.wikipedia.org/wiki/Binomial_distribution`
Find $\mathbb{P}(X = 0)$, $\mathbb{P}(X = 2)$ and $\mathbb{P}(X = 10)$. Calculate the standard deviation of X.

Solution. Variance is npq, where $p = 0.4$ and $q = 1-p = 0.6$. Thus, $npq = 0.72$. Standard deviation is the square root: $\sqrt{0.72} \approx 0.8485$. The PMF is

$$\binom{n}{k} p^k q^{n-k}$$

$$\mathbb{P}(X = 0) = \binom{3}{0} p^0 q^{3-0} = \frac{3!}{0!(3-0)!}(0.4)^0(0.6)^3 = 0.6^3 = 0.216$$
$$\mathbb{P}(X = 2) = \binom{3}{2} p^2 q^{3-2} = \frac{3!}{2!(3-2)!}(0.4)^2(0.6)^1 = 0.288$$

$\mathbb{P}(X = 10)$ does not exist since 10>3. ■

Problem 45. Let X be Poisson with parameter 4. For which value $k = 0, 1, \ldots$ does X attain the greatest probability? Calculate or estimate $\mathbb{P}(X \leq 3)$ and $\mathbb{P}(X \geq 5)$.

Solution. For $k = 0, 1, \ldots$ we have $\frac{\mathbb{P}(X=k+1)}{\mathbb{P}(X=k)} = \frac{e^{-4}4^{k+1}/(k+1)!}{e^{-4}4^k/k!} = \frac{4}{k+1}$. Thus, $\frac{\mathbb{P}(X=k+1)}{\mathbb{P}(X=k)} > 1$ for $k = 0, 1, 2$, $\frac{\mathbb{P}(X=k+1)}{\mathbb{P}(X=k)} = 1$ for $k = 3$ and $\frac{\mathbb{P}(X=k+1)}{\mathbb{P}(X=k)} < 1$ for $k = 4, 5, \ldots$ and we have $\mathbb{P}(X = 0) < \mathbb{P}(X = 1) < \mathbb{P}(X = 2) < \mathbb{P}(X = 3) = \mathbb{P}(X = 4) > \mathbb{P}(X = 5) > \ldots$. X attains with the greatest probability values 3 and 4.

■

Problem 46. Find the value of the constant c such that $f : \mathbb{R} \to \mathbb{R}$,

$$p_X(x) = \begin{cases} 0 & \text{if } x < 1 \\ \frac{c}{x^2} & \text{if } x \geq 1 \end{cases}$$

is a bona fide PDF of a continuous rv X. Calculate $\mathbb{P}(X \leq 2)$, $\mathbb{P}(X = 2)$, $\mathbb{P}(X \in [2, 3])$. Compute $\langle X^2 \rangle$ and $\langle \sqrt{X} \rangle$.

Solution. We calculate $1 = \int_{-\infty}^{\infty} p_X(x)\mathrm{d}x = \int_1^{\infty} \frac{c}{x^2}\mathrm{d}x = \int_1^{\infty} cx^{-2}\mathrm{d}x = c\frac{x^{-2+1}}{-2+1}\Big|_1^{\infty} = c(-\frac{1}{x})\Big|_1^{\infty} = c(-\frac{1}{\infty} - (-\frac{1}{1})) = c(0 + \frac{1}{1}) = c$. Therefore, $c = 1$. We have $\mathbb{P}(X \leq 2) = \int_{-\infty}^{2} p_X(x)\mathrm{d}x = \int_1^2 \frac{1}{x^2}\mathrm{d}x = (-\frac{1}{x})\Big|_1^2 = -\frac{1}{2} - (-\frac{1}{1}) = \frac{1}{2}$, $\mathbb{P}(X = 2) = \int_2^2 p_X(x)\mathrm{d}x = 0$, $\mathbb{P}(X \in [2, 3]) = \int_2^3 p_X(x)\mathrm{d}x = \int_2^3 \frac{1}{x^2}\mathrm{d}x = (-\frac{1}{x})\Big|_2^3 = -\frac{1}{3} - (-\frac{1}{2}) = \frac{1}{6}$. Next, we calculate $\langle X^2 \rangle = \int_{-\infty}^{\infty} x^2 p_X(x)\mathrm{d}x = \int_1^{\infty} x^2 \frac{1}{x^2}\mathrm{d}x = x\Big|_1^{\infty} = \infty - 1 = \infty$, thus $\langle X^2 \rangle$ does not exist. $\langle \sqrt{X} \rangle = \int_{-\infty}^{\infty} x^{1/2} p_X(x)\mathrm{d}x = \int_1^{\infty} x^{1/2}\frac{1}{x^2}\mathrm{d}x = \int_1^{\infty} x^{-3/2}\mathrm{d}x = \frac{x^{-3/2+1}}{-3/2+1}\Big|_1^{\infty} = 0 - \frac{1}{-1/2} = 2$, thus $\langle \sqrt{X} \rangle$ is finite. ■

Problem 47. Compute the fourth moment of the normal random variable.

Solution. Solutions can be found at:

`https://arxiv.org/pdf/1209.4340.pdf`

`https://www.le.ac.uk/users/dsgp1/COURSES/MATHSTAT/6normgf.pdf`

Integrals can be computed explicitly. Let $I_k(a)$ denote:

$$I_k(a) = \frac{1}{\sqrt{2\pi}} \int_a^{\infty} u^k e^{-u^2/2}\mathrm{d}u$$

The $k = 0$ case is given in terms of the standard normal CDF:

$$I_0(a) = \frac{1}{\sqrt{2\pi}} \int_a^{\infty} e^{-u^2/2}\mathrm{d}u = 1 - \Phi(a)$$

The $k = 1$ case is obtained by direct integration:

$$I_1(a) = \frac{1}{\sqrt{2\pi}} \int_a^{\infty} ue^{-u^2/2}\mathrm{d}u = -\frac{1}{\sqrt{2\pi}} \left[e^{-u^2/2}\right]_a^{\infty} = \frac{1}{\sqrt{2\pi}} e^{-a^2/2}.$$

The $k = 2$ case is obtained by integration-by-parts:

$$\begin{aligned} I_2(a) =& \frac{1}{\sqrt{2\pi}} \int_a^\infty u^2 e^{-u^2/2} \mathrm{d}u = -\frac{1}{\sqrt{2\pi}} \left[ue^{-u^2/2}\right]_a^\infty + \frac{1}{\sqrt{2\pi}} \int_a^\infty \left[e^{-u^2/2}\right] \mathrm{d}u \\ =& \frac{1}{\sqrt{2\pi}} ae^{-a^2/2} + (1 - \Phi(a)) \end{aligned}$$

These are solved using integration by parts For $k = 3$, we can also integrate by parts:

$$\begin{aligned} I_3(a) =& \frac{1}{\sqrt{2\pi}} \int_a^\infty u^3 e^{-u^2/2} \mathrm{d}u = \frac{1}{\sqrt{2\pi}} \int_a^\infty u^2 \left[ue^{-u^2/2}\right] \mathrm{d}u \\ =& -\frac{1}{\sqrt{2\pi}} \left[u^2 e^{-u^2/2}\right]_a^\infty + 2\frac{1}{\sqrt{2\pi}} \int_a^\infty u \left[e^{-u^2/2}\right] \mathrm{d}u \\ =& \frac{1}{\sqrt{2\pi}} a^2 e^{-a^2/2} + \frac{1}{\sqrt{2\pi}} 2e^{-a^2/2} \end{aligned}$$

For $k = 4$, we have

$$\begin{aligned} I_4(a) =& \frac{1}{\sqrt{2\pi}} \int_a^\infty u^4 e^{-u^2/2} \mathrm{d}u = \frac{1}{\sqrt{2\pi}} \int_a^\infty u^3 \left[ue^{-u^2/2}\right] \mathrm{d}u \\ =& -\frac{1}{\sqrt{2\pi}} \left[u^3 e^{-u^2/2}\right]_a^\infty + 3\frac{1}{\sqrt{2\pi}} \int_a^\infty u^2 \left[e^{-u^2/2}\right] \mathrm{d}u \end{aligned}$$

The last integral was already solved in the $k = 2$ case. Substituting that results gives:

$$I_4(a) = \frac{1}{\sqrt{2\pi}} a^3 e^{-a^2/2} + 3\left[\frac{1}{\sqrt{2\pi}} ae^{-a^2/2} + (1 - \Phi(a))\right]$$

We are, of course, interested in the limit $a \to -\infty$. For a normal $\mathcal{N}(\mu, \sigma^2)$ rv we simply make the substitution $u = \frac{x-\mu}{\sigma}$ and use the above formulae. Specifically,

$$\langle X^4 \rangle = \int_{-\infty}^\infty x^4 \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2} \mathrm{d}x$$

The substitution $u = \frac{x-\mu}{\sigma}$, $\mathrm{d}u = \mathrm{d}x/\sigma$:

$$\langle X^4 \rangle = \int_{-\infty}^\infty (\sigma u + \mu)^4 \frac{1}{\sqrt{2\pi}} e^{-u^2/2} \mathrm{d}u$$

Expanding

$$(\sigma u + \mu)^4 = \mu^4 + \sigma^4 u^4 + 4\sigma^3 u^3 \mu + 6\sigma^2 u^2 \mu^2 + 4\mu^3 \sigma u$$

gives

$$\begin{aligned} \langle X^4 \rangle =& \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty \left[\mu^4 + \sigma^4 u^4 + 4\sigma^3 u^3 \mu + 6\sigma^2 u^2 \mu^2 + 4\mu^3 \sigma u\right] e^{-u^2/2} \mathrm{d}u \\ =& \mu^4 I_0(-\infty) + \sigma^4 I_4(-\infty) + 6\sigma^2 \mu^2 I_2(-\infty) + 4\mu^2 \sigma I_1(-\infty) \\ =& \mu^4 + \sigma^4 \cdot 3 + 6\sigma^2 \mu^2 + 4\mu^2 \sigma \cdot 0 = \mu^4 + 3\sigma^4 + 6\sigma^2 \mu^2 \end{aligned}$$

The fourth moment of the normal distribution $\mathcal{N}(\mu, \sigma^2)$ is: $\mu^4 + 6\mu^2\sigma^2 + 3\sigma^4$. ■

Problem 48. Find the formula for $\mathbb{P}(X > t)$ of X and the CDF of X when X has the PDF:

$$p_X(x) = \begin{cases} 0 & \text{if } x < 1 \\ \frac{2}{x^3} & \text{if } x \geq 1 \end{cases}$$

Solution. The CDF is $\mathbb{P}(X \leq t) = \int_{-\infty}^{t} p_X(x)\mathrm{d}x$. For $t < 1$ we have 0 since the PDF is zero in that region. For $t \geq 1$, $\mathbb{P}(X \leq t) = \int_1^t \frac{2}{x^3}\mathrm{d}x = 2\frac{x^{-3+1}}{-3+1}\Big|_1^t = 2\left(\frac{t^{-2}}{-2} - \frac{1^{-2}}{-2}\right) = 1 - \frac{1}{t^2}$. Finally, $\mathbb{P}(X > t) = 1 - \mathbb{P}(X \leq t) = 1$ for $t < 1$ and $\frac{1}{t^2}$ for $t \geq 1$. ■

Problem 49. Let rv X be Erlang-distributed with parameters 2 and 5, see for details:
`https://en.wikipedia.org/wiki/Erlang_distribution`
Find the formula for $\mathbb{P}(X > t)$ of X and the CDF of X.

Solution. Erlang(2,5) distribution has PDF 5^2xe^{-5x}. Then, $\int xe^{-5x}dx = \int x(-\frac{1}{5}e^{-5x})'\mathrm{d}x$ = - $x\frac{1}{5}e^{-5x} + \int x'\frac{1}{5}e^{-5x}\mathrm{d}x$ = -$\frac{1}{5}xe^{-5x} + \frac{1}{5}\int e^{-5x}\mathrm{d}x$ = -$\frac{1}{5}xe^{-5x}$ - $\frac{1}{5^2}e^{-5x}$ = - $\frac{1}{25}e^{-5x}(5x+1)$. For $t > 0$, $\mathbb{P}(X > t) = \int_t^{\infty} 25xe^{-5x}\mathrm{d}x = 25\int_t^{\infty} xe^{-5x}\mathrm{d}x - e^{-5x}(5x+1)\big|_{x=t}^{\infty} = 0 + e^{-5t}(5t+1)$ while for $t \leq 0$ we have $\mathbb{P}(X > t) = 1$. The CDF of X is $\mathbb{P}(X \leq t) = 1 - \mathbb{P}(X > t)$, which equals 1 for $t < 0$ and $1 - e^{-5t}(5t+1)$ for $t \geq 0$. ■

Problem 50. Let the rv X have the following PMF ($k = 1, 2, \dots$):

$$\mathbb{P}(X = k) = \frac{1}{k^4} - \frac{1}{(k+1)^4}.$$

Find the CDF of X. Compute $\mathbb{P}(X \geq k)$ for $k = 0, 1, 2, \dots$.

Solution. For $k = 1, 2, \dots$ we have $\mathbb{P}(X \leq k) = \sum_{i=1}^{k} \mathbb{P}(X = i) = \sum_{i=1}^{k}\left(\frac{1}{i^4} - \frac{1}{(i+1)^4}\right)$ $= \frac{1}{1^4} - \frac{1}{2^4} + \frac{1}{2^4} - \frac{1}{3^4} + \dots + \frac{1}{k^4}$ - $\frac{1}{(k+1)^4} = 1 - \frac{1}{(k+1)^4}$. Now, for any $t \in \mathbb{R}$ we have $\mathbb{P}(X \leq t) = 0$ for $t < 1$. Also, $\mathbb{P}(X \leq t) = \mathbb{P}(X \leq \lfloor t \rfloor) = 1 - \frac{1}{(\lfloor t \rfloor + 1)^4}$ for $t \geq 1$. To calculate $\mathbb{P}(X \geq k)$ for $k = 1, 2, \dots$ we write $\mathbb{P}(X \geq k) = \sum_{i=k}^{\infty} \mathbb{P}(X = i) = \sum_{i=k}^{\infty}\left(\frac{1}{i^4} - \frac{1}{(i+1)^4}\right) = \frac{1}{k^4} - \frac{1}{(k+1)^4} + \frac{1}{(k+1)^4} - \frac{1}{(k+2)^4} + \dots = \frac{1}{k^4}$. ■

Problem 51. Let (X, Y) be a pair of continuous rv's whose joint density is

$$p_{XY}(x, y) = \frac{1}{2}\mathbf{1}_{[0,1]}(x)\mathbf{1}_{[0,2]}(y),$$

where $\mathbf{1}_A(x)$ is the indicator function of the set A, i.e.

$$\mathbf{1}_A(x) = \begin{cases} 1 & \text{if } x \in A \\ 0 & \text{otherwise} \end{cases}$$

Find the CDF of the vector (X, Y).

Solution. Let $s \geq 0$, $t \geq 0$. The CDF is:

$$\mathbb{P}(X < s, Y < t) = \frac{1}{2}\int_0^s \mathbf{1}_{[0,1]}(x)\mathrm{d}x \int_0^t \mathbf{1}_{[0,2]}(y)\mathrm{d}y = \frac{(s \wedge 1)(t \wedge 2)}{2}$$

where $u \wedge v$ is the minimum of u and v. ■

Problem 52. The joint PMF of (X, Y) is

	Y=1	2	3
X=0	0.2	0.1	0
1	0.1	0.3	0
2	0	0	0.3

Find the marginal probability mass functions of X and Y. Find the conditional probabilities $\mathbb{P}(X = 0|Y = 1)$, $\mathbb{P}(X = 1|Y = 1)$, $\mathbb{P}(X = 2|Y = 1)$, $\mathbb{P}(X = 0|Y = 2)$, $\mathbb{P}(X = 1|Y = 2)$, $\mathbb{P}(X = 2|Y = 2)$.

Solution. The definition of conditional probability is $\mathbb{P}(A|B) = \frac{\mathbb{P}(A\cap B)}{\mathbb{P}(B)}$. To calculate

$$\mathbb{P}(X = 0|Y = 1) = \frac{\mathbb{P}(X = 0, Y = 1)}{\mathbb{P}(Y = 1)} = \frac{0.2}{0.3} = \frac{2}{3},$$

where $\mathbb{P}(Y = 1) = 0.2 + 0.1 + 0 = 0.3$ and $\mathbb{P}(X = 0, Y = 1) = 0.2$. Other conditional probabilities are calculated similarly. We find:

$$\mathbb{P}(X = 1|Y = 1) = \frac{0.1}{0.3} = \frac{1}{3}$$
$$\mathbb{P}(X = 2|Y = 1) = \frac{0}{0.3} = 0$$
$$\mathbb{P}(X = 0|Y = 2) = \frac{0.1}{0.4} = \frac{1}{4}$$
$$\mathbb{P}(X = 1|Y = 2) = \frac{0.3}{0.4} = \frac{3}{4}$$
$$\mathbb{P}(X = 2|Y = 2) = \frac{0}{0.4} = 0$$

■

Problem 53. The random vector (X, Y) is uniformly distributed over the following region in the 2D plane:

$$D = \{(x, y) \in \mathbb{R}^2 : x^2 + y^2 \leq 2\}$$

i.e., the joint PDF is

$$p_{XY}(x, y) = \frac{1}{2\pi}\mathbf{1}_D(x, y) = \begin{cases} \frac{1}{2\pi} & \text{if } x^2 + y^2 \leq 2; \\ 0 & \text{if } x^2 + y^2 > 2. \end{cases}$$

Find the marginal densities of X and Y.

Solution. We apply the formula

$$p_X(x) = \int_{-\infty}^{\infty} p_{XY}(x,y)\mathrm{d}y = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathbf{1}_D(x,y)\mathrm{d}y$$

For $x < -\sqrt{2}$ and $x > \sqrt{2}$ we have $x^2+y^2 > 2$. Thus, $\mathbf{1}_D(x,y) = 0$ and $p_X(x) = 0$. Assume that $x \in [-\sqrt{2}, \sqrt{2}]$. We have $\mathbf{1}_D(x,y) = 1$ iff $y \in [-\sqrt{2-x^2}, \sqrt{2-x^2}]$ and otherwise $\mathbf{1}_D(x,y) = 0$. Then, $p_X(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathbf{1}_D(x,y)\mathrm{d}y = \frac{1}{2\pi}\int_{-\sqrt{2-x^2}}^{\sqrt{2-x^2}} 1\mathrm{d}y = \frac{1}{\pi}\sqrt{2-x^2}$. Similarly, $p_Y(y) = 0$ for $y < -\sqrt{2}$ and $y > \sqrt{2}$, and $p_Y(y) = \frac{1}{\pi}\sqrt{2-y^2}$ for $y \in [-\sqrt{2}, \sqrt{2}]$. ■

Problem 54. Prove that X and Y, whose joint PDF is defined in Problem 53, are statistically independent. Calculate the covariance between X and Y.

Solution. Using the marginal densities obtained in Problem 53,
$p_X(x) = \frac{1}{\pi}\sqrt{2-x^2}$ for $x \in [-\sqrt{2}, \sqrt{2}]$
$p_Y(y) = \frac{1}{\pi}\sqrt{2-y^2}$ for $y \in [-\sqrt{2}, \sqrt{2}]$,
and

$$p_{XY}(x,y) = \frac{1}{2\pi}\mathbf{1}_D(x,y) = \begin{cases} \frac{1}{2\pi} & \text{if } x^2+y^2 \le 2; \\ 0 & \text{if } x^2+y^2 > 2. \end{cases}$$
$$D = \{(x,y) \in \mathbb{R}^2 : x^2+y^2 \le 2\}$$

we find that $p_{XY}(x,y) \ne p_X(x)p_Y(y)$. Thus X and Y are not statistically independent. The covariance is defined as

$$cov(X,Y) = \langle (X - \langle X\rangle)(Y - \langle Y\rangle)\rangle = \langle XY\rangle - \langle X\rangle\ \langle Y\rangle$$

Via direct computation:

$$\begin{aligned}\langle XY\rangle =& \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{\infty} xy\,\mathbf{1}_D(x,y)\,\mathrm{d}y = \frac{1}{2\pi}\iint_D xy\,\mathrm{d}x\mathrm{d}y \\ =& \frac{1}{2\pi}\int_{-2}^{2}\mathrm{d}x\int\limits_{-\sqrt{2-x^2}}^{\sqrt{2-x^2}} xy\,\mathrm{d}y \\ =& \frac{1}{2\pi}\int_{-2}^{2} x\frac{1}{2}\left[(2-x^2)-(2-x^2)\right]\mathrm{d}x = 0\end{aligned}$$

Also, we have that $\langle X\rangle = 0$ and $\langle Y\rangle = 0$ since their marginal densities are symmetric. Therefore, $cov(X,Y) = 0$. This is an instance of two random variables that are statistically independent but uncorrelated. ■

Problem 55. Let X and Y be rv's whose joint PMF is given by:

	$Y=1$	2	3
$X=0$	0.2	0.1	0
1	0.1	0.3	0
2	0	0	0.3

Compute the covariance and correlation matrix of the random vector (X, Y).

Solution. Let $\mathbf{X} = (X, Y)$. The covariance matrix is:

$$cov(\mathbf{X}) = \begin{bmatrix} cov(X,X) & cov(X,Y) \\ cov(Y,X) & cov(Y,Y) \end{bmatrix} = \begin{bmatrix} \langle (X-\mu_X)^2 \rangle & \langle (X-\mu_X)(Y-\mu_Y) \rangle \\ \langle (Y-\mu_Y)(X-\mu_X) \rangle & \langle (Y-\mu_Y)^2 \rangle \end{bmatrix}$$

The correlation matrix is the covariance matrix whose entries are normalized (see correlation coefficient):

$$corr(\mathbf{X}) = \begin{bmatrix} \frac{\langle (X-\mu_X)^2 \rangle}{\sigma_X^2} & \frac{\langle (X-\mu_X)(Y-\mu_Y) \rangle}{\sigma_X \sigma_Y} \\ \frac{\langle (Y-\mu_Y)(X-\mu_X) \rangle}{\sigma_X \sigma_Y} & \frac{\langle (Y-\mu_Y)^2 \rangle}{\sigma_Y^2} \end{bmatrix} = \begin{bmatrix} 1 & \frac{\langle (X-\mu_X)(Y-\mu_Y) \rangle}{\sigma_X \sigma_Y} \\ \frac{\langle (Y-\mu_Y)(X-\mu_X) \rangle}{\sigma_X \sigma_Y} & 1 \end{bmatrix}$$

Computing the matrix elements:

$$\mu_X = \langle X \rangle = 0.4 + 2 * 0.3 = 1$$

$$\mu_Y = \langle Y \rangle = 1 * (0.2 + 0.1) + 2 * (0.1 + 0.3) + 3 * (0.3) = 2$$

$$\sigma_X^2 = \langle (X-\mu_X)^2 \rangle = (0.2 + 0.1) * (0-1)^2 + (0.1 + 0.3) * (1-1)^2 + 0.3 * (2-1)^2 = 0.6$$

$$\sigma_Y^2 = \langle (Y-\mu_Y)^2 \rangle = (0.2 + 0.1) * (1-2)^2 + (0.1 + 0.3) * (2-2)^2 + 0.3 * (3-2)^2 = 0.6$$

The off diagonal element is:

$$\begin{aligned} \langle (X-\mu_X)(Y-\mu_Y) \rangle =& 0.2 * (0-1)(1-2) + 0.1 * (0-1)(2-2) \\ &+ 0.1 * (1-1)(1-2) + 0.3 * (1-1)(2-2) + 0.3 * (2-1)(3-2) = 0.5 \end{aligned}$$

Thus, we arrive at:

$$cov(\mathbf{X}) = \begin{bmatrix} 1 & 0.5 \\ 0.5 & 2 \end{bmatrix}, \qquad corr(\mathbf{X}) = \begin{bmatrix} 1 & 0.25 \\ 0.25 & 1 \end{bmatrix}$$

■

Problem 56. Let rv X and Y have a joint PDF

$$p_{XY}(x,y) = \begin{cases} \frac{1}{2} & \text{if } 0 \le x \le y \le 2; \\ 0 & \text{otherwise} \end{cases}.$$

Are X and Y statistically independent? Compute the correlation matrix of the random vector (X, Y).

Solution.

$$\begin{aligned}\langle XY\rangle =&\int_{-\infty}^{\infty}\left(\int_{-\infty}^{\infty} xy\, p_{XY}(x,y)\mathrm{d}y\right)\mathrm{d}x = \int_0^2\left(\int_x^2 \frac{1}{2}\mathrm{d}y\right)\mathrm{d}x = \frac{1}{2}\int_0^2 x\left(\int_x^2 y\mathrm{d}y\right)\mathrm{d}x\\ =&\frac{1}{2}\int_0^2 x\frac{1}{2}\,y^2\big|_{y=x}^{y=2}\,\mathrm{d}x = \frac{1}{4}\int_0^2 x(4-x^2)\mathrm{d}x = \frac{1}{4}\int_0^2(4x-x^3)\mathrm{d}x = \frac{1}{4}\,(4\frac{1}{2}x^2-\frac{1}{4}x^4)\Big|_{x=0}^{x=2}\\ =&\frac{1}{4}(2\cdot 2^2-\frac{1}{4}2^4) = 1.\end{aligned}$$

Next,

$$\begin{aligned}\langle X\rangle =&\int_{-\infty}^{\infty} x\left(\int_{-\infty}^{\infty} p_{XY}(x,y)\mathrm{d}y\right)\mathrm{d}x = \int_0^2 x\left(\int_x^2 \frac{1}{2}\mathrm{d}y\right)\mathrm{d}x = \frac{1}{2}\int_0^2 x\left(\int_x^2 1\mathrm{d}y\right)\mathrm{d}x\\ =&\frac{1}{2}\int_0^2 x\cdot y|_{y=x}^{y=2}\,\mathrm{d}x = \frac{1}{2}\int_0^2 x(2-x)\mathrm{d}x = \frac{1}{2}\int_0^2(2x-x^2)\mathrm{d}x = \frac{1}{2}(2\frac{1}{2}x^2-\frac{1}{3}x^3)\Big|_{x=0}^{x=2}\\ =&\frac{1}{2}(2^2-\frac{1}{3}2^3) = \frac{2}{3}\end{aligned}$$

and

$$\begin{aligned}\langle X^2\rangle =&\int_{-\infty}^{\infty} x^2\left(\int_{-\infty}^{\infty} p_{XY}(x,y)\mathrm{d}y\right)\mathrm{d}x = \int_0^2 x^2\left(\int_x^2 \frac{1}{2}\mathrm{d}y\right)\mathrm{d}x = \frac{1}{2}\int_0^2 x^2\left(\int_x^2 1\mathrm{d}y\right)\mathrm{d}x\\ =&\frac{1}{2}\int_0^2 x^2\cdot y|_{y=x}^{y=2}\,\mathrm{d}x = \frac{1}{2}\int_0^2 x^2(2-x)\mathrm{d}x = \frac{1}{2}\int_0^2(2x^2-x^3)\mathrm{d}x\\ =&\frac{1}{2}\left(2\frac{1}{3}x^3-\frac{1}{4}x^4\right)\Big|_{x=0}^{x=2} = \frac{1}{2}\left(2\frac{1}{3}2^3-\frac{1}{4}2^4\right) = \frac{2}{3}.\end{aligned}$$

We also have

$$\begin{aligned}\langle Y\rangle =&\int_{-\infty}^{\infty} y\left(\int_{-\infty}^{\infty} p_{XY}(x,y)\mathrm{d}x\right)\mathrm{d}y = \int_0^2 y\left(\int_0^y \frac{1}{2}\mathrm{d}x\right)dy = \frac{1}{2}\int_0^2 y\left(\int_0^y 1\mathrm{d}x\right)\mathrm{d}y\\ =&\frac{1}{2}\int_0^2 y\cdot x|_{x=0}^{x=y}\,\mathrm{d}y = \frac{1}{2}\int_0^2 y^2\mathrm{d}y = \frac{1}{2}\frac{1}{3}\,y^3\big|_{y=0}^{y=2} = \frac{1}{6}2^3 = \frac{4}{3}\end{aligned}$$

and

$$\begin{aligned}\langle Y^2\rangle =&\int_{-\infty}^{\infty} y^2\left(\int_{-\infty}^{\infty} p_{XY}(x,y)\mathrm{d}x\right)\mathrm{d}y = \int_0^2 y^2\left(\int_0^y \frac{1}{2}\mathrm{d}x\right)\mathrm{d}y = \frac{1}{2}\int_0^2 y^2\left(\int_0^y 1\mathrm{d}x\right)\mathrm{d}y\\ =&\frac{1}{2}\int_0^2 y^2\cdot x|_{x=0}^{x=y}\,\mathrm{d}y = \frac{1}{2}\int_0^2 y^3\mathrm{d}y = \frac{1}{2}\frac{1}{4}\,y^4\big|_{y=0}^{y=2} = \frac{1}{8}2^4 = 2.\end{aligned}$$

Then,

$$\rho(X,Y) = \frac{cov(X,Y)}{\sigma_X\sigma_Y} = \frac{\langle XY\rangle - \langle X\rangle\langle Y\rangle}{\sqrt{\langle X^2\rangle - \langle X\rangle^2}\sqrt{\langle Y^2\rangle - \langle Y\rangle^2}}$$

$$= \frac{1 - \frac{2}{3}\frac{4}{3}}{\sqrt{\frac{2}{3} - (\frac{2}{3})^2}\sqrt{2 - (\frac{4}{3})^2}} = \frac{\frac{1}{9}}{\sqrt{\frac{2}{9}}\sqrt{\frac{2}{9}}} = \frac{1}{2}$$

and the correlation matrix of (X, Y) reads

$$\begin{bmatrix} 1 & \frac{1}{2} \\ \frac{1}{2} & 1 \end{bmatrix}.$$

Since $\rho(X, Y) \neq 0$ the variables X and Y are dependent. ■

Problem 57. There is a bridge in Durham, NC nicknamed the "can opener" bridge. Watch this 10-minutes long compilation:

`https://www.youtube.com/watch?v=USu8vT_tfdw`

The meaning of the bridge's name should be apparent from this video. Consider all oversized trucks shown in the video. The trucks either get through with significant damage (can opener) or with minimal damage. We consider 2 different scenarios:

(A) While the truck is significantly oversized, the truck driver goes through anyways, causing the truck to undergo carnage and decapitation.

(B) Truck either follows the sign and turns away, or goes through anyways and the truck suffers minimal damage (small bump, then backing out) or barely scraping under (lucky driver).

Count the number of times you observe scenarios A and B. From this data, assign probabilities for events A and B. Suppose that type A events are associated with a low IQ truck driver (IQ=60), whereas type B events are associated with a higher IQ driver (IQ=140). Compute the average IQ of a truck driver in Durham, NC. (Note: This problem is a joke; we are not implying that truck drivers from anywhere are idiots.)

Solution. Suppose we count 15 severely damaged trucks and 5 mildly damaged ones. The probability of A is

$$\mathbb{P}(A) = \frac{15}{20} = 0.75$$

The probability of B is:

$$\mathbb{P}(B) = \frac{5}{20} = 0.25$$

The average IQ is:

$$\langle IQ \rangle = IQ(A) \cdot \mathbb{P}(A) + IQ(B) \cdot \mathbb{P}(B) = 60 \cdot 0.75 + 140 \cdot 0.25 = 80.$$

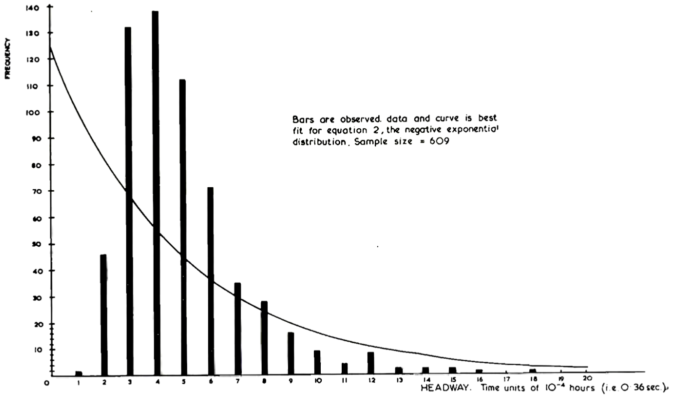
■

Problem 58. Watch 10 minutes of traffic video (preferably traffic that is not too dense, so you are able to count events). This webcam appears suitable:

`https://www.youtube.com/watch?v=5_XSYlAfJZM`

Choose a landmark such as a line on the road. Pick a lane of traffic. Count the time interval τ between consecutive vehicles crossing that lane. Plot a histogram of the time intervals. Compute the average $\langle\tau\rangle$. What distribution does τ follow? Fit the histogram to a suitable distribution. Obtain the parameters of the distribution.

Solution. An example data set is:



By inspection of this graph, $\langle\tau\rangle \approx 4 \cdot 10^{-4}$ hours. The distribution is called "headway distribution" or gap distribution. The commonly used distributions include the "displaced exponential" (for low-medium flows) and "Schuhl's composite exponential" (for normal-heavy flows) distributions. ■

Problem 59. For the traffic problem (#2) pick a time interval, say 4 minutes. Count the number of cars, n, that pass through the intersection/line (in a given lane) during that time interval. Plot of histogram of n. Find the distribution of n. Obtain the parameters of the distribution.

Solution. Suppose that we have 180 time windows (each lasting 4 seconds) and record the following observations (x: number of vehicles arriving per 4 second interval):

x	Obs. freq.	Total vehicles	Probability $P(x)$	Theoretical freq.
0	94	0	0.539	97.0
1	63	63	0.333	59.9
2	21	42	0.103	18.5
3	2	6	0.021	3.8
>3	0	0	0.004	0.8
Total	180	111	1.000	180.0

To get the histogram, we plot the vector of observed frequencies vs x. In MATLAB, we could type

```
plot([94 63 21 2 0],'o');
```

The graph doesn't quite look like an exponential decay. On the other hand, a Poisson distribution seems suitable. The probability distribution function for Poisson takes the form:

$$P(k) = \frac{m^k e^{-m}}{k!}$$

where λ is a parameter to be derived from the data. Its physical interpretation is the average number of cars per 4-second time interval. Since there are 180 time intervals in our experiment, and the total number of vehicles observed is 111:

$$m = \frac{\text{total vehicles}}{\text{total periods}} = \frac{111}{180} = 0.617; e^{-.617} = .539$$

$$P(x) = \frac{(0.617)^x}{x!}e^{-.617} = \frac{(.617)^x(.539)}{x!}$$

In the above table the column $P(x)$ is the probability calculated using the Poisson formula. The calculated "theoretical frequency" is equal to 180 $P(x)$. ■

Problem 60. For problems 57, 58 and 59 describe the probability space, the set of elementary outcomes, the random variable and the random events considered.

Solution. For problem 57, the set of possible outcomes, Ω, is the set of all possible trajectories $\omega \in \Omega$ that a given truck can take (this is best left as abstract). There are two events considered here: $A(\omega)$ (high impact), $B(\omega)$ (low or no impact). The random variable considered here is the IQ of a driver: $IQ(\omega)$, where ω refers to a particular truck/driver trajectory.

For problem 58, the set Ω of possible outcomes ($\omega \in \Omega$) is the traffic flow, i.e. all traffic scenarios giving rise to all possible gaps between consecutive cars (or some similar idea). We may consider events of the type $\{\tau = t\}$. Each of these events has probability zero (since the time intervals/bins have zero duration), however, for purposes of plotting a histogram we need to consider finite intervals of the form $\{t_1 \leq \tau \leq t_2\}$. The random variable is $\tau(\omega)$.

For problem 59, the set of outcomes is the same as in Problem 2, since the physical random experiment is the same (traffic flow). The random variable is $n(\omega)$, the number of cars in a given time interval. The events are of the form $\{n = x\}$, where x is an integer value (0, 1, 2, 3, ...). ■

Problem 61. In probability theory we often use integrals over sets. This is the same integral as you are used to, but written differently. For example, the integral of the exponential distribution, e^{-x}, over the set $[0, 1]$ is:

$$\int_{[1,3]} e^{-x}\mathrm{d}x = \int_1^3 e^{-x}\mathrm{d}x = -\, e^{-x}\big|_1^3 = e^{-1} - e^{-3} = 0.318$$

Let A be a set over the positive real numbers. Denote:

$$Q(A) = \int_A e^{-x}\mathrm{d}x$$

Compute:

(a) $Q([5,\infty))$

(b) $Q([1,3]\cup[3,5])$

(c) $Q([0,\infty))$

Solution. (a)

$$\int_5^\infty e^{-x}\mathrm{d}x = -\left.e^{-x}\right|_5^\infty = e^{-5} \approx 0.007$$

(b)

$$\int_1^3 e^{-x}\mathrm{d}x + \int_3^5 e^{-x}\mathrm{d}x = \int_1^5 e^{-x}\mathrm{d}x \approx 0.36114$$

(c)

$$\int_0^\infty e^{-x}\mathrm{d}x = 1$$

■

Problem 62. The same can be done for multiple variables. For $A \subset \mathbb{R}^n$, define the set function:

$$Q(A) = \int \cdots \int_A \mathrm{d}x_1\mathrm{d}x_2\ldots\mathrm{d}x_n,$$

provided the integral exists. For example, if $A = \{(x_1, x_2, \ldots, x_n) : 0 \le x_1 \le x_2, 0 \le x_i \le 1,$ for $i = 2, 3, \ldots, n\}$, then

$$Q(A) = \int_0^1 \left[\int_0^{x_2} \mathrm{d}x_1\right] \mathrm{d}x_2 \cdot \prod_{i=3}^{n} \left[\int_0^1 \mathrm{d}x_i\right] = \left.\frac{x_2^2}{2}\right|_0^1 \cdot 1 = \frac{1}{2}.$$

Let $B = \{(x_1, x_2, \ldots, x_n) : 0 \le x_1 \le x_2 \le \cdots \le x_n \le 1\}$. Calculate the numerical value of $Q(B)$.

Solution.

$$Q(B) = \int_0^1 \left[\int_0^{x_n} \cdots \left[\int_0^{x_3} \left[\int_0^{x_2} \mathrm{d}x_1\right] \mathrm{d}x_2\right] \ldots \mathrm{d}x_{n-1}\right] \mathrm{d}x_n = \frac{1}{n!}$$

where $n! = n(n-1)\ldots 3\cdot 2\cdot 1$. ■

Problem 63. Solve the following problems using set theory:

(a) Find the union $C_1 \cup C_2$ and the intersection $C_1 \cap C_2$ of the two sets C_1 and C_2, where $C_1 = \{(x, y) : 0 < x < 1, 0 < y < 3\}$, $C_2 = \{(x, y) : 0 < x < 2, 2 \le y < 3\}$.

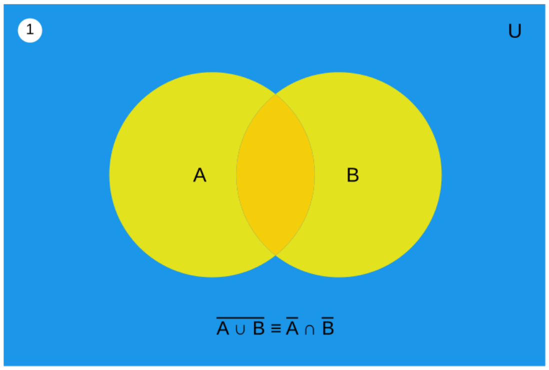
(b) Find the complement C^c of the set C with respect to the space $\mathcal{C}$ if $\mathcal{C} = \{(x, y) : x^2 + y^2 \le 1\}$, $C = \{(x, y) : |x| + |y| < 1\}$.

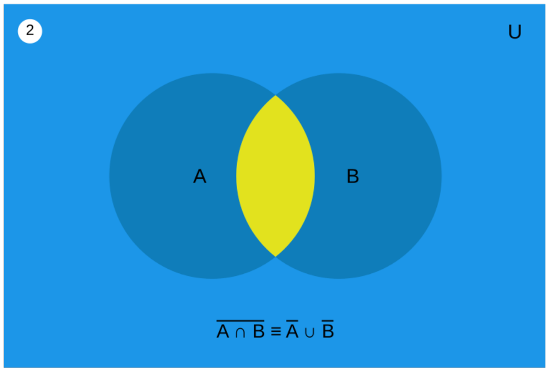
(c) Prove, using Venn diagrams, that the following statements are true:

$$(A \cap B)^c = A^c \cup B^c$$

$$(A \cup B)^c = A^c \cap B^c$$

Illustrate with an example. Generalize these statements to countable unions and intersections.





(d) Consider the space $\mathcal{C}$ to be the set of points enclosed by a rectangle containing the circles C_1, C_2 and C_3. Use Venn diagrams to compare the following sets:

$$C_1 \cup (C_2 \cap C_3) \text{ and } (C_1 \cup C_2) \cap (C_1 \cup C_3)$$

(e) Show that the following sequences of sets, $\{C_k\}$, are nondecreasing (nested upwards), i.e. $C_k \subset C_{k+1}$ for $k = 1, 2, 3, \ldots$. For such a sequence, define

$$\lim_{k\to\infty} C_k = \cup_{k=1}^{\infty} C_k.$$

Take the following sequence:

$$C_k = \{(x, y) : 1/k \leq x^2 + y^2 \leq 4 - 1/k\},\ k = 1, 2, 3, \ldots$$

Find the limit $\lim_{k\to\infty} C_k$.

(f) Show that the following sequence of sets, $\{C_k\}$, where

$$C_k = \{x : 2 < x \leq 2 + 1/k\},\ k = 1, 2, 3, \ldots,$$

is nonincreasing. A sequence of sets $\{A_n\}$ is said to be **nonincreasing** if $A_n \supset A_{n+1}$ for $n = 1, 2, 3, \ldots$. In this case, we define

$$\lim_{n\to\infty} A_n = \cap_{n=1}^{\infty} A_n.$$

Find $\lim_{k\to\infty} C_k$.

(g) For every two-dimensional set $C \subset \mathbb{R}^2$, let $Q(C) = \int\int_C (x^2 + y^2)dxdy$. If $C_1 = \{(x, y) : -1 \leq x \leq 1, -1 \leq y \leq 1\}$, $C_2 = \{(x, y) : -1 \leq x = y \leq 1\}$, and $C_3 = \{(x, y) : x^2 + y^2 \leq 1\}$, find $Q(C_1)$, $Q(C_2)$ and $Q(C_3)$.

(h) To join a club, a person must be either an idiot or a truck driver, or both. Of the 35 members in this club, 25 are idiots and 17 are truck drivers. How many persons in the club are both an idiot and a truck driver? How will these people fare when they encounter the "can opener" bridge? (Note: this problem is a joke; we are not implying that truck drivers are idiots.)

Solution. Union is a L-shaped region in the 2D plane defined by the coordinates:

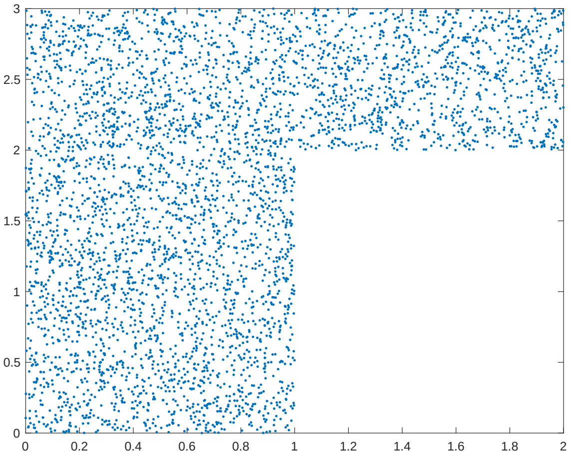
$$C_1 \cup C_2 = \{(x, y) : 0 < x < 1, 0 < y < 3 \text{ or } 0 < x < 2, 2 \leq y < 3\}$$

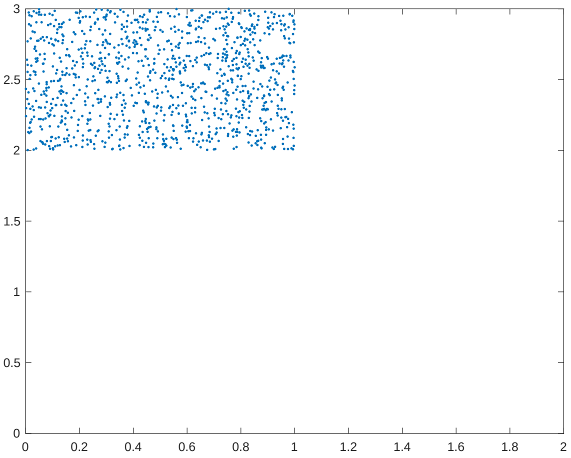
Intersection is a small square

$$C_1 \cap C_2 = \{(x, y) : 0 < x < 1, 2 \leq y \leq 3\}$$

(Notice the equality signs.)
The following MATLAB code can be used to plot the region

```
x=3*rand([1 10000]);
y=3*rand([1 10000]);
ll1=find(x>0 & x<1 & y>0 & y<3);
ll2=find(x>0 & x<2 & y>2 & y<3);
ll3=intersect(ll1,ll2);
ll3=union(ll1,ll2);
figure;
plot(x(ll3),y(ll3),'.');
axis([0 2 0 3]);
```



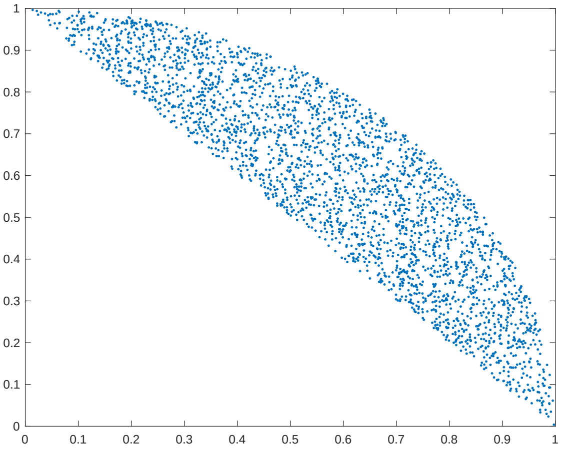


(b)

$$C^c = \{(x, y) : |x| + |y| \geq 1 \text{ and } x^2 + y^2 \leq 1\}$$

The following MATLAB code can be used to plot the region

```
x=rand([1 10000]);
y=rand([1 10000]);
ll1=find(x.^2 + y.^2 < 1);
ll2=find(abs(x) + abs(y) > 1);
ll3=intersect(ll1,ll2);
figure;
plot(x(ll3),y(ll3),’.’);
```

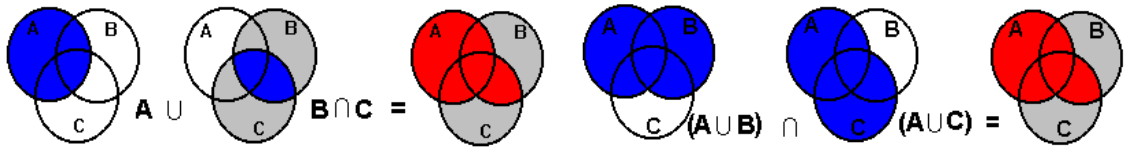


(c) Generalization is:

$$\overline{\cap_{i\in I} A_i} \equiv \cup_{i\in I} \overline{A_i}$$
$$\overline{\cup_{i\in I} A_i} \equiv \cap_{i\in I} \overline{A_i}$$

where I is some, possibly uncountable, indexing set.

(d)



(e) The sequence is nondecreasing since

$$\{(x,y) : 1/k \le x^2+y^2 \le 4-1/k\} \subset \{(x,y) : 1/(k+1) \le x^2+y^2 \le 4-1/(k+1)\}$$

for all k. The limit is

$$\{(x,y) : 0 < x^2+y^2 < 4\}$$

Note: the equality signs are gone because the end points are not part of the infinite union.

(f) The sequence is nonincreasing since

$$\{x : 2 < x \le 2+1/k\} \supset \{x : 2 < x \le 2+1/(k+1)\}$$

for all k. The limit set is:

$$\{x : 2 < x \le 2\}$$

Note: the equality sign remains because the term $1/k > 0$ for all k (even in the limit $k \to \infty$).

(g)

$$Q(C_1) = \int_{-1}^{1} \mathrm{d}x \int_{-1}^{1} (x^2+y^2)\mathrm{d}y = \frac{8}{3} \approx 2.66667$$

$$Q(C_2) = \iint_C (x^2+y^2)\mathrm{d}x\mathrm{d}y = 0 \text{ since the set } C \text{ is a thin line with zero area}$$

$$Q(C_3) = \iint_{\{(x,y)|x^2+y^2<R^2\}} (x^2+y^2)\mathrm{d}x\mathrm{d}y = \int_0^R r\mathrm{d}r \int_0^{2\pi} \mathrm{d}\theta r^2 = \frac{\pi R^4}{2} = \frac{\pi}{2}$$

(h) 25+17=42. 42-35=7. In all likelihood, the bridge shall open 7 cans of sardines. ■

Problem 64. Let Ω be the set of elementary outcomes and E a subset of Ω, called "event". Denote $\mathcal{F}$ the collection of all possible events. Technically, $\mathcal{F}$ is called a "σ-field of subsets". Let $\mathbb{P}$ be a real-valued function defined on $\mathcal{F}$. $\mathbb{P}$ is a probability set function of it satisfies the following three conditions:

(1) $\mathbb{P}(A) \ge 0$, for all $A \in \mathcal{F}$.

(2) $\mathbb{P}(\Omega) = 1$.

(3) If $\{A_n\}$ is a sequence of events in $\mathcal{F}$ and $A_m \cap A_n = \emptyset$ for all $m \neq n$, then

$$\mathbb{P}\left(\cup_{n=1}^{\infty} A_n\right) = \sum_{n=1}^{\infty} \mathbb{P}(A_n).$$

A collection of events whose members are pairwise disjoint is said to be a **mutually exclusive** collection and its union is often referred to as a **disjoint union**. The collection is further said to be **exhaustive** if the union of its events is the sample space, in which case $\sum_{n=1}^{\infty} \mathbb{P}(A_n) = 1$. We say that a mutually exclusive and exhaustive collection of events forms a **partition** of Ω.

Using the above definition of probability:

(a) Prove that for each event $A \in \mathcal{F}$, $\mathbb{P}(A) = 1 - \mathbb{P}(A^c)$.

(b) Prove that the probability of a null set is zero, i.e. $\mathbb{P}(\emptyset) = 0$.

(c) Prove that if A and B are events such that $A \subset B$, then $\mathbb{P}(A) \leq \mathbb{P}(B)$.

(d) Prove that for each $A \in \mathcal{F}$, $0 \leq \mathbb{P}(A) \leq 1$.

(e) Prove that if A and B are events in Ω, then

$$\mathbb{P}(A \cup B) = \mathbb{P}(A) + \mathbb{P}(B) - \mathbb{P}(A \cap B)$$

(f) For a finite sample space $\Omega = \{x_1, x_2, \ldots, x_m\}$ with m elements, let $p_1, p_2, \ldots, p_m$ be such that $0 \leq p_i \leq 1$ for $i = 1, 2, \ldots, m$ and $\sum_{i=1}^{m} p_i = 1$. Construct a probability set function $\mathbb{P}(A)$ on $\mathcal{F}$ (for all subsets $A \in \mathcal{F}$) such that all 3 above conditions are satisfied.

(g) Let $\Omega = \{x_1, x_2, \ldots, x_m\}$ be a finite sample space. Find the set of elementary probabilities p_i for all $i = 1, 2, \ldots, m$ such that $\mathbb{P}(A) = \#(A)/m$, where $\#(A)$ denotes the number of elements in A. Prove that $\mathbb{P}$ is a probability on Ω.

(h) Let $\Omega = \{x : 0 < x < \infty\}$. Let $C \subset \Omega$ be defined by $C = \{x : 0 < x < 10\}$. Define the function $\mathbb{P}(A) = \int_A \frac{1}{2} e^{-x/2} \mathrm{d}x$ for any event $A \subset \Omega$. Show that $\mathbb{P}(\Omega) = 1$. Evaluate $\mathbb{P}(C)$, $\mathbb{P}(C^c)$ and $\mathbb{P}(C \cap C^c)$.

Solution. (a) We have $\Omega = A \cup A^c$ and $A \cap A^c = \emptyset$. Thus from conditions 2 and 3 it follows that

$$1 = \mathbb{P}(A) + \mathbb{P}(A^c)$$

(b) Take $A = \emptyset$ so that $A^c = \Omega$. Using the result from (a),

$$\mathbb{P}(\emptyset) = 1 - \mathbb{P}(\Omega) = 1 - 1 = 0.$$

(c) Writing $B = A \cup (A^c \cap B)$ and $A \cap (A^c \cap B) = \emptyset$, condition 3 gives

$$\mathbb{P}(B) = \mathbb{P}(A) + \mathbb{P}(A^c \cap B)$$

From condition 1, $\mathbb{P}(A^c \cap B) \geq 0$. Hence, $\mathbb{P}(B) \geq \mathbb{P}(A)$.

(d) Since $\emptyset \subset A \subset \Omega$, we have by the results of part (c) that

$$\mathbb{P}(\emptyset) \leq \mathbb{P}(A) \leq \mathbb{P}(\Omega)$$

or $0 \leq \mathbb{P}(A) \leq 1$, the desired result.

(e) Each of the sets $A \cup B$ and B can be represented, respectively, as a union of nonintersecting sets as follows:

$$A \cup B = A \cup (A^c \cap B) \text{ and } B = (A \cap B) \cup (A^c \cap B).$$

These identities hold for all sets A and B, according to set theory. (You can also verify them using Venn diagrams.) From condition 3 we have

$$\mathbb{P}(A \cup B) = \mathbb{P}(A) + \mathbb{P}(A^c \cap B)$$

and

$$\mathbb{P}(B) = \mathbb{P}(A \cap B) + \mathbb{P}(A^c \cap B).$$

If the second of these quantities is solved for $\mathbb{P}(A^c \cap B)$ and this result is substituted in the first equation, we obtain

$$\mathbb{P}(A \cup B) = \mathbb{P}(A) + \mathbb{P}(B) - \mathbb{P}(A \cap B).$$

(f) We can take $p_i = 1/m$ and $\mathbb{P}(A) = \#(A)/m$. See (g).

(g) Take the equilikely distribution $p_i = 1/m$. Define:

$$\mathbb{P}(A) = \sum_{x_i \in A} \frac{1}{m} = \frac{\#(A)}{m}.$$

Then, $\mathbb{P}$ is a probability on Ω. It is trivial to check that all 3 conditions are satisfied: $\mathbb{P}(A) \geq 0$, $\mathbb{P}(\Omega) = m/m = 1$, and for disjoint sets $\mathbb{P}(A \cup B) = \mathbb{P}(A) + \mathbb{P}(B)$.

(h)

$$\mathbb{P}(\Omega) = \int_0^\infty \tfrac{1}{2} e^{-x/2} dx = \left[-e^{-x/2}\right]_0^\infty = 0 - (-1) = 1$$

■

Problem 65. You write 3 letters and in a rush, put a random letter in each envelope. (There are 3 envelopes, 3 letters, 1 letter per envelope.). What is the probability that at least one letter is in the correct envelope?

Solution. Let C_i be the event that the i-th letter is in the correct envelope. Expand $\mathbb{P}(C_1 \cup C_2 \cup C_3)$ to determine the probability:

$$\begin{aligned}\mathbb{P}(C_1 \cup C_2 \cup C_3) = \mathbb{P}(C_1) + \mathbb{P}(C_2) + \mathbb{P}(C_3) - \mathbb{P}(C_1 \cap C_2) - \mathbb{P}(C_1 \cap C_3) \\ -\mathbb{P}(C_2 \cap C_3) + \mathbb{P}(C_1 \cap C_2 \cap C_3)\end{aligned}$$

All pairwise terms $\mathbb{P}(C_1 \cap C_2)$, $\mathbb{P}(C_1 \cap C_3)$ and $\mathbb{P}(C_2 \cap C_3)$ are zero because it's not possible to have only 2 letters in correct envelopes without have all 3. Then,

$$\mathbb{P}(C_1 \cup C_2 \cup C_3) = \mathbb{P}(C_1) + \mathbb{P}(C_2) + \mathbb{P}(C_3) + \mathbb{P}(C_1 \cap C_2 \cap C_3).$$

Now the probabilities: There are 3!=6 ways to place 3 letters in 3 envelopes (order matters). There is 1 way to place letter 1 in envelope 1 (and only 1 way to place envelopes 2 and 3 in the remaining incorrect envelopes). Therefore $\mathbb{P}(C_1) = 1/6$. Same for $\mathbb{P}(C_2)$ and $\mathbb{P}(C_3)$. For the last term, $\mathbb{P}(C_1 \cap C_2 \cap C_3)$, we need to know the number of ways we can place all 3 letters in the correct envelopes. There's only 1 way to do that. Hence, $\mathbb{P}(C_1 \cap C_2 \cap C_3) = 1/6$. Thus,

$$\mathbb{P}(C_1 \cup C_2 \cup C_3) = \frac{4}{6}.$$

■

Problem 66. A random experiment consists of choosing a random number in the interval $(0, 1)$. (This number can be rational or irrational.) For any interval $(a, b) \subset (0, 1)$ it seems reasonable to define the probability $\mathbb{P}((a, b)) = b - a$, i.e. as equal to the length of the interval. Choose an appropriate sequence of subsets of $(0, 1)$ and use the following result:

$$\lim_{n\to\infty} \mathbb{P}(C_n) = \mathbb{P}(\lim_{n\to\infty} C_n) = \mathbb{P}\left(\cap_{n=1}^{\infty} C_n\right)$$

where $\{C_n\}$ is a decreasing sequence of events (i.e. $C_{n+1} \subset C_n$), to show that $\mathbb{P}(\{a\}) = 0$, for all $a \in (0, 1)$.

Solution. Construct the following decreasing sequence of events:

$$C_k = \{x : a - 1/k < x < a + 1/k\}$$

You can check that these events are open intervals $(a-1/k, a+1/k)$. Their intersection/limit is the point $\{a\}$:

$$\lim_{k\to\infty} C_k \equiv \cap_{k=1}^{\infty} C_k = \{a\}.$$

Meanwhile,

$$\mathbb{P}((a - 1/k, a + 1/k)) = a + 1/k - (a - 1/k) = 2/k.$$

Taking the limit $k \to \infty$, we see that (applying the above 'result')

$$\mathbb{P}(\lim_{k\to\infty} C_k) = \mathbb{P}(\{a\}) = \lim_{k\to\infty} \mathbb{P}((a-1/k, a+1/k)) = \lim_{k\to\infty} \frac{2}{k} = 0.$$

Therefore, $P(\{a\}) = 0$. ■

Problem 67. Calculate the following probabilities:

(a) Consider a probability space where the set of elementary outcomes is the interval $\Omega = (0,1)$, i.e. a number X (random variable) is chosen at random within that interval. Define a probability measure over that interval as

$$\mathbb{P}(X \in (a,b)) = b - a, \quad \text{for } 0 < a < b < 1.$$

Find an expression for the CDF. Derive a PDF from $\mathbb{P}$ (or the CDF). Compute the probability that X is less than an eighth or greater than seven eights. Would it be possible to use a discrete probability model for this experiment?

(b) In a random experiment we will an unbiased die. The set of outcomes is $\Omega = \{1,2,3,4,5,6\}$. Let X be the random variable that indicates the result (top face of die) of the experiment. X can take the value $\in \{1,2,3,4,5,6\}$. Its PMF is $p_i = 1/6$ for $i = 1,\ldots,6$. Plot the CDF of X, i.e. $F(x)$ vs x. Recall that the CDF is defined as $F(x) \equiv \mathbb{P}(X \in (-\infty, x])$. For $x < 1$ define $F(x) = 0$. What is the limiting value of $F(x)$ (i.e. as $x \to \infty$)? Using the CDF, can you obtain the PMF? Explain.

(c) Let X be a random variable representing a real random number chosen between 0 and 1. Obtain the CDF of X. You may assume that $\mathbb{P}(X \in (a,b)) = b - a$ for $0 < a < b < 1$. Sketch the CDF. Obtain the PDF. State the connection between CDF and PDF.

(d) Let X be a random variable with the CDF $F(x)$. Then for $a < b$, prove that the probability $\mathbb{P}(a < X \leq b) = F(b) - F(a)$.

(e) If X is a random variable and $F(x)$ its CDF, then for all a and b, if $a < b$ then $F(a) \leq F(b)$ (F is nondecreasing). Also, it can be shown that $\lim_{x\to-\infty} F(x) = 0$ (the lower limit of F is 0), $\lim_{x\to\infty} F(x) = 1$ (the upper limit of F is 1), $\lim_{x\downarrow x_0} F(x) = F(x_0)$ (F is right-continuous).

Let X be the half-life of a radioactive isotope. Assume that X has the CDF

$$F(x) = \begin{cases} 0 & x < 0 \\ 1 - e^{-x} & 0 \leq x. \end{cases}$$

Obtain the PDF of X. Show that the derivative of the CDF does not exist at $x = 0$, but that does not affect our ability to compute probabilities. Compute the probability that the half-life is between 1 and 3 years.

(f) The conditions expressed at the beginning of problem (e) show that CDFs are right-continuous and monotone. Such functions can be shown to have at most a countable number of discontinuities. For any random variable, prove that $\mathbb{P}(X = x) = F(x) - F(x-)$, for all $x \in \mathbb{R}$, where $F(x-) = \lim_{z \uparrow x} F(z)$. This results is not a mere curiosity; it allows us to deal with discontinuities in the distribution. Recall that for $\{C_n\}$ a nondecreasing sequence of events,

$$\lim_{n\to\infty} \mathbb{P}(C_n) = \mathbb{P}(\lim_{n\to\infty} C_n) = \mathbb{P}\left(\cup_{n=1}^{\infty} C_n\right)$$

Similarly for a decreasing sequence of events,

$$\lim_{n\to\infty} \mathbb{P}(C_n) = \mathbb{P}(\lim_{n\to\infty} C_n) = \mathbb{P}\left(\cap_{n=1}^{\infty} C_n\right)$$

(g) Let X have a CDF:

$$F(x) = \begin{cases} 0 & x < 0 \\ x/2 & 0 \le x < 1 \\ 1 & 1 \le x. \end{cases}$$

Compute the value $\mathbb{P}(-1 < X \le 1/2)$ and $\mathbb{P}(X = 1)$ (the value is not zero!).

(h) Let X have the PMF

$$p(x) = \begin{cases} cx & x = 1, 2, \ldots, 10 \\ 0 & \text{elsewhere} \end{cases}$$

for an appropriate constant c. Find the value c.

(i) Let X have the PDF

$$f(x) = \begin{cases} cx^3 & 0 < x < 2 \\ 0 & \text{elsewhere} \end{cases}$$

for a constant c. Compute c. Compute the probability $\mathbb{P}(1/4 < X < 1)$.

(j) Let $\Omega = \{x : 1 < x < 2\}$ be the space of X. If $D_1 = \{x : 1 < x \le 4/3\}$ and $D_2 = \{x : 4/3 < x < 2\}$, find $\mathbb{P}(D_2)$ if $\mathbb{P}(D_1) = 1/3$.

(k) Choose five cards at random and without replacement from a normal deck of playing cards. Find the PMF of X, the number of hearts in the five cards. Determine $\mathbb{P}(X \le 1)$.

Solution. (a) PDF is obtained by differentiating the CDF. CDF is

$$F(x) \equiv \mathbb{P}(X \in (0, x]) = \int_0^x dx = x.$$

Then PDF is:

$$f(x) = \begin{cases} 1 & 0 < x < 1 \\ 0 & \text{elsewhere} \end{cases}$$

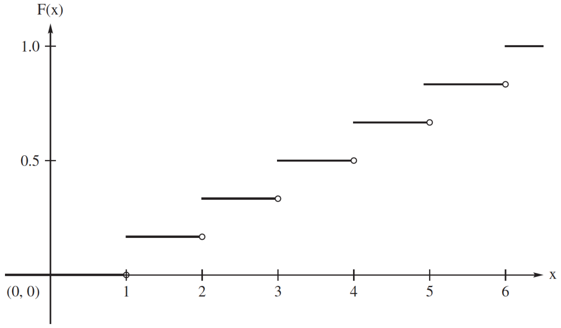
$$\mathbb{P}(\{X < 1/8\} \cup \{X > 7/8\}) = \int_0^{1/8} dx + \int_{7/8}^{1} dx = 1/4.$$

Discrete: no, because the probability $\mathbb{P}(\{X = a\}) = 0$ for all $a \in (0,1)$.

(b) The CDF is defined as the right-continuous function:

$$F(x) = \sum_{\{i : x_i \le x\}} p_i$$

where the notation $\{i : x_i \le x\}$ means "sum over all i such that $x_i \le x$". Plotting this function gives a right-continuous function:



The PMF is given to us: $\{p_i\}$. From the CDF we can obtain the PDF by differentiating:

$$f(x) = \frac{\mathrm{d}F(x)}{\mathrm{d}x} = \sum_i p_i \delta(x - x_i),$$

where $\delta(x - x_i)$ are Dirac delta functions. What about the PMF? The PMF is defined as $\mathbb{P}(X = x)$, the probability that X takes a specific value x. Obviously this is zero unless $x = x_i$, the points where the CDF "jumps" (discontinuities of F). The size of the discontinuity gives p_i. Formally, the probability of x_i is obtained by integrating the PDF:

$$\mathbb{P}(X = x_i) = \int_{\{x_i\}} f(x)\mathrm{d}x = \lim_{\epsilon \to 0} \int_{x_i - \epsilon}^{x_i + \epsilon} f(x)\mathrm{d}x = \lim_{\epsilon \to 0} \int_{x_i - \epsilon}^{x_i + \epsilon} \sum_j p_j \delta(x - x_j)\mathrm{d}x = p_i.$$

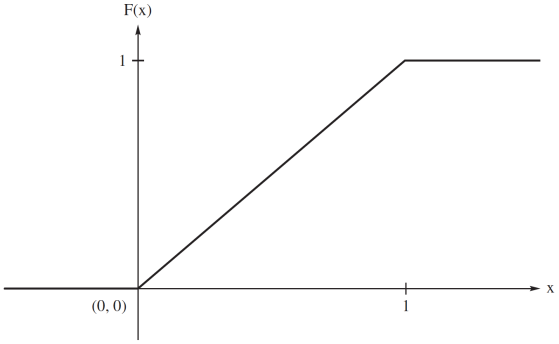
The PMF can also be obtained form the CDF as follows:

$$\mathbb{P}(X = x_i) = \lim_{\epsilon \to 0} \mathbb{P}(x_i - \epsilon < X \le x_i + \epsilon) = \lim_{\epsilon \to 0} \{F(x_i + \epsilon) - F(x_i - \epsilon)\} = p_i.$$

(c) Recall that the CDF is defined as $F(x) = \mathbb{P}(X \in (-\infty, x])$. Since the domain of definition of X is (0,1), we take 0 instead of $-\infty$ as the lower limit and we make sure that x does not exceed 1. We can take $\mathbb{P}(X \in (a,b)) = b - a$, replace a by 0 and b by x:

$$F(x) = \mathbb{P}(X \in (0,x]) = \begin{cases} 0 & x < 0 \\ x & x \in (0,1) \\ 1 & x > 1 \end{cases}$$

The graph looks like:



The PDF is obtained from the CDF by differentiating:

$$f(x) = \frac{\mathrm{d}F(x)}{\mathrm{d}x} = 1$$

where $x \in (0,1)$. This is the uniform distribution on the interval $(0,1)$.

(d) Note that

$$\{-\infty < X \leq b\} = \{-\infty < X \leq a\} \cup \{a < X \leq b\}.$$

The proof follows immediately because the union on the right side of this equation is a disjoint union.

(e) The PDF is obtained by differentiating

$$f(x) = \frac{\mathrm{d}F(x)}{\mathrm{d}x} = \begin{cases} e^{-x} & 0 < x < \infty \\ 0 & \text{elsewhere} \end{cases}$$

The derivative of a function $F(x)$ at the point a exists if the limit

$$\lim_{x \to a} \frac{F(x) - F(a)}{(x-a)}$$

exists.

That limit is also the slope of the tangent line to the curve $y = F(x)$ at $x = a$. That limit does not exist when the curve $y = F(x)$ does not have a tangent line at $x = a$ or when the curve does have a tangent line, but the tangent line has infinite slope. In the present case, there is no tangent line at $x = 0$ because this point is a sharp corner (plot the graph of $F(x)$ to see).

This is of no consequence when computing probabilities involving X because $\mathbb{P}(X=0)=0$ (see problem f below). Therefore, we can assign $f(0)=0$ without changing the probabilities involving X.

Finally,

$$\mathbb{P}(1 < X \leq 3) = F(3) - F(1) = \int_1^3 e^{-x}\mathrm{d}x.$$

(f) For any $x \in \mathbb{R}$, we have

$$\{x\} = \bigcap_{n=1}^{\infty} \left(x - \frac{1}{n}, x\right]$$

that is, $\{x\}$ is the limit of a decreasing sequence of sets. Hence,

$$\begin{aligned}\mathbb{P}(X=x) = \mathbb{P}\left(\bigcap_{n=1}^{\infty}\{x - \frac{1}{n} < X \leq x\}\right) &= \lim_{n\to\infty} \mathbb{P}(x - 1/n < X \leq x) \\ = \lim_{n\to\infty} [F(x) - F(x - 1/n)] &= F(x) - F(x-)\end{aligned}$$

which is the desired result. The difference, $F(x) - F(x-)$ measures the discontinuity at x.

(g)

$$\mathbb{P}(-1 < X \leq 1/2) = F(1/2) - F(-1) = \frac{1}{4} - 0 = \frac{1}{4}.$$
$$\mathbb{P}(X=1) = F(1) - F(1-) = 1 - \frac{1}{2} = \frac{1}{2}.$$

(h)

$$1 = \sum_{x=1}^{10} p(x) = \sum_{x=1}^{10} cx = c(1 + 2 + \cdots + 10) = 55c.$$

Hence, $c = 1/55$.

(i)

$$1 = \int_0^2 cx^3\mathrm{d}x = x\left[\frac{x^4}{4}\right]_0^2 = 4c.$$

Hence, $c = 1/4$. Also,

$$\mathbb{P}(1/4 < X < 1) = \int_{1/4}^1 \frac{x^3}{4}\mathrm{d}x = \frac{255}{4096} = 0.06226.$$

(j) The two sets are disjoint, $D_1 \cap D_2 = \emptyset$. Since, $D_1 \cup D_2 = \Omega$, the collection of sets $\{D_1, D_2\}$ forms a partition of Ω. Then,

$$\mathbb{P}(D_1 \cup D_2) = \mathbb{P}(D_1) + \mathbb{P}(D_2) = \mathbb{P}(\Omega) = 1.$$

Hence,

$$\mathbb{P}(D_2) = 1 - \mathbb{P}(D_1) = 1 - 1/3 = 2/3.$$

(k) Let's assume a standard 52-card deck. There are 4 suits, 13 cards per suit. The number of ways to choose 5 cards without replacement, and without regard to order is:

$$\binom{52}{5} = \frac{52!}{(52-5)!5!} = 2,598,960.$$

First we consider the case $X = 1$. The number of ways to choose a heart is $\binom{13}{1}$. Cards 2-5: number of ways to choose 4 non-hearts is $\binom{51}{4}$. Number of ways to choose 1 heart, 4 non-hearts:

$$\binom{13}{1}\binom{39}{4}.$$

The probability of $X = 1$ is

$$\mathbb{P}(X = 1) = \frac{\binom{13}{1}\binom{39}{4}}{\binom{52}{5}} \approx 0.4114$$

Similarly,

$$\mathbb{P}(X = 2) = \frac{\binom{13}{2}\binom{39}{3}}{\binom{52}{5}} \approx 0.2743$$

$$\mathbb{P}(X = 3) = \frac{\binom{13}{3}\binom{39}{2}}{\binom{52}{5}} \approx 0.0815$$

$$\mathbb{P}(X = 4) = \frac{\binom{13}{4}\binom{39}{1}}{\binom{52}{5}} \approx 0.0107$$

$$\mathbb{P}(X = 5) = \frac{\binom{13}{5}\binom{39}{0}}{\binom{52}{5}} \approx 0.0005$$

For $\mathbb{P}(X \leq 1)$ we need to consider two disjoint events: $\{X = 0\}$ and $\{X = 1\}$. Then,

$$\mathbb{P}(X \leq 1) = \mathbb{P}(\{X = 0\}) \cup \{X = 1\}) = \mathbb{P}(X = 0) + \mathbb{P}(X = 1)$$

■

Problem 68. Let X have the PMF

$$p_X(x) = \begin{cases} \frac{3!}{x!(3-x)!}\left(\frac{2}{3}\right)^x\left(\frac{1}{3}\right)^{3-x} & x = 0, 1, 2, 3 \\ 0 & \text{elsewhere} \end{cases}$$

Find the PMF $p_Y(y)$ of the random variable $Y = X^2$.

Solution. The transformation $y = g(x) = x^2$ maps the set $\{x : x = 0, 1, 2, 3\}$ into $\{y : y = 0, 1, 4, 9\}$. In general, $y = x^2$ does not define a one-to-one transformation. Here, however, it does, as there are no negative values of x in the set (for x). That is, we have the single-valued inverse function $x = g^{-1}(y)$ (not $-\sqrt{y}$), and so

$$p_Y(y) = p_X(\sqrt{y}) = \frac{3!}{(\sqrt{y})!(3-\sqrt{y})!}\left(\frac{2}{3}\right)^{\sqrt{y}}\left(\frac{1}{3}\right)^{3-\sqrt{y}}, \quad y = 0, 1, 4, 9$$

■

Problem 69. Consider a sequence of independent flips of a coin, each resulting in a head (H) or a tail (T). On each flip, we assume that H and T are equally likely. The sample space consists of sequences TTHTHTHTHT.... Let the random variable X equal to the number of flips needed to obtain the first head. For example, $X(\mathrm{TTHTHHT}\cdots) = 3$. The space of X is $\Omega = \{1, 2, 3, 4, \dots\}$. We see what $X = 1$ when the sequence begins with an H and $\mathbb{P}(x = 1) = \frac{1}{2}$. Likewise, $X = 2$ when the sequence begins with TH, which has probability $\mathbb{P}(X = 2) = (\frac{1}{2})(\frac{1}{2}) = \frac{1}{4}$ (assuming statistical independence). More generally, if $X = x$, where $x = 1, 2, 3, 4, \dots,$ there must be a string of $x - 1$ tails followed by a head. That is, TT$\cdots$TH, where there are $x - 1$ tails in TT$\cdots$T. Thus, from independence,

$$\mathbb{P}(X = x) = \left(\frac{1}{2}\right)^{x-1}\left(\frac{1}{2}\right) = \left(\frac{1}{2}\right)^{x}, \quad x = 1, 2, 3, \dots$$

the space of which is countable. Calculate the probability of the event that the first head appears on an odd number of flips, i.e. $X \in \{1, 3, 5, \dots\}$. Let $Z = (X - 2)^2$. Compute the PMF of Z.

Solution. For the first part of the question,

$$\mathbb{P}\left(X \in \{1, 3, 5, \dots\}\right) = \sum_{x=1}^{\infty}\left(\frac{1}{2}\right)^{2x-1} = \frac{1}{2}\sum_{x=1}^{\infty}\left(\frac{1}{4}\right)^{x-1} = \frac{1/2}{1-(1/4)} = \frac{2}{3}.$$

For $Z = (X - 2)^2$, the space of Z is $\{0, 1, 4, 9, 16, \dots\}$. Note that $Z = 0$ if and only if $X = 2$. $Z = 1$ if and only if $X = 1$ or $X = 3$. For the other values of the space there is a one-to-one correspondence given by $x = \sqrt{z} + 2$, for $z \in \{4, 9, 16, \dots\}$. Hence, the PMF of Z is

$$p_Z(z) = \begin{cases} p_X(2) = \frac{1}{4} & \text{for } z = 0 \\ p_X(1) + p_X(3) = \frac{5}{8} & \text{for } z = 1 \\ p_X(\sqrt{2} + 2) = \frac{1}{4}\left(\frac{1}{2}\right)^{\sqrt{z}} & \text{for } z = 4, 9, 16, \dots \end{cases}$$

You can show that the PMF of Z sums to 1 over its space. ■

Problem 70. Suppose that we have a unit circle and select a point at random within the interior of the circle. Let X be the distance of the point to the origin (Euclidean distance). The sample space for the random point is $\Omega = \{(w, y) : w^2 + y^2 < 1\}$. If the points (chosen at random) have equal probability, write down a formula for the probability of the point landing within an area A contained within the interior of the circle. The event $\{X \leq x\}$ means the point lies in a circle of radius x. Compute the probability $\mathbb{P}(X \leq x)$. Write down the CDF of X. Obtain the PDF of X. Calculate the numerical value of $\mathbb{P}(1/4 < X \leq 1/2)$.

Solution.

$$\mathbb{P}(A) = \frac{\text{area of } A}{\pi}$$

For $0 < x < 1$, the event $\{X \leq x\}$ is equivalent to the point lying in a circle of radius x. By this probability rule, $\mathbb{P}(X \leq x) = \pi x^2/\pi = x^2$. Hence, the CDF of X is

$$F(x) = \begin{cases} 0 & x < 0 \\ x^2 & 0 \leq x < 1 \\ 1 & 1 \leq x \end{cases}$$

■

Problem 71. Suppose that a phone company operates a computerized switchboard designed to route phone calls across the busy telephone network. Let X be the random variable that is the time in seconds between (consecutive) incoming telephone calls. Suppose that the PDF of X is

$$f(x) = \begin{cases} \frac{1}{4}e^{-x/4} & 0 < x < \infty \\ 0 & \text{elsewhere} \end{cases}$$

Show that $f(x)$ is normalized (to 1) and that $f(x) \geq 0$. Calculate the probability that the time between successive phone calls exceeds 4 seconds, i.e. $\mathbb{P}(X > 4)$. Plot this PDF and illustrate the area under the graph that corresponds to this probability. Is this distribution skewed? Compute the skewness of the distribution and explain the value obtained.

Solution.

$$f(x) = \begin{cases} \frac{1}{4}e^{-x/4} & 0 < x < \infty \\ 0 & \text{elsewhere} \end{cases}$$

$$\mathbb{P}(X > 4) = \int_4^\infty \frac{1}{4}e^{-x/4}\mathrm{d}x = e^{-1} = 0.3679.$$

■

Problem 72. Obtain the distribution of $Y = X^2$, where the CDF of X is

$$F_X(x) = \begin{cases} 0 & x < 0 \\ x^2 & 0 \leq x < 1 \\ 1 & 1 \leq x \end{cases}$$

Both X and Y have the same support, i.e., the interval $(0, 1)$.

Solution. Let y be the support of Y, i.e., $0 < y < 1$. The CDF of Y is

$$F_Y(y) = \mathbb{P}(Y \leq y) = \mathbb{P}(X^2 \leq y) = \mathbb{P}(X \leq \sqrt{y}) = F_X(\sqrt{y}) = \sqrt{y}^2 = y.$$

It follows that the PDF of Y is

$$f_Y(y) = \begin{cases} 1 & 0 < y < 1 \\ 0 & \text{elsewhere} \end{cases}$$

■

Problem 73. Let X be a continuous random variable with PDF

$$f(x) = \frac{e^x}{(1+5e^x)^{1.2}}, \quad -\infty < x < \infty.$$

Obtain the CDF of X. Plot the PDF. Compute the 3 quantiles: 0.25, 0.50 and 0.75 for X. Indicate on the graph of the PDF the position of the 3 quantiles. Definition (quantile): Let $0 < p < 1$. The quantile of order p of X is a value ξ_p such that $\mathbb{P}(X < \xi_p) \leq p$ and $\mathbb{P}(X \leq \xi_p) \geq p$. It is known as the $(100p)$th percentile of X.

Solution. The CDF of X is

$$F(x) = 1 + (1+5e^x)^{-.2} \qquad -\infty x < \infty,$$

which is confirmed by differentiation, $F'(x) = f(x)$. The quantiles are

$$q_1 = -0.4419242$$

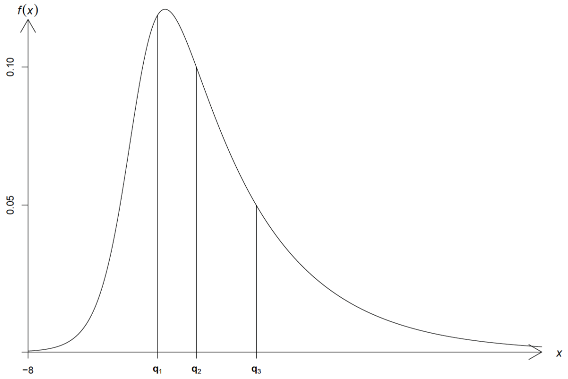
for 25%,

$$q_2 = 1.824549$$

for 50% and

$$q_3 = 5.321057$$

for 75%.



■

Problem 74. Let $f_X(x) = 1/2$, $-1 < x < 1$, zero elsewhere, be the PDF of X. X has uniform distribution within the interval of support $(-1,1)$. Define $Y = X^2$. Find the PDF and CDF of Y.

Solution. If $y \geq 0$, the probability $\mathbb{P}(Y \leq y)$ is equivalent to

$$\mathbb{P}(X^2 \leq y) = \mathbb{P}(-\sqrt{y} \leq X \leq \sqrt{y}).$$

Accordingly, the CDF of Y is given by

$$F_Y(y) = \begin{cases} 0 & y < 0 \\ \int_{-\sqrt{y}}^{\sqrt{y}} \frac{1}{2}\mathrm{d}x = \sqrt{y} & 0 \leq y < 1 \\ 1 & 1 \leq y \end{cases}$$

■

Problem 75. Let X have a distribution

$$F(x) = \begin{cases} 0 & x < 0 \\ \frac{x+1}{2} & 0 \leq x < 1 \\ 1 & 1 \leq x \end{cases}.$$

Calculate the value $\mathbb{P}(-3 < X \leq 1/2)$ and $\mathbb{P}(X = 0)$ (not zero!). Plot the graph of $F(x)$. Comment on any discontinuities and on the discrete (or non-discrete) nature of the distribution.

Solution.

$$\mathbb{P}(-3 < x \leq 1/2) = F(1/2) - F(-3) = \frac{3}{4} - 0 = \frac{3}{4}$$

$$\mathbb{P}(X = 0) = F(0) - F(0-) = \frac{1}{2} - 0 = \frac{1}{2}.$$

■

Problem 76. Compute the following expectation values of X:

(a) Let X have the PDF

$$f(x) = \begin{cases} 4x^3 & 0 < x < 1 \\ 0 & \text{elsewhere} \end{cases}$$

(b) For $x = 1, 2, 3, 4$ the corresponding PMF is $p(x)$=4/10, 1/10, 3/10 and 2/10, respectively. Here, $p(x) = 0$ if x is not equal to one of the first four positive integers.

(c) Let X be continuous rv with PDF $f(x) = 2x$, which has support on the interval $(0, 1)$. Suppose $Y = 1/(1 + X)$. Find $\langle X \rangle$ and $\langle Y \rangle$.

(d) Let X have the PDF

$$f(x) = \begin{cases} 2(1 - x) & 0 < x < 1 \\ 0 & \text{elsewhere} \end{cases}$$

Calculate $\langle X \rangle$, $\langle X^2 \rangle$ and $\langle 6X - 3X^2 \rangle$.

(e) Let X have the PMF

$$p(x) = \begin{cases} \frac{x}{6} & x = 1, 2, 3 \\ 0 & \text{elsewhere} \end{cases}$$

Compute $\langle 6X^3 + X \rangle$.

(f) Divide randomly a line segment of length 5 into two parts. If X is the length of the left-hand part, it is reasonable to assume that X has the PDF

$$f(x) = \begin{cases} \frac{1}{5} & 0 < x < 5 \\ 0 & \text{elsewhere} \end{cases}$$

Compute the expected value of the length $\langle X \rangle$. Calculate $\langle 5 - X \rangle$. Calculate also $\langle X(5-X) \rangle$ (expectation value of their product). Explain why $\langle X(5-X) \rangle \neq \langle X \rangle \cdot \langle 5 - X \rangle$. In the physical sciences, we often encounter situations like this where the product of expectation values is not the same as the expectation value of the product. A famous example is the spatial dependence of the dipole-dipole interaction, which scales as $1/r^3$. In general, $\langle 1/r^3 \rangle \neq \langle 1/r \rangle^3$.

Solution. (a)

$$\langle X \rangle = \int_0^1 x(4x^3)\mathrm{d}x = \int_0^1 4x^4 \mathrm{d}x = \left.\frac{4x^5}{5}\right|_0^1 = \frac{4}{5}.$$

(b)

$$\langle X \rangle = (1)\frac{4}{10} + (2)\frac{1}{10} + (3)\frac{3}{10} + (4)\frac{2}{10} = \frac{23}{10} = 2.3$$

(c)

$$\langle Y \rangle = \int_0^1 \frac{2x}{1+x}\mathrm{d}x = \int_1^2 \frac{2u-2}{u}\mathrm{d}u = 2(1 - \log 2).$$

(d)

$$\langle X \rangle = \int_{-\infty}^{\infty} x f(x)\mathrm{d}x = \int_0^1 (x)2(1-x)\mathrm{d}x = \frac{1}{3}$$
$$\langle X^2 \rangle = \int_{-\infty}^{\infty} x^2 f(x)\mathrm{d}x = \int_0^1 (x^2)2(1-x)\mathrm{d}x = \frac{1}{6}$$
$$\langle 6X + 3X^2 \rangle = 6(\frac{1}{3}) + 3(\frac{1}{6}) = \frac{5}{2}.$$

(e)

$$\langle 6X^3 + X \rangle = 6\langle X^3 \rangle + \langle X \rangle = 6\sum_{x=1}^{3} x^3 p(x) + \sum_{x=1}^{3} x p(x) = \frac{301}{3}$$

(f)

$$\langle X(5-x)\rangle = \int_0^5 x(5-x)(\frac{1}{5})\mathrm{d}x = \frac{25}{6} \neq (\frac{5}{2})^2.$$

■

Problem 77. Suppose that we have an amplifier that takes a voltage and amplifies it by a factor of 10×, i.e. $f(x) = 10x$. Suppose that we feed this amplifier the following input voltages:

$$X = \{2.53, 2.55, 2.45, 2.49, 2.50, 2.52, 2.47, 2.48, 2.56, 2.49\}$$

(a) What is the sample variance at the *output* of the amplifier?

(b) Suppose that we have two rv's, X and Y and they are statistically independent. Furthermore, suppose that $var(X)$=2.7 and $var(Y)$=2.5. Compute the value of $var(X+Y)$ and $var(X-Y)$.

(c) Given that $var(X)$=2.7, $var(Y)$=2.5 and $\rho(X,Y)$=0.9 (correlation coefficient), what is $var(X+Y)$ and $var(X-Y)$?

(d) If X, Y and Z are statistically independent and $var(X)$=1.7, $var(Y)$=2.3 and $var(Z)$=1.4. What is $var(0.3X + 0.7Y + 0.5Z)$?

Solution. (a) First, calculate the sample variance of X and then multiply by 100. Then multiply each X_i by 10 and then calculate the sample variance of the multiplied values. The sample variance of the X's is 0.001249. Multiply this by 100 to get 0.1249. Multiplying each X by 10 and taking the sample variance we get 0.1249, which is the same as the first method. From this we confirmed the validity of the formula $var(aX) = a^2 var(X)$.

(b) By statistical independence we have

$$var(X+Y) = var(X) + var(Y) = 2.7 + 2.5 = 5.2.$$

Then from

$$var(aX + bY) = a^2 var(X) + b^2 var(Y),$$

with $a = 1$ and $b = -1$ we have

$$var(X-Y) = (1)^2 var(X) + (-1)^2 var(Y) = var(X) + var(Y) = 2.7 + 2.5 = 5.2.$$

From this, we conclude that when X and Y are statistically independent, $var(X+Y) = var(X-Y) = var(X) + var(Y)$. ■

Statistical Foundations of Thermodynamics

2.1. Probability Distributions in Statistical Mechanics

2.1.1. Boltzmann distribution. In classical mechanics the momentum $\mathbf{p}$ of a particle with mass m in a gas may be considered as a (three-dimensional) random variable. For the density distribution one obtains

$$\rho(\mathbf{p}) = \frac{1}{A}\exp\left(-\beta\frac{\mathbf{p}^2}{2m}\right), \quad \text{where} \quad \beta = \frac{1}{k_B T}.$$

Here T represents the temperature, k_B is the Boltzmann's constant and A is a normalization constant. The density $\rho(\mathbf{p})$ is thus given by a three-dimensional Gaussian distribution. The general n-dimensional Gaussian distribution is

$$\rho(\boldsymbol{\mu}, \mathsf{A}; \mathbf{x}) = \frac{(2\pi)^{-n/2}}{(\det \mathsf{A})^{1/2}}\exp\left(-\frac{1}{2}(\mathbf{x}-\boldsymbol{\mu})_i(\mathsf{A}^{-1})_{ij}(\mathbf{x}-\boldsymbol{\mu})_j\right).$$

Here we have used the summation convention, i.e. one has to sum over all indices appearing twice. The vector $\boldsymbol{\mu}$ and the matrix A are parameters of this distribution.

As our second example of a multivariate distribution we consider a gas of N particles characterized by the momenta and positions of all particles:

$$(\mathbf{p}, \mathbf{q}) = (\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{q}_1, \ldots, \mathbf{q}_N).$$

We will describe this state at each instant by a $6N$-dimensional random vector. When the volume and the temperature of the gas are specified, one obtains for the probability density in statistical mechanics

$$\rho(\mathbf{p},\mathbf{q}) = \frac{1}{A} e^{-\beta \mathcal{H}(\mathbf{p},\mathbf{q})}, \qquad \beta = \frac{1}{k_B T},$$

where again T denotes the temperature, k_B Boltzmann's constant and A is a normalization constant. Furthermore, $\mathcal{H}(\mathbf{p},\mathbf{q})$ is the Hamiltonian function for the particles in the volume V. This density is also called the Boltzmann distribution.

2.1.2. Marginal Densities. When one integrates over some of the variables of a multidimensional probability density, one obtains a probability density describing the probability for the remaining variables, irrespective of the values for those variables which have been integrated over. Let, for instance,

$$\rho'(x_1) = \int dx_2 \ldots dx_n \rho(x_1, x_2, \ldots, x_n),$$

then $\rho'(x_1)dx_1$ is the probability of finding X_1 in the interval $[x_1, x_1 + dx_1]$, irrespective of the outcome for the variables $X_2, \ldots, X_n$. This may be illustrated for the case of the Boltzmann distribution. With the Hamiltonian function

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + V(\mathbf{q}_1, \ldots, \mathbf{q}_N),$$

one obtains, after taking the integral over $\mathbf{p}_2, \ldots, \mathbf{p}_N, \mathbf{q}_1, \ldots, \mathbf{q}_N$, the probability density for a single particle, in this case in the form

$$\rho'(\mathbf{p}_1) = \frac{1}{A'} \exp\left(-\beta \frac{\mathbf{p}_1^2}{2m}\right).$$

2.1.3. Conditional Probabilities and Bayes' Theorem. With the Boltzmann distribution we have already met a distribution where certain given parameters need to be included explicitly, for instance, the temperature T and the volume V. The number of particles N may also be counted among these given parameters. In probability theory one writes $A|B$ for an event A under the condition that B is given. So the probability $\mathbb{P}(A)$ is then more precisely denoted by $\mathbb{P}(A|B)$, i.e., the probability of A when B is given. $\mathbb{P}(A|B)$ is called the conditional probability.

This notion extends to the probability densities. The Boltzmann distribution can therefore be written as

$$\rho(\mathbf{p},\mathbf{q}|T,V,N),$$

or in words, the probability density for the positions and momenta at given temperature, volume, and number of particles. In the same way,

$$\rho(p_x|p_y,p_z)$$

is the probability density for the x-component of the momentum of a particle under the condition that the y- and z-components are given.

One may form

$$\mathbb{P}(A,B)=\mathbb{P}(A|B)\mathbb{P}(B), \tag{2.1}$$

which is the joint probability for the occurrence of A and B. If B is an event in the same Borel space as A, then the joint probability $\mathbb{P}(A,B)$ is equivalent to $\mathbb{P}(A\cap B)$.

One may also define the conditional probability by

$$\mathbb{P}(A|B)=\frac{\mathbb{P}(A,B)}{\mathbb{P}(B)}.$$

If the denominator $\mathbb{P}(B)$ vanishes, it is not meaningful to consider the conditional probability $\mathbb{P}(A|B)$.

Similarly, conditional densities might also be introduced by using the multivari- ate probability densities, e.g.,

$$\rho(p_x|p_y,p_z)=\frac{\rho(p_x,p_y,p_z)}{\rho(p_y,p_z)}.$$

Example: consider a fair die and $B=\{2,4,6\}$, $A=\{2\}$. (Here A and B belong to the same Borel space.). Then

$$\mathbb{P}(A|B)=\frac{\mathbb{P}(A\cap B)}{\mathbb{P}(B)}=\frac{\mathbb{P}(A)}{\mathbb{P}(B)}=\frac{1/6}{1/2}=\frac{1}{3}.$$

The probability for the event $\{2\}$, given the number of points is even, is $1/3$. Obviously also $\mathbb{P}(B|A)=1$.

We note that if

$$\cup_{i=1}^{N}B_i=\Omega$$

is a disjoint, complete partition of Ω (such that $B_i\cap B_j=\emptyset$ and the union of all B_i is equal to the total set Ω), then obviously

$$\mathbb{P}(A)=\mathbb{P}(A,\Omega)=\sum_{i=1}^{N}\mathbb{P}(A,B_i)=\sum_{i=1}^{N}\mathbb{P}(A|B_i)\mathbb{P}(B_i),$$

where in the last step we have invoked Eq. (2.1). This should be compared with the formula

$$\rho_{X_1}(x_1)=\int dx_2\,\rho_{X_1,X_2}(x_1,x_2)=\int dx_2\,\rho(x_1|x_2)\rho_{X_2}(x_2).$$

2.1.4. Statistical Independence. We can define the concept of statistical independence starting from a slightly different point. Let A_1 and A_2 be two events (in the same, or possibly different Borel spaces). A_1 is said to be independent of A_2 if the probability for the occurrence of A_1 is independent of A_2, i.e.

$$\mathbb{P}(A_1|A_2)=\mathbb{P}(A_1).$$

In light of the definition of conditional probability, $\mathbb{P}(A_1|A_2)=\frac{\mathbb{P}(A_1,A_2)}{\mathbb{P}(A_2)}$, we have:

$$\mathbb{P}(A_1,A_2)=\mathbb{P}(A_1)\mathbb{P}(A_2).$$

If A_1 is independent of A_2, then A_2 is also independent of A_1: statistical independence is always mutual. Similarly, the joint density of two independent random variables may be written as

$$\rho_{X_1,X_2}(x_1,x_2) = \rho_{X_1}(x_1)\rho_{X_2}(x_2).$$

2.1.5. Bayes' Theorem. From

$$\mathbb{P}(A,B) = \mathbb{P}(A|B)\mathbb{P}(B) = \mathbb{B}|\mathbb{A}\mathbb{P}(A)$$

it follows that

$$\mathbb{P}(B|A) = \frac{\mathbb{P}(A|B)\mathbb{P}(B)}{\mathbb{P}(A)}.$$

Hence $\mathbb{P}(B|A)$ can be determined from $\mathbb{P}(A|B)$, if the a priori probabilities $\mathbb{P}(A)$ and $\mathbb{P}(B)$ are known.

Bayes' theorem is a very useful relation for determining the a posteriori probabilities P.B j A/. It has enormous numbers of applications.

Example: A company which produces chips owns two factories : Factory A produces 60% of the chips, factory B 40%. So, if we choose at random one chip from the company, this chip originates from factory A with a probability of 60%. We further suppose that 35% of the chips coming from factory A are defective, but only 25% of those coming from factory B.

Using Bayes' theorem one can determine the probability that a given defective chip comes from factory A. Let d be the event 'the chip is defective', A the event 'the chip comes from factory A', and $B = (= A^c)$ the event 'the chip comes from factory B'. From Bayes' theorem we then have

$$\mathbb{P}(A|d) = \frac{\mathbb{P}(d|A)\mathbb{P}(A)}{\mathbb{P}(d)} = \frac{\mathbb{P}(d|A)\mathbb{P}(A)}{\mathbb{P}(d|A)\mathbb{P}(A) + \mathbb{P}(d|B)\mathbb{P}(B)}.$$

Inserting the numbers $\mathbb{P}(A) = 0.60$, $\mathbb{P}(d|A) = 0.35$, $\mathbb{P}(d|B) = 0.25$ yields a value of $\mathbb{P}(A|d) = 0.68$.

2.1.6. Entropy.

2.1.6.1. *Entropy for a discrete set of events.* Let $\{A_1, \dots, A_N\}$ be a complete, disjoint set of events, i.e.

$$A_1 \cup A_2 \cup \cdots \cup A_N = \Omega.$$

Furthermore, let $\mathbb{P}$ be a probability defined on those events. We define the entropy as

$$S = -k \sum_{i=1}^{N} \mathbb{P}(A_i) \log \mathbb{P}(A_i).$$

Here k represents a factor which we set equal to 1 for the moment. In statistical mechanics k will be Boltzmann's constant k_B.

We observe:

- The entropy is defined for a complete, disjoint set of events of a random variable, irrespective of whether this partition of Ω into events can be refined or not. If Ω is the real axis, we might have, e.g., $N = 2$, $A_1 = (-\infty, 0)$, $A_2 = [0, \infty)$.
- Since $0 \leq \mathbb{P}(A_i) \leq 1$ we always have $S \geq 0$.
- If $\mathbb{P}(A_j) = 1$ for a certain j and $\mathbb{P}(A_i) = 0$ otherwise, then $S = 0$. This means that if the event A_j occurs with certainty the entropy is zero.
- If an event has occurred, then, $-\log_2 \mathbb{P}(A_j)$ is a good measure of the number of questions to be asked in order to find out that it is just A_j which is realized. In this context, 'question' refers to questions which can be answered by 'yes' or 'no', i.e., the answer leads to a gain of information of 1 bit. Hence, on average the required number of yes-or-no questions is

  $$S' = -\sum_{j=1}^{N} \mathbb{P}(A_j) \log_2 \mathbb{P}(A_j) = S + \mathit{const}.$$

  The entropy is thus a measure of the missing information needed to find out which result is realized.

  To show that $-\log_2 \mathbb{P}(A_j)$ is just equal to the number of required yes-or-no questions, we first divide Ω into two disjoint domains Ω_1 and Ω_2 such that

  $$\sum_{A_i \in \Omega_1 |} \mathbb{P}(A_i) = \sum_{A_i \in \Omega_2} \mathbb{P}(A_i) = \frac{1}{2}.$$

  The first question is now: Is A_j in Ω_1? Having the answer to this question we next consider the set containing Aj and multiply the probabilities for the events in this set by a factor of 2. The sum of the probabilities for this set is now again equal to 1, and we are in the same position as before with the set Ω: We divide it again and ask the corresponding yes-or-no question. This procedure ends after k steps, where k is the smallest integer such that $2^k \mathbb{P}(A_j)$ becomes equal to or larger than 1. Consequently, $-\log_2 \mathbb{P}(A_j)$ is a good measure of the number of yes-or-no questions needed.
- If the probabilities of the events are equal, i.e.,

  $$\mathbb{P}(A_i) = \frac{1}{N},$$

  we have

  $$S = \log N.$$

  Any other distribution of probabilities leads to a smaller S. This will be shown later.

The above observations suggest that the entropy may be considered as a lack of information when a probability density is given. On average it would require the answers to S yes-or-no questions to figure out which event has occurred. This lack is zero for a density which describes the situation where one event occurs with certainty. If all events are equally probable, this lack of information about which event will occur in a realization is maximal.

A less subjective interpretation of entropy arises when we think of it as a measure for uncertainty. If the probability is the same for all events, the uncertainty is maximal.

2.1.6.2. *Entropy for a continuous space of events.* In a similar manner we define the entropy for a random variable X , where the space of events is a continuum, by

$$S[\rho_X] = -k \int dx \rho_X(x) \log\left(\frac{\rho_X(x)}{\rho_0}\right).$$

When $\rho_X(x)$ has a physical dimension, the denominator ρ_0 in the argument of the logarithm cannot simply be set to 1. Since the physical dimension of $\rho_X(x)$ is equal to the dimension of $1/dx$, the physical dimension of ρ_0 has to be the same, in order that the argument of the logarithm will be dimensionless.

It is easy to see that a change of ρ_0 by a factor α leads to a change of the entropy by an additive term $k \log \alpha$. Such a change of ρ_0 only shifts the scale of S. Notice that we no longer have $S \geq 0$.

We now calculate[1] the entropy for a Gaussian random variable $N(\mu, \sigma^2)$. We obtain (for $k = 1$, $\rho_0 = 1$)

$$S = \int dx \left(\frac{(x-\mu)^2}{2\sigma^2} + \frac{1}{2}\log(2\pi\sigma^2)\right)\rho_X(x) = \frac{1}{2}(1 + \log(2\pi\sigma^2)).$$

The entropy increases with the width σ^2 of the probability density, i.e., with the spreading around the expectation value. In this case we again find that the broader the distribution, the larger our ignorance about which event will occur in a realization, and the larger the entropy. Again, entropy means a lack of information or uncertainty.

2.1.7. Relative Entropy. The relative entropy of a density function $p(x)$ with respect to a second density function $q(x)$ is defined by

$$S[p|q] = -k \int dx p(x) \log\left(\frac{p(x)}{q(x)}\right).$$

Obviously, $p(x) = q(x)$ iff $S[p|q] = 0$. However, while the entropy for a complete and disjoint set of events is positive semi-definite, the relative entropy of a density function $p(x)$ with respect to a given density function $q(x)$ is negative semi-definite, i.e.,

$$S[p|q] \leq 0.$$

This is easy to see: We use the inequality

$$\log z \leq z - 1$$

for $z = \frac{q(x)}{p(x)}$, multiply by $p(x)$, integrate over x, and obtain

$$-\int dx p(x) \log\left(\frac{p(x)}{q(x)}\right) \leq \int dx (q(x) - p(x)) = 0.$$

---

[1] The first term is trivial (requires no computation), because it is just the variance of the Gaussian, i.e. $\int dx\,(x - \mu)^2 \rho_X(x) \equiv var(X)$.

The inequality follows from $\log z \leq z - 1$ with $z = q/p$. The last step follows since both densities are normalized, causing the integrals on the right-hand side to be equal, from which $S[p|q] \leq 0$ follows.

Remarks: The notion of entropy was first introduced into thermodynamics as an extensive quantity, conjugate to temperature. The revealing discovery of the connection between this quantity and the probability of microstates was one of the great achievements of L. Boltzmann, and his equation $S = k \log W$. The introduction of entropy as a measure of the uncertainty of a density originated from Shannon (1948). Kullback and Leibler (1951) were the first to define the relative entropy, for which reason it is sometimes called Kullback–Leibler entropy. The relation between thermodynamics and information theory has been discussed extensively by Jaynes (1982).

2.1.8. Proof of the inequality $\log z \leq z-1$**.** A proof of the inequality $\log(z) \leq z-1$ can be obtained by considering the function $f(z) = z - 1 - \log(z)$ for $z > 0$ and its derivative, $f'(z) = 1 - \frac{1}{z}$. We find the critical points by setting $f'(z) = 0$, which gives $1 - \frac{1}{z} = 0$ or $z = 1$. We then apply the second derivative test using $f''(z) = \frac{1}{z^2}$. Since $f''(z) > 0$ for $z > 0$, $f(z)$ is concave up, indicating that $z = 1$ is a local minimum. We then evaluate $f(z)$ at $z = 1$ and obtain $f(1) = 1 - 1 - \log(1) = 0$. Since $z = 1$ is a local minimum and $f(z)$ is concave up for $z > 0$, $f(z)$ is non-negative for $z > 0$ and $f(z) = z - 1 - \log(z) \geq 0$, which leads to the desired result, $\log(z) \leq z - 1$.

2.1.9. Applications of Entropy. Using the inequality $S[p|q] \leq 0$ satisfied by the relative entropy it will now be easy to see that a constant density distribution always has maximum entropy. Notice, however, that such a constant density distribution is only possible if Ω, the set of possible outcomes, is a compact set, e.g., a finite interval.

Let $q(x) \equiv q_0$ be the constant density on Ω and $\rho(x)$ be an arbitrary density. The entropy of this density can also be written as[2]

$$S[\rho] = S[\rho|q_0] - k \log\left(\frac{q_0}{\rho_0}\right).$$

From $S[\rho|q_0] \leq 0$ and $S[\rho|q_0] = 0$ for $\rho \equiv q_0$ follows: $S[\rho]$ is maximal for $\rho \equiv q_0$

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[2] Using the definition

$$S[\rho|q_0] = -k \int dx\rho(x) \log\left(\frac{\rho(x)}{q_0}\right) = -k \int dx\rho(x) \log \rho(x) + k \int dx\rho(x) \log q_0$$

we find

$$S[\rho] = -k \int dx\rho(x) \log\left(\frac{\rho(x)}{\rho_0}\right) = -k \int dx\rho(x) \log \rho(x) + k \int dx\rho(x) \log \rho_0$$

which simplifies to

$$= S[\rho|q_0] - k \int dx\rho(x) \log q_0 + k \int dx\rho(x) \log \rho_0$$

and

$$= S[\rho|q_0] - k \log(q_0/\rho_0).$$

As a second application we now consider two random variables X_1, X_2, their densities $\rho_{X_1}(x)$, $\rho_{X_2}(x)$, and the joint density $\rho_{X_1,X_2}(x_1,x_2)$. For the relative entropy

$$S[\rho_{X_1,X_2}|\rho_{X_1}\dot{\rho}_{X_2}] = -\int dx_1 dx_2 \rho_{X_1,X_2}(x_1,x_2)\log\left(\frac{\rho_{X_1,X_2}(x_1,x_2)}{\rho_{X_1}(x_1)\rho_{X_2}(x_2)}\right) \equiv S_{12}$$

a short calculation yields[3]

$$S[\rho_{X_1,X_2}|\rho_{X_1}\rho_{X_2}] = S_{12} - S_1 - S_2,$$

where S_i is the entropy for the density $\rho_{X_i}(x)$, $i = 1,2$ and S_{12} the entropy of the joint density $\rho_{X_1,X_2}(x_1,x_2)$. As the relative entropy is always smaller than or equal to zero, one always has

$$S_{12} \leq S_1 + S_2.$$

Hence, the entropy of the joint density is always smaller than or equal to the sum of the entropies of the single densities. Equality holds iff

$$\rho_{X_1,X_2}(x_1,x_2) = \rho_{X_1}(x_1)\rho_{X_2}(x_2),$$

i.e., if the two random variables are independent: the entropies of independent random variables add up[4]. For independent random variables the total entropy is maximal. Any dependence between the random variables reduces the total entropy and lowers the uncertainty for the pair of random variables, i.e. any dependency corresponds to an information about the pair of random variables. The relative entropy $S[\rho_{X_1,X_2}|\rho_{X_1}\rho_{X_2}]$ is also known as mutual information.

In the remainder of this section we address the maximum entropy principle. We are looking for the density function $\rho(x)$ which has maximum entropy and satisfies the supplementary conditions

$$\langle g_i(X)\rangle \equiv \int dx g_i(x)\rho(x) = \eta_i, \qquad i = 1,\ldots,n. \tag{2.2}$$

Here $g_i(x)$ are given functions and η_i are given real numbers. From the proposition about the relative entropy proven above, one finds that the density function with maximum

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[3] Simply expand the expression for $S[\rho_{X_1,X_2}|\rho_{X_1}\dot{\rho}_{X_2}]$ given in the previous line. The logarithm becomes $\log(\rho_{X_1,X_2}) - \log\rho_{X_1} - \log\rho_{X_2}$. This leads to 3 terms. The first term is $S_{12} = -\int dx_1 dx_2 \rho_{X_1,X_2}(x_1,x_2)\log\rho_{X_1,X_2}(x_1,x_2)$. The second term, $S_1 = \int dx_1 dx_2 \rho_{X_1,X_2}(x_1,x_2)\log\rho_{X_1}(x_1)$. Integration over dx_2 gives a marginal density, so that the term becomes $S_1 = \int dx_1 \rho_{X_1}(x_1)\log\rho_{X_1}(x_1)$. Same story for the third term, $S_2 = \int dx_1 dx_2 \rho_{X_1,X_2}(x_1,x_2)\log\rho_{X_2}(x_2)$. Integration over dx_1 gives a marginal density, so that $S_2 = \int dx_2 \rho_{X_2}(x_2)\log\rho_{X_2}(x_2)$.

[4] The proof is trivial:

$$-\int dx_1 dx_2 \rho_{X_1}(x_1)\rho_{X_2}(x_2)\log\frac{\rho_{X_1}(x_1)\rho_{X_2}(x_2)}{\rho_0^2} = -\int dx_1 dx_2 \rho_{X_1}(x_1)\rho_{X_2}(x_2)\log\frac{\rho_{X_1}(x_1)}{\rho_0}$$
$$-\int dx_1 dx_2 \rho_{X_1}(x_1)\rho_{X_2}(x_2)\log\frac{\rho_{X_2}(x_2)}{\rho_0} = S[\rho_{X_1}] + S[\rho_{X_2}].$$

entropy satisfying the supplementary conditions (2.2) has the form

$$\rho(x) = \frac{1}{A} e^{-\lambda_1 g_1(x) - \lambda_2 g_2(x) - \cdots - \lambda_n g_n(x)}. \tag{2.3}$$

Here A is a normalization factor and $\{\lambda_i\}$ may be calculated from $\{\eta_i\}$. With the help of this maximum entropy principle we can determine density functions.

Proof. For the density function (2.3) one obtains (with $k = 1$)

$$S[\rho] = \log(A\rho_0) + \sum_{i=1}^{n} \lambda_i \eta_i,$$

where ρ_0 represents the factor which might be necessary for dimensional reasons. Let $\varphi(x)$ be a second density satisfying the supplementary conditions (2.2). Then, according to $S[p|q] \leq 0$,

$$S[\varphi|\rho] \leq 0,$$

i.e.

$$S[\varphi|\rho] = -k \int dx \varphi(x) \log \frac{\varphi(x)}{\rho(x)} = -\int \varphi \log \varphi + \int \varphi \log \rho + \log \rho_0 - \log \rho_0 \leq 0,$$

which leads to

$$\int \varphi \log(\varphi/\rho_0) \leq \int \varphi \log(\rho/\rho_0)$$

and therefore

$$\begin{aligned} S[\varphi] &= -\int dx \varphi(x) \log\left(\frac{\varphi(x)}{\rho_0}\right) \\ &\leq \int dx \varphi(x) \log\left(\frac{\rho(x)}{\rho_0}\right) \\ &= \int dx \varphi(x) \left[\log(A\rho_0) + \sum_{i=1}^{n} \lambda_i g_i(x)\right] \\ &= \log(A\rho_0) + \sum_{i=1}^{n} \lambda_i \eta_i \equiv S[\rho], \end{aligned}$$

where the third line follows from Eq. (2.3). Hence, $\rho(x)$ given by (2.3) is the density with maximum entropy.

Let us look at the two examples. First we seek the density defined on $[0, \infty)$ which has maximum entropy and satisfies the supplementary condition

$$\langle X \rangle = \eta.$$

We immediately find this density as

$$\rho(x) = \frac{1}{A} e^{-\lambda x} \qquad \text{for } x \geq 0.$$

The normalization factor A is given by

$$A = \int_0^\infty dx e^{-\lambda x} = \frac{1}{\lambda},$$

and λ is determined by η according to

$$\eta = \langle X \rangle = \int_0^\infty dx x \lambda e^{-\lambda x} = -\lambda \frac{\partial}{\partial \lambda} \int_0^\infty dx e^{-\lambda x} = \frac{1}{\lambda}.$$

Therefore,

$$\rho(x) = \frac{1}{\eta} e^{-x/\eta}.$$

As a second example we seek the density $\rho(\mathbf{p}, \mathbf{q})$, defined on the $6N$-dimensional phase space for N classical particles, which has maximum entropy and satisfies the supplementary condition

$$\langle \mathcal{H}(\mathbf{p}, \mathbf{q}) \rangle = E,$$

where $\mathcal{H}(\mathbf{p}, \mathbf{q})$ is the Hamiltonian function for the N particles. One obtains

$$\rho(\mathbf{p}, \mathbf{q}) = \frac{1}{A} e^{-\lambda \mathcal{H}(\mathbf{p}, \mathbf{q})}, \tag{2.4}$$

i.e., the Boltzmann distribution. We still have to determine A and λ. The former follows from the normalization condition

$$A = \int_\Gamma d^{3N}\mathbf{p}\, d^{3N}\mathbf{q}\, e^{-\lambda \mathcal{H}(\mathbf{p}, \mathbf{q})}, \tag{2.5}$$

where Γ is the phase space domain

$$\Gamma = \{(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{q}_1, \ldots, \mathbf{q}_N) : \mathbf{q}_i \in V, \mathbf{p}_i \in \mathbb{R}^3, \forall i = 1, \ldots, N\}.$$

In particular, we find

$$-\frac{1}{A} \frac{\partial A}{\partial \lambda} = \langle \mathcal{H}(\mathbf{p}, \mathbf{q}) \rangle. \tag{2.6}$$

λ follows from the supplementary condition:

$$E = \langle \mathcal{H}(\mathbf{p}, \mathbf{q}) \rangle = \frac{1}{A} \int_\Gamma d^{3N}\mathbf{p}\, d^{3N}\mathbf{q}\, \mathcal{H}(\mathbf{p}, \mathbf{q})\, e^{-\lambda \mathcal{H}(\mathbf{p}, \mathbf{q})}. \tag{2.7}$$

The right-hand side yields a function $f(\lambda, N, V)$ which has to be equal to E. The resulting equation has to be solved for λ to obtain $\lambda = \lambda(E, N, V)$.

The meaning of λ becomes more obvious when we consider the entropy. We have[5]

$$S[\rho] = \log(A\rho_0) + \lambda E$$

---

[5] This is easily seen as follows:

$$S[\rho] = -\int dx \frac{1}{A} e^{-\lambda H(x)} \log \frac{A^{-1} e^{-\lambda H(x)}}{\rho_0} = \log(A\rho_0) + \lambda \langle H \rangle,$$

where $\langle H \rangle = E$.

and therefore, using (2.6), we find[6]

$$\frac{\partial S[\rho]}{\partial E} = \frac{\partial \lambda}{\partial E}\frac{\partial}{\partial \lambda}\log(A\rho_0) + \frac{\partial \lambda}{\partial E}E + \lambda = \lambda.$$

The quantity λ indicates the sensitivity of the entropy to a change in energy. In statistical mechanics we introduce the temperature as being proportional to the inverse of this quantity λ and we will consider a system of N particles in a volume V, for which the temperature, i.e. the parameter λ, is held fixed by contact with a heat bath. In this system, which will be called the canonical system, we will obtain the Boltzmann distribution as the probability density for the positions and momenta of the particles. In the present context it results from the requirement of maximum entropy under the supplementary condition $\langle \mathcal{H}(\mathbf{x}) \rangle = E$.

This has a twofold significance: First, that the energy is not fixed, but the system may exchange energy with the environment (i.e. the heat bath), and second, that $\langle \mathcal{H}(\mathbf{x}) \rangle$ is independently given, which is equivalent to fixing the temperature in the canonical system. Both approaches to the Boltzmann distribution proceed from the same physical situation.

If we were looking for a system with maximum entropy which satisfies the supplementary conditions

$$\langle \mathcal{H}(\mathbf{x}) \rangle = E \qquad \text{and} \qquad \langle \mathcal{H}^2(\mathbf{x}) \rangle = C,$$

we would construct a system where both $\langle \mathcal{H}(\mathbf{x}) \rangle$ and $\langle \mathcal{H}^2(\mathbf{x}) \rangle$ are independently given. In the canonical system, however, one can determine $\langle \mathcal{H}^2(\mathbf{x}) \rangle$ as a function of E, N, V or T, N, V.

2.1.10. Ideal Gas: Average Kinetic Energy. The ideal gas is defined as a non-interacting ensemble of particles. The Hamiltonian contains a kinetic energy term, but no potential energy:

$$\mathcal{H}(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}$$

The density associated with the canonical ensemble (fixed T, V, N) is given by Eq. (2.4), the Boltzmann distribution, $\rho(\mathbf{p}, \mathbf{q}) = \frac{1}{A}e^{-\lambda \mathcal{H}(\mathbf{p}, \mathbf{q})}$. Using this density, we may compute various quantities of interest. For example, consider the kinetic energy of a single particle:

$$\frac{\mathbf{p}_1^2}{2m} = \frac{p_{x1}^2 + p_{y1}^2 + p_{z1}^2}{2m}$$

The average is computed using the density:

$$\langle \mathbf{p}_1^2 \rangle = \langle p_{x1}^2 + p_{y1}^2 + p_{z1}^2 \rangle = \langle p_{x1}^2 \rangle + \langle p_{y1}^2 \rangle + \langle p_{z1}^2 \rangle = 3\langle p_{x1}^2 \rangle,$$

---

[6] Note that

$$\frac{\partial}{\partial \lambda}\log A = \frac{1}{A}\frac{\partial A}{\partial \lambda} = -\langle H \rangle = -E.$$

where in the last step we have used the fact that all directions are equivalent, so that $\langle p_{x1}^2\rangle = \langle p_{y1}^2\rangle = \langle p_{z1}^2\rangle$. Let us therefore compute the average $\langle p_{x1}^2\rangle$:

$$\langle p_{x1}^2\rangle = \frac{1}{A}\int_\Gamma d^{3N}\mathbf{p}\, d^{3N}\mathbf{q}\, p_{x1}^2\, e^{-\beta\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}} = \frac{1}{A}\int_\Gamma d^{3N}\mathbf{p}\, d^{3N}\mathbf{q}\, p_{x1}^2 \prod_{i=1}^N e^{-\beta\frac{p_{xi}^2+p_{yi}^2+p_{zi}^2}{2m}}.$$

Integration over $\mathbf{q}$ is trivial because the integrand does not depend on $\mathbf{q}$. We get a factor V^N from it. We are left with

$$\langle p_{x1}^2\rangle = \frac{V^N}{A}\int_{\mathbb{R}^{3N}} d^{3N}\mathbf{p}\, p_{x1}^2 \prod_{i=1}^N e^{-\beta\frac{p_{xi}^2+p_{yi}^2+p_{zi}^2}{2m}}.$$

Next, notice that all remaining integrals except dp_{x1} are identical, let's call them $\xi = \int_\mathbb{R} dp_{ji} e^{-\beta p_{ji}^2/2m} = \sqrt{\frac{2\pi m}{\beta}}$. There are $3N-1$ such factors, leaving us with

$$\langle p_{x1}^2\rangle = \frac{V^N\xi^{3N-1}}{A}\int_\mathbb{R} dp_{x1}\, p_{x1}^2\, e^{-\beta\frac{p_{x1}^2}{2m}} = \frac{V^N\xi^{3N-1}}{A}\sqrt{2\pi}(\frac{2}{\beta})^{3/2},$$

where we used the fact that the remaining integral is proportional to the variance of the Gaussian, i.e.

$$\int_\mathbb{R} dp_{x1}\, p_{x1}^2\, e^{-\beta\frac{p_{x1}^2}{2m}} \times \frac{\sqrt{2\pi\sigma^2}}{\sqrt{2\pi\sigma^2}} = \sqrt{2\pi\sigma^2}\, var(p_{x1}) = \sqrt{2\pi m/\beta}\frac{m}{\beta} = \sqrt{2\pi}(\frac{m}{\beta})^{3/2}$$

with $\sigma^2 = m/\beta$. Now for A, we have

$$A = \int_\Gamma d^{3N}\mathbf{p}\, d^{3N}\mathbf{q}\, e^{-\beta\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}} = V^N\xi^{3N}.$$

Putting it all together:

$$\langle p_{x1}^2\rangle = \frac{V^N\xi^{3N-1}}{V^N\xi^{3N}}\sqrt{2\pi}(\frac{2}{\beta})^{3/2} = \frac{1}{\xi}\sqrt{2\pi}(\frac{m}{\beta})^{3/2} = \sqrt{\frac{\beta}{2\pi m}}\sqrt{2\pi}(\frac{m}{\beta})^{3/2} = k_BTm.$$

Therefore,

$$\langle\frac{\mathbf{p}_1^2}{2m}\rangle = \frac{1}{2m}\cdot 3\langle p_{x1}^2\rangle = \frac{3}{2m}k_BTm = \frac{3}{2}k_BT,$$

independent of mass. This result is for 1 particle. For N particles, we have:

$$\langle KE\rangle = \frac{3}{2}Nk_BT.$$

2.1.11. Maxwell-Boltzmann Velocity Distribution. Suppose that we have 3 independent random variables X_1, X_2, X_3 with standard normal distributions and set

$$Z = \sqrt{X_1^2 + X_2^2 + X_3^2}.$$

The density of Z is given by

$$\rho_Z(z) = \int dx_1 dx_2 dx_3\, \delta(z - \sqrt{x_1^2 + x_2^2 + x_3^2})\, \rho(x_1, x_2, x_3),$$

where

$$\rho(x_1, x_2, x_3) = (2\pi\sigma^2)^{-3/2} e^{-\frac{1}{2\sigma^2}(x_1^2+x_2^2+x_3^2)},$$

where $\sigma^2 = k_B T/m$. Using a property of the Dirac delta function:

$$\int_{\mathbb{R}^n} f(\mathbf{x})\,\delta(g(\mathbf{x}))\,d\mathbf{x} = \int_{g^{-1}(0)} \frac{f(\mathbf{x})}{|\nabla g|}\,d\sigma(\mathbf{x})$$

where the integral is over the $(n-1)$-dimensional surface defined by $g(\mathbf{x}) = 0$. Here, we are interested in the speed of a molecule, which depends on the components of the 3D velocity vector:

$$\begin{aligned} \mathbf{x} &= (v_x, v_y, v_z) \\ g(\mathbf{x}) &= v - \sqrt{v_x^2 + v_x^2 + v_z^2} \\ \nabla g(\mathbf{x}) &= -\frac{(v_x, v_y, v_z)}{\sqrt{v_x^2 + v_x^2 + v_z^2}} = -\frac{\mathbf{x}}{|\mathbf{x}|} \\ |\nabla g(\mathbf{x})| &= 1. \end{aligned}$$

Since the integrand only depends on the distance to the origin (isotropic) we can use spherical coordinates. The volume element is $dV = r^2 dr d\Omega$ and the surface element is $dS = r^2 d\Omega$, where $d\Omega = \sin\theta d\theta d\phi$. The surface integral has fixed $r = v$:

$$\int_{g^{-1}(0)} \frac{f(\mathbf{x})}{|\nabla g|}\,dS(\mathbf{x}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta e^{-\frac{mv^2}{2k_B T}} v^2 = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T}\right)^{3/2} e^{-\frac{1}{2}\frac{mv^2}{k_B T}} v^2.$$

The integral here was completely trivial, since the integrand does not depend on θ, ϕ. The PDF for the Maxwell speed distribution is therefore,

$$\rho_V(v) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T}\right)^{3/2} e^{-\frac{1}{2}\frac{mv^2}{k_B T}} v^2.$$

Using this distribution you should be able to compute the r.m.s. speed of a gas molecule and recover the result you learned in freshman chemistry.

2.1.12. The Microcanonical Ensemble. One of the original motivations for the development of statistical mechanics was to provide a rigorous justification for thermodynamics by taking into account the microscopic origins of the constituents of matter. Statistical mechanics and thermodynamics are essentially macroscopic theories describing the average behavior of all N-body systems with the same macroscopic constraints. Thermodynamics presents an economic but reduced description of a N-body system with a typical size of $N \sim 10^{23}$ particles in terms of a few ($M \sim$ 3-8) “macroscopic” degrees of freedom as control parameters.

In microcanonical statistics, there is no restriction to the number of particles. We may treat, for example, some 100 particles such as a sequence of amino acids in a peptide. We always assume, however, that $6N \gg M$ (the factor ‘6’ indicates six degrees of freedom per particle in 3D space: three position coordinates and three momenta). To determine the M parameters leaves $6N - M$ undetermined variables. The statistical theory should simultaneously describe all N-body systems with the same macroscopic constraints (e.g. thermodynamical parameters).

These systems define an ensemble Ω of points in the N-body phase space. Thermodynamics describes only the average behavior of this whole group of systems, i.e. it is a probabilistic theory. From this point of view, we call thermodynamics "statistical mechanics" or "thermostatistics".

The dynamics of the N-body system are governed by a Hamiltonian H. Let's assume that the system is trapped in a volume V and only the total energy (E) and number of particles (N) are conserved. The macroscopic variables of this ensemble which are held constant in its thermodynamic description are therefore: E, N and V. The triple (E, N, V) describes a *macrostate.*

2.1.12.1. *Phase space.* In the classical mechanics the motion in time of all points of the ensemble follows trajectories in N-body phase space $\{q_i(t), p_i(t)\}$, $i = 1, \dots, N$. The set of trajectories solve the Hamilton-Jacobi equations

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}, \qquad i = 1, \dots, N$$

with some initial conditions $\{q_i(0) = q_{i0}; p_i(0) = p_{i0}\}$.

2.1.12.2. *Microcanonical ensemble.* The total energy (E) is conserved in classical mechanics. Therefore, the trajectories never leave this $(6N-1)$-dimensional shell of constant energy. This manifold – the subset of phase space where total energy remains constant – is called the *microcanonical ensemble.*

The *area* $W(N, V, E)$ of this manifold in the N-body phase space is also denoted by Boltzmann ($k \equiv k_B$):

$$W(N, V, E) = e^{S/k},$$

or, as written on his grave:

$$S = k \log W. \tag{2.8}$$

Boltzmann has shown that $S(N, V, E)$ is the *entropy* of the system. Thus, entropy has a geometric interpretation. The formula $S = k \log W$ enabled Boltzmann to deduce thermodynamics. It is called Boltzmann's principle.

2.1.12.3. *Microstates.* The Boltzmann principle is often taken to be an axiom in the theory of statistical mechanics. Precisely, W is the number of *microstates* of the N-body system at a given energy E in the spatial volume V (setting $k = 1$ for now):

$$W(N, V, E) = \mathrm{Tr}[\delta(E - \mathcal{H}(\mathbf{p}, \mathbf{q}))] = \int_\Gamma \frac{d^{3N}\mathbf{q}\, d^{3N}\mathbf{p}}{N! h^{3N}} \delta(E - \mathcal{H}(\mathbf{p}, \mathbf{q})) = \int_\Gamma \delta(E - \mathcal{H}(\mathbf{x})) d\mathbf{x}.$$

Due to the presence of the δ function in the second equality, $W(E)$ is akin to a measure of the *surface area* of a manifold defined by the constraint $\mathcal{H}(\mathbf{p}, \mathbf{q}) = E$ in the $6N$-dimensional phase space[7]. Here, Γ is the phase space domain

$$\Gamma = \{(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{q}_1, \ldots, \mathbf{q}_N) : \mathbf{q}_i \in V, \mathbf{p}_i \in \mathbb{R}^3, \forall i = 1, \ldots, N\}.$$

In the second equality we have introduced a multiplicative constant $(N!h^{3N})^{-1}$ to make W dimensionless. The constant $N!$ is called the Gibbs factor. It accounts for indistinguishability of classical particles[8]. The factor h^{3N} has to do with getting the correct units when working with the partition function. It comes from the quantum mechanical uncertainty principle $\Delta x \Delta p \geq h$, which leads to the "minimum" phase-space volume $(\Delta x)^{3N}(\Delta p)^{3N} = h^{3N}$. This is needed in order for the phase space volumes to match those obtained in quantum mechanics. It was not used in Eqs. (2.5) and (2.7) because these factors cancel out when computing averages.

The variable $\mathbf{x}$ was implicitly defined in order to absorb the factor $\frac{1}{N!h^{3N}}$. Some authors call W the *characteristic state function* of the microcanonical ensemble. The reader should verify that the units of h are angular momentum. The units of $\mathbf{pq}$ or $d^{3N}\mathbf{q}\, d^{3N}\mathbf{p}$ are also angular momentum, since the latter is defined as $\mathbf{L} = \mathbf{r} \times \mathbf{p}$.

The $3N$ positions $\{q_i\}$ are restricted to the volume V, whereas the $3N$ momenta $\{p_i\}$ are unrestricted. The set of outcomes in the probability space is

$$\Omega = V^N \otimes \mathbb{R}^{3N}.$$

A *microstate* is a point $(\mathbf{p}, \mathbf{q})$ (a $6N$-fimensional vector) in the phase space, or equivalently, a particular outcome $\omega \in \Omega$ in the probability space.

2.1.12.4. *Temperature.* The absolute temperature T in the microcanonical ensemble is defined by

$$\frac{1}{T} = \frac{\partial S(E)}{\partial E}.$$

2.1.12.5. *Example: spins in a magnetic field.* To illustrate these ideas, let us consider the simplest possible example: classical spins in a magnetic field (B). The two possible orientations s_i for each spin are: $\uparrow$ and $\downarrow$. Taking $\hat{z}$ as the axis of quantization, the energy of two noninteracting spins is:

$$E = -\gamma \hbar B(m_{S1} + m_{S2}).$$

A *microstate* is the pair (s_1, s_2) consistent with the energy E. The allowed values of m_{Si} $i = 1, 2$ are $\pm 1/2$. A spin i points along B if $m_S = +1/2$, which corresponds to a state of low energy.

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[7] This analogous to the space $\mathbb{R}^3$, where a constraint is imposed, such as $x^2 + y^2 + z^2 = 1$, defining a surface, except that here the embedding space is $\mathbb{R}^{6N}$.

[8] It is related to the Gibbs paradox. The Gibbs paradox refers to a conceptual issue in classical statistical mechanics concerning the entropy change associated with the mixing of identical particles. According to classical thermodynamics, mixing two different ideal gases leads to an increase in entropy. However, if the gases are identical, classical calculations yield a non-zero entropy change, which contradicts the intuition that identical particles should not contribute to an entropy increase upon mixing. The paradox is resolved by postulating that the gas particles are in fact indistinguishable. This means that all states that differ only by a permutation of particles should be considered as the same state.

The phase space volume is,

$$W(E) = \sum_{\{\mathbf{x}:E=\mathcal{H}(\mathbf{x})\}} 1 \approx \sum_{\{\mathbf{x}:E<\mathcal{H}(\mathbf{x})<E+\delta E\}} 1 \approx \text{ number of microstates with energy } E$$

The possible states are: $(\uparrow\uparrow)$, $(\uparrow\downarrow)$, $(\downarrow\uparrow)$, $(\downarrow\downarrow)$. These correspond to 3 possible energies:

Energy (E)	Allowed microstates	Multiplicity $W(E)$	Entropy ($S = \log W$)
$-\gamma\hbar B$	$\uparrow\uparrow$	1	0
0	$\uparrow\downarrow, \downarrow\uparrow$	2	$\log(2) \approx 0.7$
$\gamma\hbar B$	$\downarrow\downarrow$	1	0

Table 2.1. Two spins in a magnetic field.

2.1.12.6. *Entropy is a measure of uncertainty.* Recall that the macrostate is specified by a triple (N, V, E) but it is possible that more than one *microstates* (e.g. pairs (s_1, s_2) in the previous example) are consistent with a given macrostate. In fact, W gives the number of microstates consistent with a fixed energy E. We say that the entropy ($S = k \log W$) is a measure of the uncertainty about the system.

In the previous example, if we measure the total energy of the system to be -2, then we know for sure that the state of the system must be $(\uparrow\uparrow)$, according to the above table. Likewise, if we measure the energy to be 2, then we know the system is in the state $(\downarrow\downarrow)$. On the other hand, if we know that the energy is 0, then we can't tell for sure whether the "state" is $(\uparrow\downarrow)$ or $(\downarrow\uparrow)$. There is uncertainty about the system and the entropy is therefore higher. Uncertainty is measured by the entropy via Boltzmann's principle $S = k \log W$.

In other words, we know the macroscopic state E, but we do not know with complete certainty which microstate gives rise to the measured value E. We can only guess, or at best, state which microstate the system is in, and assign a probability for it.

In the previous example of spins in a magnetic field, which energy level is characterized by the largest uncertainty and therefore, maximum entropy?

2.1.12.7. *Non-additivity of entropy.* Since entropy is an extensive quantity we know that, in the thermodynamic limit (large volume, large number of particles), for two systems that are brought together and interact minimally, entropy is additive:

$$S_{1+2} = S_1 + S_2.$$

For a small number of particles, as may be the case in the microcanonical ensemble, entropy is not additive:

$$S_{1+2} = S_1 + S_2 + S_{1,2}.$$

where $S_{1,2}$ is a measure of non-additivity. We shall illustrate this by way of a simple example. Consider a system of three spins in a magnetic field. The possible configurations and energies are as follows:

Energy (E)	Allowed microstates	Multiplicity $W(E)$	Entropy ($S = \log W$)
-3	↑↑↑	1	0
-1	↑↑↓, ↓↑↑, ↑↓↑	3	$\log(3) \approx 1.1$
1	↑↓↓, ↓↑↓, ↓↓↑	3	$\log(3) \approx 1.1$
3	↓↓↓	1	0

Table 2.2. Three spins in a magnetic field

Non-additivity: Consider the two systems: two spins (s_1, s_2) combined with a third spin, s_3, to give three spins in total: (s_1, s_2, s_3). The corresponding table for the third spin is:

Energy (E)	Allowed microstates	Multiplicity $W(E)$	Entropy ($S = \log W$)
-1	↑	1	0
1	↓	1	0

Table 2.3. Single spin in a magnetic field

For the energy level $E = -1$, we would have for the total entropy

System 1 microstate	W_1	System 2 microstate	W_2	Combined system W_1W_2
↑↑	1	↓	1	1
↑↓	2	↑	1	2
↓↑	2	↑	1	2

Table 2.4. Combining a two spin system with a third spin to give a total energy $E = -1$ (two spins up, one spin down). From Table 2.2 we know this combined system should have $W = 3$.

In fact, the correct way to combine the entropies is by calculating the number of accessible states via combinatorics:

$$W(E) = \sum_{E_0 \le E_1 \le E} W_1(E_1)W_2(E - E_1) = \sum_{E_0 \le E_2 \le E} W_1(E - E_2)W_2(E_2),$$

where $E = E_1 + E_2$ and E_0 is the lowest energy value in the spectrum of E_1 or E_2 in the above formulae (sums 1 and 2, respectively). In the case where the energy spectrum is continous, we have:

$$W(E) = \int_{E_0}^{E} dE_1\, W_1(E_1)\, W_2(E - E_1).$$

For the combined three-spins system, $E = -1$, and let the summation run over $E_2 = +1, -1$. There are two terms in the sum:

$$W = 2 \cdot 1 + 1 \cdot 1 = 3.$$

The entropy of the combined system according to this summation is log(3), in agreement with the entropy of the combined system found in Table 2.2.

2.1.12.8. *Principle of equal a priori probability.* Because the only thing we know is the total energy E, and that each microstate gives rise to the same energy E, the best we can do is assign equal probability of occurrence to all microstates consistent with E.

Since a measurement of the total energy in the laboratory must occur in a finite time, we can even think of the system evolving over time and hopping between the different microstates. It may do so as long as the total energy remains constant.

For the microstates consistent with a given value of E, hopping would be plausible because it costs zero energy to hop from state to state, i.e. from $\uparrow\downarrow$ to $\downarrow\uparrow$. This is really just an intuitive argument and does not imply that hopping takes place. One would need a certain type of coupling between the two spins to permit this sort of transition. But it helps make the argument for equal probabilities plausible.

In the case of a continuous phase space, the argument is much more complicated and invokes more elaborate theorems which will not be covered here. See Kubo and Toda for more details. We will content ourselves by taking this principle of equal probabilities as an axiom of the theory.

Mathematically, this principle is expressed in terms of a probability distribution that is constant over the region where the energy equals E. If the state space is discrete, we have:

$$P_E(\mathbf{x}_i) = \frac{1}{W(E)},$$

and if the state space is continuous we have the density:

$$p(\mathbf{x}) = \frac{\delta(E - \mathcal{H}(\mathbf{x}))}{W(E)}.$$

2.1.13. Microcanonical density matrix. Density matrices are used to describe the statistical properties of ensembles in quantum mechanics. For example, average values of observables are calculated as follows:

$$\langle A \rangle = \mathrm{Tr}\left[A\rho\right],$$

where A is the quantum mechanical observable and ρ is the density matrix.

Suppose that $|E'\rangle$ is an eigenvector of the Hamiltonian operator $\hat{\mathcal{H}}$ corresponding to the energy E':

$$\hat{\mathcal{H}}\,|E'\rangle = E'\,|E'\rangle\,.$$

The density matrix which represents a microcanonical distribution with energy E is

$$\hat{\rho}_{E,V,N} = \sum_{E<E'<E+\delta E} \frac{|E'\rangle\,\langle E'|}{W_{\delta E}(E)}.$$

where

$$W_{\delta E}(E) = \sum_{\{\mathbf{x}: E < \mathcal{H}(\mathbf{x}) < E+\delta E\}} 1$$

is the microcanonical partition function. As always, it is tacitly understood that one eventually takes the limit $\delta E \to 0$.

In the example of a spin in a magnetic field, we have, for $|\uparrow\rangle = (1\ 0)$ and $|\downarrow\rangle = (0\ 1)$,

$$\rho_{E=-1} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \qquad \rho_{E=+1} = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}.$$

2.1.13.1. *Microcanonical average: discrete state space.* Given the probability distribution we may calculate the average value of an observable. For the example of a spin in a magnetic field, let us calculate the average magnetization when $E = -\gamma\hbar\beta B/2$. This implies only one possibility $m_{S1} = 1/2$. The principle of equal probability states that the probability of the microstate $m_{S1} = 1/2$ equals 1. Then

$$\langle m_{S1} \rangle = (1/2) \cdot 1 = 1/2.$$

In the case of two spins, let us calculate the average of the total magnetization $m_{S1} + m_{S2}$ for the case $E = 0$. There are two possible microstates: ↑↓ and ↓↑, each with probability 1/2. Then,

$$\langle m_{S1} + m_{S2} \rangle = 0 \cdot \frac{1}{2} + 0 \cdot \frac{1}{2} = 0.$$

For the energy $E = -\gamma\hbar\beta B$, we have the sole microstate ↑↑ and the average total magnetization $\langle m_{S1} + m_{S2} \rangle$ evaluates to $\frac{1}{2} + \frac{1}{2} = 1$.

2.1.13.2. *Microcanonical average: continuous state space.* We calculate the properties of our ensemble by averaging over states with energies in a shell $[E, E + \delta E]$ in the limit $\delta E \to 0$. Another way of writing W is

$$W(E) = \frac{1}{\delta E} \int\limits_{\{\mathbf{x}: E < \mathcal{H}(\mathbf{x}) < E+\delta E\}} d\mathbf{x} = \frac{1}{\delta E} \int_{\mathbb{R}^{6N}} I_{\{\mathbf{x}: E < \mathcal{H}(\mathbf{x}) < E+\delta E\}}(\mathbf{x}) d\mathbf{x}.$$

This can be rewritten in terms of the derivative with respect to energy of the phase-space volume (rather than the shell). We first note that the indicator function

$$I_{\{\mathbf{x}: E < \mathcal{H}(\mathbf{x}) < E+\delta E\}}(\mathbf{x})$$

equals 1 inside the energy shell and zero everywhere else. It can be written as the difference of two indicator functions:

$$I_{\{\mathbf{x}: \mathcal{H}(\mathbf{x}) < E+\delta E\}}(\mathbf{x}) - I_{\{\mathbf{x}: \mathcal{H}(\mathbf{x}) < E\}}(\mathbf{x}).$$

We also note that the following ratio converges to the limit:

$$\lim_{\delta E \to 0} \frac{I_{\{\mathbf{x}: \mathcal{H}(\mathbf{x}) < E+\delta E\}}(\mathbf{x}) - I_{\{\mathbf{x}: \mathcal{H}(\mathbf{x}) < E\}}(\mathbf{x})}{\delta E} = \frac{\partial}{\partial E} I_{\{\mathbf{x}: \mathcal{H}(\mathbf{x}) < E\}}(\mathbf{x}).$$

Therefore, we have:

$$W(E) = \frac{\partial}{\partial E}\int_{\mathbb{R}^{6N}} I_{\{\mathbf{x}:\mathcal{H}(\mathbf{x})<E\}}(\mathbf{x})\,d\mathbf{x} = \frac{\partial}{\partial E}\underbrace{\int\limits_{\{\mathbf{x}:\mathcal{H}(\mathbf{x})<E\}} d\mathbf{x}}_{\mathcal{V}(E)}.$$

Using this formalism, the expectation value of an observable φ:

$$\langle\varphi\rangle_E = \frac{1}{W(E)\cdot\delta E}\int\limits_{\{\mathbf{x}:E<\mathcal{H}(\mathbf{x})<E+\delta E\}} \varphi(\mathbf{x})\,d\mathbf{x}$$

can be expressed as:

$$\langle\varphi\rangle_E = \frac{1}{W(E)}\frac{\partial}{\partial E}\int_{\mathbb{R}^{6N}} \varphi(\mathbf{x})I_{\{\mathbf{x}:\mathcal{H}(\mathbf{x})<E\}}(\mathbf{x})\,d\mathbf{x} = \frac{1}{W(E)}\frac{\partial}{\partial E}\int\limits_{\{\mathbf{x}:\mathcal{H}(\mathbf{x})<E\}} \varphi(\mathbf{x})\,d\mathbf{x}.$$

And because the derivative of the step function $I_{\{\mathbf{x}:\mathcal{H}(\mathbf{x})<E\}}(\mathbf{x})$ with respect to E is a Dirac delta function:

$$\frac{\partial}{\partial E}I_{\{\mathbf{x}:\mathcal{H}(\mathbf{x})<E\}}(\mathbf{x}) = \delta(E-\mathcal{H}(\mathbf{x})),$$

we may rewrite this average as:

$$\langle\varphi\rangle_E = \frac{1}{W(E)}\int_{\mathbb{R}^{6N}} \varphi(\mathbf{x})\delta(E-\mathcal{H}(\mathbf{x}))\,d\mathbf{x},$$

where

$$p(\mathbf{x}) = \frac{\delta(E-\mathcal{H}(\mathbf{x}))}{W(E)}$$

is the probability density of the microcanonical ensemble.

2.1.13.3. *Transition to the canonical ensemble: the thermodynamic limit.* We may now proceed toward the thermodynamic limit. Instead of fixed (N,V,E) let us look at the case of fixed temperature (N,V,T). This is the canonical ensemble. Let us separate the phase space into the components of two systems, 1 and 2, and compute the following average

$$\langle\varphi\rangle = \frac{1}{W(E)\cdot\delta E}\int\limits_{\{(\mathbf{x}_1,\mathbf{x}_2):E<\mathcal{H}_1(\mathbf{x}_1)+\mathcal{H}_2(\mathbf{x}_2)<E+\delta E\}} \varphi(\mathbf{x_1})d\mathbf{x}_1 d\mathbf{x}_2$$

The heat bath has temperature T_2 and is not affected by small changes in the energy of system 1 (if the heat bath is large, the small variations $E_1-\langle E_1\rangle$ will not change its temperature). Therefore the temperature is fixed:

$$\frac{1}{T_2} = \frac{\partial S_2(E_2)}{\partial E_2}.$$

Using the definition $S_2(E_2) = k_B\log W_2(E_2)$, we get:

$$\frac{1}{T_2} = \frac{\partial}{\partial E_2}k_B\log W_2(E_2) = k_B\frac{1}{W_2(E_2)}\frac{\partial W_2(E_2)}{\partial E_2},$$

or equivalently,

$$-\frac{W_2(E-E_1)}{k_BT_2} = \frac{\partial W_2(E-E_1)}{\partial E_1}.$$

This is a first-order differential equation. Integrating with respect to dE_1 from $\langle E_1\rangle$ to E_1 gives the solution:

$$W_2(E-E_1) = W_2(E-\langle E_1\rangle)e^{-(E_1-\langle E_1\rangle)/k_BT_2}.$$

This gives:

$$\begin{aligned}
W(E) = \int\limits_{E_0}^{E_{max}} dE_1\ W_1(E_1)\underbrace{W_2(E-E_1)} &= \int\limits_{E_0}^{E_{max}} dE_1\ W_1(E_1)\underbrace{W_2(E-\langle E_1\rangle)e^{-(E_1-\langle E_1\rangle)/k_BT_2}} \\
&= W_2(E-\langle E_1\rangle)e^{\langle E_1\rangle/k_BT_2}\underbrace{\int\limits_{E_0}^{E_{max}} dE_1\ W_1(E_1)e^{-E_1/k_BT_2}}_{Z}. \\
&= W_2(E-\langle E_1\rangle)e^{\langle E_1\rangle/k_BT_2}Z.
\end{aligned}$$

Substitution of $W(E)$ and $W_2(E-E_1)$ with $E_1 = \mathcal{H}_1(\mathbf{x}_1)$ into the expression for $\langle\varphi\rangle$ gives:

$$\begin{aligned}
\langle\varphi\rangle =& \frac{1}{\underbrace{W(E)}}\int_{\Gamma_1}\varphi(\mathbf{x_1})d\mathbf{x}_1\underbrace{W_2(E-\mathcal{H}_1(\mathbf{x}_1))} \\
=& \frac{1}{W_2(E-\langle E_1\rangle)e^{\langle E_1\rangle/k_BT}Z}\int_{\Gamma_1}\varphi(\mathbf{x_1})d\mathbf{x}_1\cdot W_2(E-\langle E_1\rangle)e^{-(\mathcal{H}_1(\mathbf{x}_1)-\langle E_1\rangle)/k_BT} \\
=& \frac{1}{Z}\int_{\Gamma_1}\varphi(\mathbf{x}_1)\cdot e^{-\mathcal{H}_1(\mathbf{x}_1)/k_BT}d\mathbf{x}_1
\end{aligned}$$

where Γ_1 is the volume of phase space for subsystem 1, i.e.

$$\Gamma_1 = \{(\mathbf{p}_1,\ldots,\mathbf{p}_{N_1},\mathbf{q}_1,\ldots,\mathbf{q}_{N_1}) : \mathbf{q}_i \in V, \mathbf{p}_i \in \mathbb{R}^3, \forall i = 1,\ldots,N_1\}.$$

Thus, integrating over the bath coordinates $d\mathbf{x}_2$ has turned the microcanonical distribution into a canonical ensemble. This process is called ”integrating out” or ”tracing out” over the bath degrees of freedom.

2.1.13.4. *Microcanonical ensemble: classical ideal gas.* Consider a gas of N particles confined to a volume V. The Hamiltonian is:

$$\mathcal{H} = \sum_{i=1}^{3N}\frac{p_i^2}{2m} = \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m},$$

where $\mathbf{p}_i = (p_{xi}, p_{yi}, p_{zi})$ is the momentum vector of particle i. Then

$$\mathcal{V}(E,V,N) = \int\limits_{\{(\mathbf{p},\mathbf{q}):\mathcal{H}(\mathbf{p},\mathbf{q})<E\}} \frac{\prod_{i=1}^{3N} dp_i dq_i}{N!h^{3N}} = \frac{V^N}{N!h^{3N}} \int\limits_{\{\mathbf{p}:\sum_{i=1}^{N}\mathbf{p}_i^2<2mE\}} d^{3N}\mathbf{p},$$

where the factor V^N is the result of integrating over space ($d^{3N}\mathbf{q}$). The momentum integral is precisely the volume of a $3N$-dimensional sphere with radius $R = \sqrt{2mE}$. We therefore have:

$$\mathcal{V}(E,V,N) = \frac{V^N(2\pi mE)^{3N/2}}{N!h^{3N}(3N/2)\Gamma(3N/2)}.$$

From this, we may compute the entropy:

$$S = k_B \log \frac{\partial}{\partial E}\mathcal{V}(E,V,N) = k_B \left\{ N \log\left[V(2\pi mE)^{3/2}\right] - \log\left[\Gamma(3N/2)\right] - \log E - \log(N!h^{3N}) \right\}.$$

The equation of state for the ideal gas is obtained with the help of the first law[9] of thermodynamics [$dU = TdS - pdV$ or $dS = (1/T)(dU + PdV)$],

$$P = T\left(\frac{\partial S}{\partial V}\right)_E = T\frac{Nk_B}{V}.$$

which gives the familiar result $PV = Nk_BT$.

We can also solve for the temperature as a function of E, V and N:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = \frac{3Nk_B}{2E}.$$

This gives the usual relation $E = (3/2)Nk_BT$ for the energy of a monoatomic classical ideal gas.

2.1.14. Supplemental Readings. For a more in-depth coverage of stochastic processes in physics and chemistry, you are referred to:

- A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics*, Dover (1960)
- M. Toda, R. Kubo, N. Saito, *Statistical physics I*, 2nd edition, Springer (1998)

2.1.15. Canonical ensemble. The canonical ensemble is one in which the macrostate is specified by the parameters (N, V, T). The probability density for such a system is given

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[9] Recall from multivariable calculus the definition of total differential of a function of two variables:

$$df(x,y) = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy$$

where dx and dy are arbitrary "infinitesimals". In the present case,

$$dS(U,V) = \frac{\partial S}{\partial U}dU + \frac{\partial S}{\partial V}dV.$$

Since dU and dV are arbitrary, we can match their coefficients. Thus, together with the first law, $dS = (1/T)(dT + PdV)$, we obtain $(1/T) = \frac{\partial S}{\partial U}$ from matching the coefficients of dU, and $P/T = \frac{\partial S}{\partial V}$ by matching the coefficients of dV.

by the Gibbs measure:

$$p(\mathbf{x}_1) = \frac{1}{Z} e^{-\mathcal{H}_1(\mathbf{x}_1)/k_B T},$$

where $\mathcal{H}_1(\mathbf{x}_1)$ is the Hamiltonian of the subsystem held at fixed temperature, i.e. in contact with a bath of temperature T, and

$$Z(N, V, T) = \int_{E_0}^{E_{max}} dE_1 W_1(E_1) e^{-E_1/k_B T},$$

is the canonical partition function written as a "sum" over energies. We now drop the subscript "1" from the notation. For discrete energy levels, the partition function is:

$$Z = \sum_{E_i} W(E_i) e^{-E_i/k_B T},$$

where the summation runs over all discrete energy levels E_i, each counted only once. And because $W(E_i)$ is the number of states with energy E_i, we may write this as a sum over states

$$Z = \sum_i e^{-E_i/k_B T},$$

where the summation now runs over all states, meaning that if several microstates correspond to energy E_i, there is one term for each of these microstates.

As an example, consider a spin in a magnetic field. The Hamitonian is $\mathcal{H} = -\gamma\hbar\vec{B} \cdot \vec{S}$, where $\vec{B} = B\hat{z}$, $S_z |Sm_S\rangle = m_S |Sm_S\rangle$, $m_S = \pm 1/2$. The partition function is:

$$Z = e^{-\gamma\hbar B/2k_B T} + e^{\gamma\hbar B/2k_B T} = 2\cosh(\gamma\hbar B/2k_B T).$$

For the case of two spins in a magnetic field, $\mathcal{H} = -\gamma\hbar\vec{B} \cdot (\vec{S}_1 + \vec{S}_2) = -\gamma\hbar B(m_{S1} + m_{S2})$, the sum over energies is:

$$Z = \sum_{E_i} W(E_i) e^{-E_i/k_B T} = e^{-\gamma\hbar B/k_B T} + 2\underbrace{e^0}_{1} + e^{\gamma\hbar B/k_B T} = 2[1 + \cosh(\gamma\hbar B/k_B T)],$$

and the sum over states gives the same result

$$Z = \sum_i e^{-E_i/k_B T} = e^{-\gamma\hbar B/k_B T} + 1 + 1 + e^{\gamma\hbar B/k_B T} = 2[1 + \cosh(\gamma\hbar B/k_B T)].$$

2.1.15.1. *Canonical density matrix.* The density matrix which represents a canonical ensemble at temperature $\beta = 1/k_B T$ is

$$\hat{\rho}_{T,V,N} = \frac{e^{-\beta\hat{\mathcal{H}}}}{\text{Tr}\left[e^{-\beta\hat{\mathcal{H}}}\right]} = \frac{1}{Z} \sum_{E'} e^{-\beta E'} |E'\rangle \langle E'|,$$

where $Z = \text{Tr}\left[e^{-\beta\hat{\mathcal{H}}}\right] \equiv \sum_{E'} e^{-\beta E'}$ (summation is over all microstates of a given energy – not a sum over energies) is the canonical partition function.

Consider a two-level spin in a magnetic field B. The Hamiltonian, expressed in units of the magnetic field, $\hat{\mathcal{H}} = -\gamma\vec{B} \cdot \vec{S}$, so that the energy eigenvalues are $E = -\gamma B m_S$. The spin operator S_z is proportional to the Pauli matrix:

$$S_z = \frac{1}{2}\hat{\sigma}_z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}$$

The density matrix is therefore:

$$\hat{\rho} = \frac{e^{-\gamma\hbar\beta\hat{H}}}{\mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}}]} = \frac{1}{e^{\gamma\hbar\beta B/2} + e^{-\gamma\hbar\beta B/2}} \begin{pmatrix} e^{\gamma\hbar\beta B/2} & 0 \\ 0 & e^{-\gamma\hbar\beta B/2} \end{pmatrix}.$$

The statistical average of S_z is

$$\langle S_z \rangle = \mathrm{Tr}[\hat{\rho} S_z] = \frac{1}{2}\frac{e^{\gamma\hbar\beta B/2} - e^{-\gamma\hbar\beta B/2}}{e^{\gamma\hbar\beta B/2} + e^{-\gamma\hbar\beta B/2}} = \frac{1}{2}\tanh[\gamma\hbar\beta B/2].$$

With the identification

$$M = N\langle \mu_z \rangle,$$

where M is the magnetization, N is the number density of magnetic moments and $\langle \mu_z \rangle = I_z$ is the average moment. We have just derived the *Langevin paramagnetic equation.* In the approximation $\tanh x \approx x$ (high temperatures), this gives the *Curie law.*

This is the canonical ensemble average of the magnetic polarization due to an applied field. We note that the canonical statistical average here means the average in a state of thermal equilibrium. Even though we have used the Zeeman interaction of a single spin $\vec{S}$ to derive this result, the statistical average is over an entire ensemble.

Entropy in quantum mechanics is often defined in terms of density matrices $\hat{\rho}$:

$$S = -k_B \mathrm{Tr}[\hat{\rho}\log\hat{\rho}].$$

This formula is identical to the Gibbs-Shannon entropy (below). In the present example, the entropy evaluates to:

$$S = 2e^{\beta\epsilon}\cosh(\beta\epsilon)\left[\log(1 + e^{-2\beta\epsilon}) + e^{2\beta\epsilon}\log(1 + e^{2\beta\epsilon})\right],$$

where $\epsilon = \gamma\hbar B/2$. With these formulas, many more thermodynamic relations can be derived.

2.1.15.2. *Gibbs-Shannon Entropy.* The Gibbs-Shannon entropy in statistical mechanics is defined, for a probability distribution $\{p_i\}$ as:

$$S = -k_B \sum_i p_i \log p_i.$$

If we maximize S over all possible p_i subject to the constraint $\sum_i p_i = 1$ (see homework problem), we find that $p_i = const.$ In the microcanonical ensemble, this probability must be related to the phase-space volume according to

$$p_i = \frac{1}{N} = \frac{1}{W(E)}.$$

This leads to the result that

$$S = -k_B \sum_i p_i \log p_i = -k_B N \cdot \frac{1}{N} \log 1/N = k_B \log W(E).$$

We see that the Boltzmann entropy is the special case where the Gibbs entropy is maximized with respect to the probability distribution $\{p_i\}$.

2.1.16. Thermodynamic Limit. Before we delve too deeply in our discussions of thermodynamic ensembles, it is important to define what is meant by the "thermodynamic limit". So far, we have worked with the microcanonical ensemble, which does not require a thermodynamic limit. However, other ensembles do. The thermodynamic limit is defined as:

$$N \to \infty, \quad V \to \infty \quad \text{with} \quad \frac{N}{V} = \text{constant}.$$

In other words, we increase the size of our system so that it becomes macroscopic while enforcing the constraint that the density $\frac{N}{V}$ remains constant.

2.1.17. Entropy becomes additive in the thermodynamic limit. The second law of thermodynamics states that the entropy of an isolated system never decreases. We can derive this principle using the definition of entropy in the microcanonical ensemble. Consider a composite of two systems in contact with each other. The total energy

$$E = E_1 + E_2$$

is fixed, but E_1 and E_2 can fluctuate. The energy spectrum is divided into steps of level spacing Δ. This situation is illustrated in Figure 2.1.

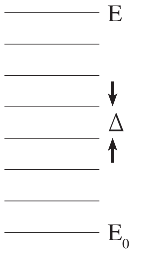

Figure 2.1. Energy levels start at E_0 and end at E with energy gap Δ.

The total number of accessible states is given by

$$W(E) = \sum_{E_0 < E_1 < E} W_1(E_1) W_2(E - E_1)$$

where the sum extends over the possible values of E_1 in steps of Δ. The total entropy is given by

$$S(E) = k_B \log \sum_{E_0<E_1<E} W_1(E_1)W_2(E - E_1) \tag{2.9}$$

For a macroscopic system, we will show that E_1 hovers near one value only, the value that maximizes the entropy.

Among the E/Δ terms in the sum, let the maximal term be denoted $E_1 = \tilde{E}_1$. Since all terms are positive, the value of the sum lies between the largest term and E/Δ times the largest term:

$$k_B \log \left[W_1(\tilde{E}_1)W_2(E - \tilde{E}_1)\right] < S(E) < k_B \log \left[W_1(\tilde{E}_1)W_2(E - \tilde{E}_1)\right] + k_B \log(E/\Delta)$$

In a macroscopic system of N particles, we expect S and E both to be of order N. Therefore, the last term on the right hand side is $\mathcal{O}(\log N)$ and may be neglected as $N \to \infty$. Thus

$$S(E) = k_B \log W_1(\tilde{E}_1) + k_B \log W_2(E - \tilde{E}_1) + \mathcal{O}(\log N)$$

Neglecting the last term, we have

$$S(E) = S_1(\tilde{E}_1) + S_2(\tilde{E}_2) \tag{2.10}$$

The principle of maximum entropy emerges when we compare (2.9) and (2.10). The former shows that the division of energy among subsystems have a range of possibilities. The latter indicates that, neglecting fluctuations, the energy is divided such as to maximize the entropy of the system.

A corollary to the principle of maximum entropy is that the temperatures of the two subsystems are equal $T_1 = T_2$. This is left as an exercise. *Hint:* differentiate Eq. 2.10 with respect to $\tilde{E}_1$ and apply the definition of temperature $T^{-1} = \frac{\partial S(E)}{\partial E}$ together with the chain rule $\frac{\partial}{\partial \tilde{E}_1} = \frac{\partial \tilde{E}_2}{\partial \tilde{E}_1}\frac{\partial}{\partial \tilde{E}_2} = -\frac{\partial}{\partial \tilde{E}_2}$ (applied to the second term) since $E = \tilde{E}_1 + \tilde{E}_2$.

2.1.17.1. *Connection with thermodynamics.* In the microcanonical ensemble, the connection with thermodynamics is made by defining the entropy of the closed system by:

$$S(E, V, N) = k_B \log W(E, V, N).$$

In the canonical ensemble, the connection with thermodynamics is established through the Helmholtz free energy

$$F(T, V, N) = -k_B T \log Z(T, V, N).$$

2.1.17.2. *Products of partition functions.* When two systems with free energies A_1 and A_2 are brought together, their total energy is the sum of energies plus an interaction term

$$F = F_1 + F_2 + F_{12}.$$

In the “dilute” limit, the interaction term is negligible $F_{12} \to 0$. According to the thermodynamic connection, the partition function of the combined system a product of partition functions for each individual system:

$$Z(\beta) = e^{-\beta F} = e^{-\beta(F_1+F_2)} = e^{-\beta F_1}e^{-\beta F_2} = Z_1(\beta) \cdot Z_2(\beta).$$

This idea is general and applies to any degree of freedom which are statistically independent. For example, molecules in a gas have energies that depend on rotational, vibrational, electronic and nuclear wave functions. The total energy is the sum of all these contributions:

$$F = F_{rot} + F_{vib} + F_{el} + F_{nuc}.$$

The partition function is a product of all these contributions:

$$Z = Z_{rot} \cdot Z_{vib} \cdot Z_{el} \cdot Z_{nuc}.$$

This implies that the entropies are additive, in the thermodynamic limit:

$$S = S_{rot} + S_{vib} + S_{el} + S_{nuc}.$$

2.1.18. Thermodynamic Ensembles (macroscopic) vs Partition Functions (microscopic). The transformation between ensembles can be opaque at first. The partition functions are obtained from one another via Laplace transformation, whereas the thermodynamics potentials are obtained from one another via Legendre transformation. In this section, we will explore how the Laplace transform gives rise to the Legendre transform in the thermodynamic limit. In a sense, we will learn that the Legendre transformation is a special case of the Laplace transform (in the thermodynamic limit).

2.1.18.1. *Saddle Point Approximation.* Suppose we have an integral of the form

$$I(\lambda) = \int_0^\infty dx\, \rho(x) e^{-A(x)/\lambda}.$$

Such integrals can be approximated using the saddle point method, which is based on the observation that at the saddle point x_0 the largest contribution comes from the integrand evaluated at x_0. All other points contribute far less to the integral.

Consider the Taylor expansions:

$$A(x) = A(x_0) + (x - x_0)A'(x_0) + \frac{1}{2}(x - x_0)^2 A''(x_0) + O(|x - x_0|^3)$$
$$\rho(x) = \rho(x_0) + (x - x_0)\rho(x_0) + \ldots$$

It can be shown that since $(x - x_0)$ is small, $\rho(x) \approx \rho(x_0)$ is a good approximation. At an extremum, $A'(x_0)$ and we are left with $A(x) = A(x_0) + \frac{1}{2}(x - x_0)^2 A''(x_0)$. The extremum is of course, obtained by finding $x = x_0$ such that $A'(x) = 0$. Inserting this into the integral $I(\lambda)$ gives:

$$I(\lambda) = \rho(x_0)e^{-A(x_0)/\lambda} \int dx e^{-\frac{1}{2}(x-x_0)^2 A''(x_0)/\lambda} = \rho(x_0)e^{-A(x_0)/\lambda}\sqrt{\frac{2\pi\lambda}{A''(x_0)}},$$

where in the last step we have extended the lower limit to $-\infty$ and made use of $\int e^{-ay^2} dy = \sqrt{\pi/a}$. Extension of the integration limits is permitted because the added contribution is negligible (i.e., $e^{-\frac{1}{2}(x-x_0)^2 A''(x)/\lambda}$ is small when $|x-x_0|$ is large). The usefulness of this approximation lies in our ability to avoid integrating and instead replace the integral by the largest value of its integrand (value at the saddle point). When taking logs of such expressions involving the saddle-point approximation the term $\sqrt{\frac{2\pi\lambda}{A''(x_0)}}$ becomes unimportant in the thermodynamic limit because it does not scale as N.

2.1.18.2. *Laplace Transform Relationship Among Partition Functions.* In thermodynamics we have the familiar expression "defining" Helmholtz free energy F from the internal energy E

$$F(S,V,T) = E(S,V,N) - TS(N,V,E),$$

which has the structure of a Legendre transform with conjugate variables T and S. Some authors[10] also express it as a Legendre transform from S to F with conjugate variables T and S. In terms of the dimensionless quantities $\mathcal{S} \equiv S/k_B$ and $\mathcal{F} \equiv \beta F$,

$$\mathcal{F}(\beta) = \beta E - \mathcal{S}(E)$$

where the conjugate variables are now β and E. The Laplace transform of

$$W(N,V,E) = \int_\Gamma \delta(E - \mathcal{H}(\mathbf{x}))\, d\mathbf{x}$$

is

$$\int_{E_0}^{E_{max}} W(E) e^{-\beta E} dE = \int_{E_0}^{E_{max}} dE \int_\Gamma d\mathbf{x}\, \delta(E - \mathcal{H}(\mathbf{x})) e^{-\beta E} = \int_\Gamma d\mathbf{x}\, e^{-\beta \mathcal{H}(\mathbf{x})},$$

which we recognize to be the canonical partition function $Z(\beta)$. Here, Γ is the phase space domain

$$\Gamma = \{(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{q}_1, \ldots, \mathbf{q}_N) : \mathbf{q}_i \in V, \mathbf{p}_i \in \mathbb{R}^3, \forall i = 1, \ldots, N\}.$$

The latter is therefore seen to be the Laplace transform of the microcanonical partition function $W(E)$.

2.1.18.3. *Statistical Mechanics lead to Thermodynamics.* The result from the previous section can be expressed as

$$Z(\beta) = \int_{E_0}^{E_{max}} W(E) e^{-\beta E} dE.$$

Using the Laplace inversion formula, this can be inverted to give:

$$W(E) = \int_\mathcal{C} Z(\beta) e^{\beta E} d\beta.$$

where $\mathcal{C}$ is the Bromwich contour in the complex plane (vertical line with real part $\Re[\mathcal{C}] > 0$). Invoking the Boltzmann definition of entropy, $\mathcal{S}(E) = \log W(E)$, as well as the statistical thermodynamical definition of Helmholtz free energy, $\mathcal{F}(\beta) = -\log Z(\beta)$, this becomes:

$$e^{\mathcal{S}(E)} = \int_\mathcal{C} e^{-\mathcal{F}(\beta) + \beta E} d\beta.$$

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[10] Zia, Redish, McKay, Making sense of the Legendre transform, arXiv:0806.1147v2 [physics.ed-ph]

Let us now solve this integral by the saddle point method. We find the saddle point $\tilde{\beta}$ by taking the derivative of the argument of the exponential and setting it to zero:

$$\frac{\partial}{\partial\beta}(-\mathcal{F}(\beta)+\beta E) = E - \frac{\partial\mathcal{F}(\beta)}{\partial\beta} = 0 \qquad \Rightarrow \qquad E = \frac{\partial\mathcal{F}(\beta)}{\partial\beta},$$

which we begin to recognize as the definition of conjugate variables in a Legendre transform. The integral is then approximated by its integrand at the saddle point

$$\int_{\mathcal{C}} e^{-\mathcal{F}(\beta)+\beta E} d\beta \approx e^{-\mathcal{F}(\tilde{\beta})+\tilde{\beta}E}\sqrt{2\pi/A''(\tilde{\beta})},$$

where $A''(\tilde{\beta}) = \frac{\partial^2}{\partial\beta^2}(\mathcal{F}(\beta)-\beta E)\Big|_{\beta=\tilde{\beta}} = \frac{\partial^2\mathcal{F}(\beta)}{\partial\beta^2}\Big|_{\beta=\tilde{\beta}}$. Taking the logs of both sides leads to

$$\mathcal{S}(E) = -\mathcal{F}(\tilde{\beta}) + \tilde{\beta}E + \frac{1}{2}\log(2\pi) - \frac{1}{2}\log A''(\tilde{\beta})$$

Taking the thermodynamic limit ($N \to \infty$), the last two terms become negligible, since they are $O(1)$ and $O(\log N)$, respectively, whereas $\mathcal{S}$, $\mathcal{F}$ and E are all $O(N)$. This leaves us with

$$\boxed{\mathcal{F}(\tilde{\beta}) = \tilde{\beta}E - \mathcal{S}(E) \quad \text{(in the thermodynamic limit)}}$$

where $\tilde{\beta}$ is the (inverse) temperature that minimizes the free energy. The free energy is minimized when choosing $\beta = \tilde{\beta}$ because the saddle-point method requires $A'' > 0$, whereas $A''(\tilde{\beta}) = \frac{\partial^2\mathcal{F}(\beta)}{\partial\beta^2}\Big|_{\beta=\tilde{\beta}} > 0$ (i.e., $\mathcal{F}(\beta)$ is concave up, reaching a minimum at $\beta = \tilde{\beta}$). Inspection of the result $\mathcal{F}(\tilde{\beta}) + \mathcal{S}(E) = \tilde{\beta}E$ suggests that, in the thermodynamic limit, a minimum in the free energy ($\beta = \tilde{\beta}$) corresponds to a maximum in the entropy. According to Section 9.12.6, Appendix), the Legendre transform (see Section 9.15) preserves the convexity of functions (see Eq. 9.12). We can express this Legendre transform pair as

$$\mathcal{S}(E) = \max_{\beta}\{\beta E - \mathcal{F}(\beta)\} = \tilde{\beta}E - \mathcal{F}(\tilde{\beta}),$$

where $\tilde{\beta}$ is the particular value of β that maximizes $\beta E - \mathcal{F}(\beta)$.

Thus, according to Eq. 9.12), if the mapping $\mathcal{F}(\beta) : X \to \mathbb{R}$ on a convex set[11] $X \in \mathbb{R}^n$ is convex, then $\mathcal{S}(E)$ is the convex conjugate of $\mathcal{F}(\beta)$. Conversely,

$$\mathcal{F}(\beta) = \max_{E}\{\beta E - \mathcal{S}(E)\} = \tilde{\beta}\tilde{E} - \mathcal{S}(\tilde{E}),$$

where $\tilde{E}$ is the particular value of E that maximizes $\beta E - \mathcal{S}(E)$. It is obtained by solving $\beta = \partial_E\mathcal{S}(E)$ for E in terms of β. We have therefore proven that the relationship between thermodynamic potentials (as related by Legendre transform) is a consequence of the Laplace transform relationship between partition functions. We may (loosely) say that the Legendre transform is a special case[12] of the Laplace transform.

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[11] Here, $X \in \mathbb{R}^+$, since β is the inverse temperature.

[12] The special case is that of the thermodynamic limit.

2.1.19. The Grand Canonical Ensemble. The grand canonical ensemble describes an *open* system, whose volume is fixed, in equilibrium with a reservoir with which it can exchange both energy and particles. A macroscopic state is characterized by its volume V, temperature T and chemical potential μ. A microstate is specified by $(N, \mathbf{p}, \mathbf{q})$ and its density (PDF) is

$$\rho(\mathbf{p}, \mathbf{q}, N) = \frac{1}{\mathcal{Z}} e^{\beta\mu N - \beta\mathcal{H}(\mathbf{p},\mathbf{q})}.$$

where $\mathcal{Z} \equiv \mathcal{Z}(T, V, \mu)$ is called the *grand canonical partition function*

$$\mathcal{Z}(T, V, \mu) = \sum_N \int_\Gamma \frac{d^{3N}\mathbf{p}\, d^{3N}\mathbf{q}}{N! h^{3N}} e^{\beta\mu N - \beta\mathcal{H}(\mathbf{p},\mathbf{q})} = \sum_N e^{\beta\mu N} Z(T, V, N),$$

where $Z(T, V, N)$ is the canonical partition function discussed previously. The quantity $e^{\beta\mu}$ is called the *fugacity*.

The statistical mechanical connection with thermodynamics is established by defining the Landau (grand) potential:

$$\Omega(T, V, \mu) \equiv k_B T \log \mathcal{Z}(T, V, \mu). \tag{2.11}$$

The Landau (grand) potential in classical thermodynamics is defined by the Legendre transform of the Helmholtz free energy:

$$\Omega = -F + \mu N. \tag{2.12}$$

A proof of Eq. (2.12) can be found in Section 2.1.22 (see Eq. 2.14).

2.1.19.1. *Grand Canonical Density Matrix.* The density matrix which corresponds to a grand canonical ensemble has the form:

$$\hat{\rho}_{\mu,T,V} = \frac{e^{-\beta(\hat{\mathcal{H}} - \mu\hat{N})}}{\mathrm{Tr}\left[e^{-\beta(\hat{\mathcal{H}} - \mu\hat{N})}\right]},$$

where $\hat{N}$ is the quantum operator corresponding to the particle number. This density matrix acts on a generalized Hilbert space called the *Fock space*, which is the direct sum of Hilbert spaces with fixed particle numbers:

$$F(H) = H(1) \oplus H(2) \oplus \cdots \oplus H(\infty),$$

where $H(n)$ is the symmetrized tensor product of single-particle Hilbert spaces, i.e. $H(n) = S \cdot \bigotimes_{i=1}^n H_1$ (S is a symmetrization operator describing particles obeying bosonic or fermionic statistics).

2.1.20. Isobaric Ensemble. Another ensemble which is useful for a system of exactly N particles whose pressure is held fixed while its volume is allowed to fluctuate, is the isobaric ensemble. Its partition function corresponding to the density

$$\rho(\mathbf{p}, \mathbf{q}, V) = \frac{1}{\Theta} e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q}) - \beta PV},$$

with $\Theta \equiv \Theta(T, P, N)$ is the Laplace transform of Z:

$$\Theta(T, P, N) = \int dV \int_\Gamma \frac{d^{3N}\mathbf{p}\, d^{3N}\mathbf{q}}{N! h^{3N}} e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q}) - \beta PV} = \int dV e^{-\beta PV} Z(T, V, N),$$

and the connection with thermodynamics is through the Gibbs free energy

$$G(T, P, N) \equiv -k_B T \log \Theta(T, P, N).$$

2.1.21. Relations Between Partition Functions. If we rewrite the above partition functions as integrals (integrals can always be reduced to summations as a special case of a discrete measure), an interesting relationship is found. Starting from the entropy in the microcanonical ensemble, the partition function is:

$$W(E, V, N) = e^{(1/k_B)S(E,V,N)} \qquad \text{microcanonical}$$

while the remaining partition functions are:

$$\begin{aligned} Z(T, V, N) &= \int dE\, W(E, V, N) e^{-\beta E} && \text{canonical} \\ \mathcal{Z}(T, V, \mu) &= \sum_N Z(T, V, N) e^{\beta\mu N} && \text{grand canonical} \\ \Theta(T, P, N) &= \int dV\, Z(T, V, N) e^{-\beta PV} && \text{isobaric} \end{aligned}$$

We see that they can all be obtained from each other by Laplace transformation. This is not unrelated to the Legendre transformations that define the thermodynamic potentials:

$U(S, V, N)$	Internal energy	
$S(E, V, N)$	Entropy	
$F(T, V, N) = U - TS$	Helmholtz free energy	canonical
$G(T, P, N) = F + PV$	Gibbs potential	isobaric, isothermal
$H(P, S, N) = U + PV$	Enthalpy	isobaric, isentropic
$\Omega(T, V, \mu) = - F + \mu N$	Landau (grand) potential	grand canonical

2.1.22. Laplace Inversion of the Grand Canonical Partition Function. Starting from

$$\mathcal{Z}(T, V, \mu) = \sum_N e^{\beta\mu N} Z(T, V, N),$$

let us rewrite it as

$$\mathcal{Z}(z) = \sum_N z^N Z(T, V, N),$$

where $z = e^{\beta\mu}$. This can be inverted by taking the N-th derivative of $\mathcal{Z}(z)$ at the point $z = 0$ and dividing by $1/N!$:

$$Z(T, V, N) = \frac{1}{N!} \frac{d^N \mathcal{Z}(z)}{dz^N}.$$

However, the N-th derivative of a holomorphic (infinitely differentiable) function is given by the Cauchy differential formula:

$$f^{(n)}(a) = \frac{n!}{2\pi i} \oint_\gamma \frac{f(z)}{(z-a)^{n+1}}\, dz.$$

where $f^{(n)}(a)$ is the n-derivative of f evaluated at the point a. Therefore,

$$Z(T,V,N) = \frac{1}{2\pi i} \oint_\gamma \frac{dz}{z^{N+1}} \mathcal{Z}(z),$$

where the contour of integration γ is around $z = 0$. Since $z^{-N} = e^{-N \log z}$, we can rewrite it as

$$Z(T,V,N) = \frac{1}{2\pi i} \oint_\gamma \frac{dz}{z} e^{\log \mathcal{Z}(z) - N \log z},$$

and this integral can be solved using the method of steepest descent. The point of steepest descent is obtained from the condition:

$$\frac{\partial}{\partial z} \{\log \mathcal{Z}(z) - N \log z\} = 0, \tag{2.13}$$

$$\frac{\partial}{\partial z} \log \mathcal{Z}(z) = \frac{N}{z},$$

which, under the assumption that $\log \mathcal{Z}(z)$ is proportional to V, becomes, in the thermodynamic limit (dividing by V/z):

$$\frac{1}{V} z \frac{\partial}{\partial z} \log \mathcal{Z}(z) = \rho,$$

where $\rho = N/V$ in the limit $N \to \infty$, $V \to \infty$. The value of z which solves this equation is written $z = e^{\mu\beta}$, where μ is called the chemical potential. We thus find

$$Z(T,V,N) \sim e^{\log \mathcal{Z}(z) - (N+1)\log z} \sqrt{\frac{2\pi}{\partial^2 \log \mathcal{Z}(z)/\partial z^2}}.$$

From $Z(T,V,N) = e^{-\beta F(V,T)}$ we have in the thermodynamic limit

$$-\beta F(V,T) = \log \mathcal{Z}(z) - (N+1)\log z$$

Substituting $z = e^{\mu\beta}$ as well as the statistical-thermodynamic connection formula for grand potential, $\Omega(T,V,\mu) = k_B T \log \mathcal{Z}(z)$ (Eq. 2.11), we have

$$-\beta F(V,T) = \beta\Omega(T,V,\mu) - (N+1)\mu\beta$$

and since $N+1 \approx N$ as $N \to \infty$:

$$-\beta F(V,T) = \beta\Omega(T,V,\mu) - N\mu\beta, \tag{2.14}$$

which proves the Legendre transform relation $\Omega(T,V,\mu) = \mu\tilde{N} - F(T,V,\tilde{N})$ (Eq. 2.12), where $\tilde{N}$ denotes the particular value of N that minimizes $\mu N - F$. Note: the saddle point equation (Eq. 2.13) differentiates with respect to $z = e^{\mu\beta}$, which we view as (a function of) the chemical potential. The variable that is solved for is $\tilde{N}$.

Also from $P = -\frac{\partial F}{\partial V}$,

$$P = -\frac{\partial}{\partial V}\{-\beta^{-1}\log Z(T,V,N)\} \sim \beta^{-1}\frac{\partial}{\partial V}\left\{\log \mathcal{Z}(z) - (N+1)\log z\right\}.$$

Recalling that $\log \mathcal{Z}(z)$ is $O(V)$ we may use[13]

$$\frac{\partial}{\partial V}\log \mathcal{Z}(z) = \frac{1}{V}\log \mathcal{Z}(z)$$

and the fact that z is independent of V to obtain the result

$$\frac{P}{k_B T} = \lim_{V\to\infty}\frac{1}{V}\log \mathcal{Z}(z).$$

Moreover, we find

$$U = \langle H\rangle = \frac{1}{Z(\beta)}\int H(\mathbf{x})e^{-\beta H(\mathbf{x})}\,d\mathbf{x} = -\frac{\partial \log Z(\beta)}{\partial \beta},$$

$$U = \frac{\partial}{\partial\beta}\beta F(V,T,N) = F(V,T,N) - T\frac{\partial}{\partial T}F(V,T,N),$$

where we used the chain rule

$$\frac{\partial}{\partial\beta}F(T,V,N) = \frac{\partial F}{\partial T}\frac{\partial T}{\partial \beta} = \frac{\partial F}{\partial T}\frac{\partial(\beta k_B)^{-1}}{\partial\beta} = \frac{\partial F}{\partial T}(-1)\frac{1}{(k_B\beta)^2}k_B = -\frac{\partial F}{\partial T}k_B T^2.$$

From $U = \frac{\partial}{\partial\beta}\beta F(V,T,N)$ and $F(V,T,V) = -k_B T\log Z(T,V,N)$, we have

$$\frac{U}{V} = -\frac{1}{V}\frac{\partial}{\partial\beta}\log Z(T,V,N) = -\frac{\partial}{\partial\beta}\lim_{V\to\infty}\frac{1}{V}\log\mathcal{Z}(z).$$

2.1.23. Restatement of the Thermodynamic Potentials in the Language of Legendre Transformations. In thermodynamics when we write $F = U - TS$ it is understood that in the context of the Legendre transformation, such statements have the meaning:

$$U(S,V,N) = \min_T\{F(T,V,N) + TS\} = F(\tilde{T},V,N) + \tilde{T}S,$$

where $\tilde{T}$ is a particular choice of T that minimizes the free energy $F - TS$. $S \to U(S,V,N)$ is concave if $T \to F(T,V,N)$ is concave[14]. If there are no abrupt phase transitions, the thermodynamic potentials are differentiable. Differentiation with respect the T gives the condition for an extremum:

$$\frac{\partial F}{\partial T} + S = 0,$$

---

[13] For example, if $\log\mathcal{Z}(z) = const\times V$, the derivative $\frac{\partial}{\partial V}const\times V = \frac{const\times V}{V} = const$.

[14] Recall our definition of Legendre transformation:

$$H(p) = \max_q\{p\cdot q - L(q)\}$$

where maximization of $p\cdot q - L(q)$ involves the negative of $L(q)$. If instead L appeared with a positive sign, the convexity would be reversed (convex → concave) and we would be searching for the minimum instead of the maximum.

as well as the new variable, which is conjugate to temperature:

$$S = -\frac{\partial F}{\partial T}.$$

With U now being a function of S, V, N, we can write:

$$dU(S, V, N) = TdS - pdV + \mu dN.$$

The independent variables are S, V and N. The corresponding derivatives are

$$T = \frac{\partial U}{\partial S}, \qquad p = -\frac{\partial U}{\partial V}, \qquad \mu = \frac{\partial U}{\partial N}.$$

If the internal energy is known as a function of entropy, volume and number of particles, then temperature, pressure and chemical potential can be computed.

Conversely, we may also write, in the case where the mapping $S \to U(S, V, N)$ is concave:

$$F(T, V, N) = \min_S \{U(S, V, N) - TS\} = U(\tilde{S}, V, N) - T\tilde{S},$$

where $\tilde{S}$ is a particular choice of S that minimizes $U - TS$. It then follows that $T \to F(T, V, N)$ is concave. In the absence of abrupt phase transitions, the mapping is differentiable (smooth) and the derivative of $\{\cdot\}$ with respect to S vanishes:

$$\frac{\partial}{\partial S}\{U(S, V, N) - TS\} = 0,$$

which implies that

$$T = \frac{\partial U}{\partial S}.$$

Likewise, we have the following Legendre transform pair:

$$G(T, P, N) = \min_V \{F(T, V, N) + PV\} = F(T, \tilde{V}, N) + P\tilde{V}$$

where $\tilde{V}$ is a particular choice of V that minimizes $F + PV$, and

$$F(T, V, N) = \min_P \{G(T, P, N) - PV\} = G(T, \tilde{P}, N) - \tilde{P}V,$$

where $\tilde{P}$ is a particular choice of P such that $G - PV$ is minimized. We also have the pair:

$$H(P, S, N) = \min_V \{U(S, V, N) + PV\} = U(S, \tilde{V}, N) + P\tilde{V}$$

and

$$U(S, V, N) = \min_P \{H(P, S, N) - PV\} = H(\tilde{P}, S, N) - \tilde{P}V.$$

Finally, the grand potential:

$$\Omega(T, V, \mu) = \max_N \{-F(T, V, N) + \mu N\} = \mu\tilde{N} - F(T, V, \tilde{N})$$

and

$$F(T, V, N) = \max_\mu \{-\Omega(T, V, \mu) - \mu N\} = -\tilde{\mu}N - \Omega(T, V, \tilde{\mu}).$$

2.1.23.1. *From microcanonical to canonical.* To see this, we begin with the microcanonical partition function $W(E, V, N)$, which is a function of the entropy S/k_B. Rewriting the Helmholtz free energy as

$$\beta F = \beta U - S/k_B,$$

which says that we may pass from the thermodynamic quantity S/k_B to βF by performing the Legendre transform to eliminate the energy U and replace it by its conjugate variable β (inverse temperature). It is a transformation of a function of (E, V, N) to a new function of the variables (β, V, N) or (T, V, N). This passage from the microcanonical ensemble to the canonical ensemble is obtained by taking the Laplace transform of $W(E, N, V)$ with respect to the energy E. The conjugate variable is β, the inverse temperature:

$$Z(T, V, N) = \int_{E_0}^{E_{max}} dE\, W(E, V, N) e^{-\beta E}$$

For historic reasons, in thermodynamics, the variables chosen for the Legendre transforms are not always conjugate pairs. This obscures the symmetry between the quantities. By contrast, if we define the dimensionless quantities

$$\mathcal{S} = S/k_B \qquad \text{and} \qquad \mathcal{F} = \beta F,$$

the Legendre transform takes the symmetric form:

$$\mathcal{F}(\beta) + \mathcal{S}(E) = \beta \cdot E,$$

which expresses the duality between β (inverse temperature) and energy E. This shows that the dimensionless entropy $\mathcal{S}$ is the conjugate potential to the dimensionless Helmholtz free energy $\mathcal{F}$. The former is a function of inverse temperature $\mathcal{F}(\beta)$ while the latter is a function of the energy $\mathcal{S}(E)$.

2.1.23.2. *From canonical to grand canonical.* In a similar way, we may transform from the canonical ensemble with variables (T, V, N) to the grand canonical ensemble with variables (T, V, μ). The thermodynamic potential is called the grand canonical potential

$$\Omega = -F + \mu N,$$

and the corresponding grand canonical partition function is obtained by the Laplace transform of Z with respect to N, and introducing its conjugate variable μ,

$$\mathcal{Z}(T, V, \mu) = \int dN\, Z(T, V, N) e^{\beta \mu N}.$$

To be strictly correct, the above transform is from N to the conjugate variable $\beta\mu$, resulting in a function of $(T, V, \beta\mu)$. However, the β in $\beta\mu$ is redundant if T is known. The unique set of variables is (T, V, μ).

To make this more transparent, it helps to define the following dimensionless quantities:

$$\tilde{\Omega} = \beta\Omega \qquad \text{and} \qquad \mathcal{F} = \beta F \qquad \text{and} \qquad \tilde{\mu} = \beta\mu.$$

The Legendre transform $\Omega = -F + \mu N$ can be written in a form that highlights the role of the dimensionless conjugate variables:

$$\tilde{\Omega}(\mu) - \mathcal{F}(N) = \tilde{\mu} \cdot N.$$

2.1.23.3. *From canonical to isobaric.* The Legendre transform relation

$$G = F + PV$$

becomes, in dimensionless form (let $\mathcal{G} = \beta G$, $\mathcal{F} = \beta F$ and $\mathcal{P} = \beta P$)

$$\mathcal{G}(\mathcal{P}) - \mathcal{F}(V) = \mathcal{P} \cdot V.$$

2.1.23.4. *Link between Legendre transform and Laplace transform.* Starting from the Legendre transform relationship between free energy $\mathcal{F}$ and entropy $\mathcal{S}$:

$$-\mathcal{F}(\beta) = \mathcal{S}(U) - \beta \cdot U,$$

and exponentiating,

$$e^{-\mathscr{F}(\beta)} = e^{\mathcal{S}(U) - \beta \cdot U},$$

we recognize the left hand side as the canonical partition function:

$$Z(\beta, V, N) = e^{-\mathcal{F}(\beta)}.$$

In the thermodynamic limit, the right hand side is approximately equal to:

$$e^{\mathcal{S}(U) - \beta \cdot U} \approx \int_0^\infty dE \, e^{\mathcal{S}(E) - \beta \cdot E} = \int_0^\infty dE \, W(E) e^{-\beta \cdot E},$$

where the last step follows from the substitution $W(E) = e^{\mathcal{S}(E)}$. Therefore, we get that the canonical partition function $Z(\beta)$ is the Laplace transform of $W(E)$:

$$Z(\beta) = \int_0^\infty dE \, W(E) e^{-\beta \cdot E}.$$

2.1.24. Supplemental Readings. The following textbooks are recommended reading:

- A.I. Khinchin, *Mathematical Foundations of Statistical Mechanics*, Dover (1960)
- M. Toda, R. Kubo, N. Saito, *Statistical physics I*, 2nd edition, Springer (1998)
- D.A. McQuarrie, *Statistical Mechanics*, 2nd edition, University Science Books (2000)
- K. Huang, *Statistical Mechanics*, 2nd edition, Wiley (1987)

2.1.25. Solving problems of thermostatistics using statistical ensembles. Most problems in thermostatistics begin with the partition function. For example, let's take the canonical partition function. Written down as a sum over states:

$$Z = \sum_i e^{-\beta E_i}$$

where $\beta = \frac{1}{k_B T}$ and E_i is the energy of the i-th state. The Helmholtz free energy F is related to Z by:

$$F(T, V, N) = -k_B T \log Z$$

This relationship establishes the link between thermodynamics (LHS) and statistical mechanics (RHS). A thermodynamic potential is a scalar quantity from which all thermodynamic variables can be derived. In the context of a system in equilibrium at constant temperature and volume, the Helmholtz free energy serves as the relevant thermodynamic potential

$$F = U - TS - \mu N$$

where μ is the chemical potential, N, the number of particles, U is the internal energy and T is the temperature. S is the entropy of the system. The Helmholtz free energy is commonly employed to calculate work done on or by the system, excluding work done by expansion or contraction (i.e., PdV work). The minimization of $F(T, V, N)$ at constant T, N and V indicates a state of equilibrium.

Considering F as a function of T and V, $F(T, V, N)$, partial derivatives yield other thermodynamic properties:

$$dF = -SdT - PdV - \mu dN.$$

From this, we identify the coefficients of dT, dV and dN as $-S$, $-P$ and $-\mu$, respectively. The relations are:

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P, \quad \left(\frac{\partial F}{\partial T}\right)_{V,N} = -S, \quad \left(\frac{\partial F}{\partial N}\right)_{T,V} = -\mu.$$

Other quantities can also be obtained. For example, the average energy can be obtained by differentiating the partition function with respect to β:

$$\frac{\partial}{\partial \beta} Z(T, V, N) = \int_\Gamma \left[\frac{\partial}{\partial \beta} e^{-\beta \mathcal{H}(\mathbf{p},\mathbf{q})}\right] \frac{d^{3N}\mathbf{p}\ d^{3N}\mathbf{q}}{N! h^{3N}} = \int_\Gamma \left[-\mathcal{H}(\mathbf{p}, \mathbf{q}) e^{-\beta \mathcal{H}(\mathbf{p},\mathbf{q})}\right] \frac{d^{3N}\mathbf{p}\ d^{3N}\mathbf{q}}{N! h^{3N}}$$

and so dividing this by $-Z$ is the statistical definition of the average $\langle \mathcal{H}(\mathbf{p}, \mathbf{q}) \rangle$. Therefore,

$$U \equiv \langle \mathcal{H}(\mathbf{p}, \mathbf{q}) \rangle = -\frac{\partial}{\partial \beta} \log Z(T, V, N) = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}.$$

2.1.25.1. *Canonical ensemble: the classical ideal gas.* The Hamiltonian is

$$\mathcal{H}(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}.$$

The partition function is:

$$Z(T, V, N) = \int_\Gamma e^{-\beta \sum_{i=1}^{3N} p_i^2/2m} \frac{d^{3N}\mathbf{p}\ d^{3N}\mathbf{q}}{N! h^{3N}},$$

where the sum has $3N$ terms to account for N particles and 3 components per particle, i.e. $p_{1x}, p_{1y}, p_{1z}, p_{2x}, \ldots,\ p_{Nx}, p_{Ny}, p_{Nz}$. The integral over the position variables gives a factor

V^N, are we are left with the task of evaluating Gaussian integrals:

$$Z(T,V,N) = \frac{V^N}{N!h^{3N}}\left[\int_{-\infty}^{\infty} d^3\mathbf{p}e^{-\beta\mathbf{p}^2/2m}\right]^N,$$

where $\mathbf{p}^2 = p_x^2 + p_y^2 + p_z^2$. Integrating using the formula $\int_{\mathbb{R}} \exp(-\alpha x^2)dx = \sqrt{\pi/\alpha}$, the result is:

$$Z(T,V,N) = \frac{V^N}{N!h^{3N}}\left(\frac{2\pi m}{\beta}\right)^{3N/2}.$$

We immediately find, for the energy:

$$U = -\frac{\partial}{\partial\beta}\log Z(T,V,N) = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = \frac{3}{2}Nk_BT.$$

We note that the factor $(N!h^{3N})^{-1}$ was not needed because computing U involved taking a partial derivative with respect to β. For the pressure, we get:

$$P = k_BT\frac{\partial}{\partial V}\log Z(T,V,N) = \frac{Nk_BT}{V}.$$

Same comment here, $(N!h^{3N})^{-1}$ was not needed.

2.1.25.2. *Grand canonical ensemble: the classical ideal gas.* The grand canonical partition function is the Laplace transform of the canonical partition function:

$$\mathcal{Z}(T,V,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,V,N),$$

But we have already calculated the canonical partition function in the previous exercise:

$$Z(T,V,N) = \frac{V^N}{N!h^{3N}}\left(\frac{2\pi m}{\beta}\right)^{3N/2}.$$

Thus,

$$\mathcal{Z}(T,V,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N}\frac{V^N}{N!h^{3N}}\left(\frac{2\pi m}{\beta}\right)^{3N/2}.$$

We recognize the Taylor expansion of the exponential function. Therefore,

$$\mathcal{Z}(T,V,\mu) = \exp\left[e^{\beta\mu}\frac{1}{h^3}V\left(\frac{2\pi m}{\beta}\right)^{3/2}\right] = \exp\left[e^{\mu/k_BT}V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right].$$

The grand canonical potential is:

$$\Omega(T,V,\mu) = k_BT\log\mathcal{Z}(T,V,\mu) = k_BTe^{\mu/k_BT}V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}.$$

The equations of state can be found by differentiation,

$$S(T,V,\mu) = \left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}, \qquad P(T,V,\mu) = \left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}, \qquad N(T,V,\mu) = \left(\frac{\partial\Omega}{\partial\mu}\right)_{V,T}.$$

These latter relations are easily calculated. They are also easily derived from the definition of the Landau (grand) potential

$$\Omega = -F + \mu N = -U + TS + \mu N = -PV \qquad \text{with} \qquad U = TS - PV + \mu N.$$

2.1.25.3. *Microcanonical ensemble: classical harmonic oscillators.* The Hamiltonian of a set of N classical harmonic oscillators is

$$\mathcal{H}(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{m\omega^2}{2} q_i^2 \right).$$

The volume of phase space is

$$\mathcal{V}(N, V, E) = \int\limits_{\{\mathbf{x}:\mathcal{H}(\mathbf{x})<E\}} d\mathbf{x},$$

and can be computed using the substitutions

$$p_i = \sqrt{2m}\ y_i \qquad\qquad i = 1, \ldots, 3N$$

$$q_i = \sqrt{\frac{2}{m\omega^2}}\ y_{3N+i} \qquad\qquad i = 1, \ldots, 3N$$

where we omitted the Gibbs factor $(N! h^{3N})^{-1}$ since it plays no role when computing classical thermodynamical quantities. In terms of these variables, the energy constraint is

$$E = \sum_{i=1}^{6N} y_i^2.$$

The volume is:

$$\mathcal{V}(N, V, E) = \left(\frac{2}{\omega}\right)^{3N} \int\limits_{\{\mathbf{x}:H(\mathbf{x})<E\}} \prod_{i=1}^{6N} dy_i = \left(\frac{2}{\omega}\right)^{3N} \frac{\pi^{3N}}{3N\Gamma(3N)} E^{3N}.$$

where $\Gamma(z) = \int_0^\infty r^{z-1} e^{-r} dr$ is the Gamma function and we have used the volume of a $6N$-dimensional sphere with radius $R = \sqrt{E}$. To compute the entropy,

$$S = k_B \log \frac{\partial \mathcal{V}(N, V, E)}{\partial E} = k_B \log \left(\frac{2}{\omega}\right)^{3N} \frac{\pi^{3N}}{\Gamma(3N)} E^{3N-1}.$$

Using Stirling's formula, we obtain:

$$S \approx 3Nk_B \left[\log \left(\frac{2\pi E}{3\omega N} \right) + 1 \right].$$

The temperature is given by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_N = \frac{3Nk_B}{E}.$$

Thus, the average energy per oscillator is $3k_BT$, in agreement with the equipartition theorem.

2.1.25.4. *Microcanonical ensemble: defects in a solid.* This example can be found in Huang:

- K. Huang, *Lectures on statistical physics and protein folding*, World Scientific (2005)

Consider a lattice with N sites, each occupied by one atom. There are M possible interstitial locations where atoms can be misplaced, and it costs an energy Δ to misplace an atom, as shown in Figure (2.2). Assume $N, M \to \infty$, and the number of displaced atoms n is a small fraction of N. Let's calculate the thermodynamic properties of this system.

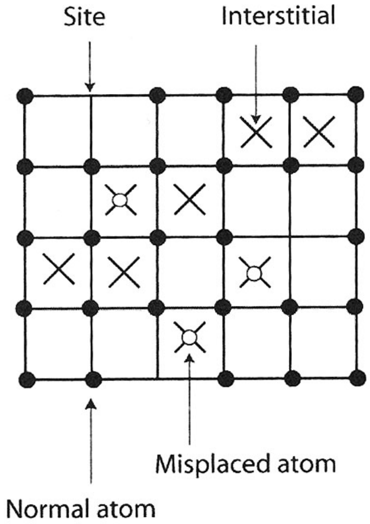

Figure 2.2. Model of defects in a solid.

The given macroscopic parameters are N, M, n. The energy is

$$E = n\Delta.$$

The number of states in the microcanonical ensemble is:

$$W(E) = \left[\frac{N!}{n!(N-n)!}\right] \cdot \left[\frac{M!}{n!(M-n)!}\right].$$

The first factor is the number of ways to choose the n atoms to be removed from N sites, and the second factor is the number of ways to place the n atoms on the M interstitial positions. We can use Stirling's formula

$$\log \log N! \approx N \log N - N.$$

The entropy is

$$\frac{S(E)}{k_B} = \log W(E) \approx n \log \frac{N}{n} - (N-n) \log \left(1 - \frac{n}{N}\right) + n \log \frac{M}{n} - (M-n) \log \left(1 - \frac{n}{M}\right).$$

The temperature is given by

$$\frac{1}{T} = \frac{\partial S(E)}{\partial E} = k_B \frac{\partial \log W(E)}{\partial E} = \frac{1}{\Delta} \frac{\partial \log W(E)}{\partial n}.$$

This leads to

$$\frac{\Delta}{k_B T} = \frac{\partial}{\partial n} \log W(E) = \log\left(\frac{N}{n} - 1\right) + \log\left(\frac{M}{n} - 1\right).$$

Exponentiating both sides, we have

$$\frac{n^2}{(N-n)(M-n)} = \exp\left(-\frac{\Delta}{k_B T}\right).$$

The low and high temperature limits are:

$$\begin{aligned} n &\approx \sqrt{NM}\exp(-\Delta/2k_B T) && (k_B T \ll \Delta) \\ \frac{1}{n} &\approx \frac{1}{N} + \frac{1}{M} && (k_B T \gg \Delta). \end{aligned}$$

As a model for defects in solids, we set $N = M$ and $n \ll N, M$, and $\Delta = 1$ eV. Then,

$$\frac{n}{N} \approx \exp(-\Delta/2k_B T).$$

For T=300 K, $n/N \approx 2 \times 10^{-9}$. (Note: $k_B T$ is approx. equal to 0.03 eV.)
For T=1000 K, $n/N \approx 2 \times 10^{-3}$. In the high temperature limit $T \to \infty$, $n/N \approx 0.5$.

2.1.25.5. *Canonical ensemble: unwinding of DNA.* This example can be found in Huang:

- K. Huang, *Lectures on statistical physics and protein folding*, World Scientific (2005)

The unwinding of a double-stranded DNA molecule is like unraveling a zipper. The DNA has N links, each of which can be in one of two states: a closed state with energy 0, and an open state with energy Δ. A link can be opened only if all the links to its left are already open, as illustrated in Figure (2.3). Due to thermal fluctuations, links will spontaneously open and close. We want to calculate the average number of open links.

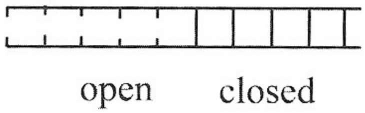

Figure 2.3. Zipper model for DNA.

The possible states are labeled by the number of open links $n = 0, 1, 2, \ldots, N$. The energy with n open links is

$$E_n = n\Delta.$$

The partition funciton is

$$Z_N = \sum_{n=0}^{N} e^{-\beta n\Delta} = \frac{1 - e^{-\beta(N+1)\Delta}}{1 - e^{-\beta\Delta}}.$$

The average number of open links is:

$$\langle n \rangle = \frac{\sum_{n=0}^{N} n e^{-\beta n\Delta}}{\sum_{n=0}^{N} e^{-\beta n\Delta}} = -\frac{1}{\Delta}\frac{\partial \log Z_N}{\partial \beta} = \frac{e^{-\beta\Delta}}{1 - e^{-\beta\Delta}} - \frac{(N+1)e^{-\beta(N+1)\Delta}}{1 - e^{-\beta(N+1)\Delta}}.$$

At low temperatures $\beta\Delta \gg 1$, and there are few open links:

$$\langle n \rangle \approx e^{-\beta\Delta}.$$

At high temperatures $\beta\Delta \ll 1$, almost all the links are open:

$$\langle n \rangle \approx N.$$

2.1.25.6. *Grand canonical ensemble: chemical equilibria.* This example can be found in Sethna's book:

- J.P. Sethna, *Statistical Mechanics: Entropy, Order Parameters and Complexity*, Oxford University Press (2006)

In studying chemical reactions, we are often interested in the number of molecules of various types as a function of time, and not interested in observing properties depending on the positions and momenta of the molecules.

Ammonia can be produced from hydrogen and nitrogen through the reaction

$$3\mathrm{H}_2 + \mathrm{N}_2 \leftrightharpoons 2\mathrm{NH}_3.$$

In *chemical equilibrium*, we know the concentrations satify the *law of mass-action*

$$K_{eq}(T) = \frac{[\mathrm{NH}_3]^2}{[\mathrm{N}_2][\mathrm{H}_2]^3}.$$

This law of mass-action implies that all reactions proceed by simultaneous three-body collisions, as shown in Figure (2.4), i.e. the probability of one nitrogen and three hydrogen molecules colliding in a small region is proportional to the nitrogen concentration and to the cube of the hydrogen concentration. This gives the forward rate as $K_F[\mathrm{N}_2][\mathrm{H}_2]^3$. Similarly the backward reaction occurs at a rate $K_B[\mathrm{NH}_3]^2$. Balancing (equating) these two rates and letting $K_{eq} = K_F/K_B$ gives the law of mass-action. This argument is flawed for general chemical reactions because it neglects the possibility of reaction intermediates involving multiple collisions. Let us derive the law of mass-action from statistical mechanics.

Since we are not interested in the position and momentum, consider instead the Helmholtz free energy:

$$F(T, V, N_{\mathrm{H}_2}, N_{\mathrm{N}_2}, N_{\mathrm{NH}_3}).$$

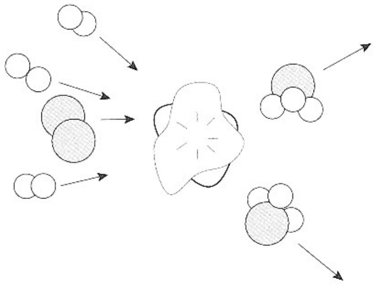

Figure 2.4. Ammonia collision: the simple motivating argument for the law of mass-action views the reaction as a simultaneous collision of all three reactants.

When the chemical reaction takes place, this changes the number of molecules, and the free energy of the system changes according to:

$$\begin{aligned}\Delta F =& \frac{\partial F}{\partial N_{\mathrm{H}_2}} \Delta N_{\mathrm{H}_2} + \frac{\partial F}{\partial N_{\mathrm{N}_2}} \Delta N_{\mathrm{N}_2} + \frac{\partial F}{\partial N_{\mathrm{NH}_3}} \Delta N_{\mathrm{NH}_3}. \\ =& -3\mu_{\mathrm{H}_2} - \mu_{\mathrm{N}_2} + 2\mu_{\mathrm{NH}_3},\end{aligned}$$

where $\mu_X = \partial F/\partial N_X$ is the chemical potential of molecule X. The reaction will proceed until the free energy is at a minimum, i.e.

$$-3\mu_{\mathrm{H}_2} - \mu_{\mathrm{N}_2} + 2\mu_{\mathrm{NH}_3} = 0 \tag{2.15}$$

in equilibrium.

To derive the law of mass-action, we must now make an assumption: that the molecules are uncorrelated in space. This makes each molecular species into a separate ideal gas. The Helmholtz free energies of the gases are of the form[15]

$$F(N,V,T) = N k_B T \left[\log((N/V)\lambda^3) - 1\right] + N F_0,$$

where $\lambda = h/\sqrt{2\pi m k_B T}$ is the thermal deBroglie wavelength. The first two terms give the contribution to the partition function from the positions and momenta of the mlecules. The last term NF_0 comes from the internal free energy of the molecules. So the chemical potential is

$$\begin{aligned}\mu(N,V,T) \equiv& \frac{\partial F}{\partial N} = k_B T \left[\log((N/V)\lambda^3) - 1\right] + N k_B T (1/N) + F_0 \\ =& k_B T \log((N/V)\lambda^3) + F_0 \\ =& k_B T \log(N/V) + c + F_0, \end{aligned} \tag{2.16}$$

---

[15] We previously derived the canonical partition function $Z = (L/\lambda)^{3N}/N!$ with $V = L^3$, $\lambda = h/\sqrt{2\pi m k_B T}$ for the ideal gas. The free energy is $F = -k_B T \log((L/\lambda)^{3N}/N!)$, which reduces to $-N k_B T \log(V/\lambda^3) + k_B T \log(N!)$. Using Stirling, this becomes $-N k_B T \log(V/\lambda^3) + k_B T(N \log N - N)$, or $-N k_B T \left[\log(V/N\lambda^3) + 1\right]$.

where the constant $c = k_B T \log(\lambda^3)$ is independent of density. Using Eq. (2.16) into Eq. (2.15), dividing by $k_B T$, writing concentrations $[X] = N_X/V$ and pulling terms independent of concentrations to the right, we find the law of mass-action

$$-3\log[\mathrm{H_2}] - \log[\mathrm{N_2}] + 2\log[\mathrm{NH_3}] = \log K_{eq},$$

$$K_{eq} = \frac{[\mathrm{NH_3}]^2}{[\mathrm{H_2}]^3[\mathrm{N_2}]}.$$

We also find that the equilibrium constant depends exponentially on the net internal free energy difference

$$\Delta F_{net} = -3F_0^{\mathrm{H_2}} - F_0^{\mathrm{N_2}} + 2F_0^{\mathrm{NH_3}}$$

between reactants and products:

$$K_{eq} = K_0 \exp(-\Delta F_{net}/k_B T)$$

with a prefactor

$$K_0 = \frac{\lambda_{\mathrm{H_2}}^9 \lambda_{\mathrm{N_2}}^3}{\lambda_{\mathrm{NH_3}}^6} = \frac{h^6 m_{\mathrm{NH_3}}^3}{8\pi^3 k_B^3 T^3 m_{\mathrm{H_2}}^{9/2} m_{\mathrm{N_2}}^{3/2}} \propto T^{-3}.$$

that depends weakly on temperature. The factor $e^{-\Delta F_{net}/k_B T}$ represents the Boltzmann factor favoring a final state with molecular free energy ΔF_{net} lower than the initial state. Thus,

$$K_{eq} \propto e^{-\Delta E_{net}/k_B T}.$$

with $\Delta E_{net} = 92.4$ kJ/mol for the ammonia synthesis reaction (exothermic).

An M-atom chemical reaction is a trajectory in $3M$-dimensional configuration space. In chemistry we usually plot the energy as a function of the "reaction coordinate" X (see Figure 2.5. The energy barrier B separates the reactants from the products. The atomic configuration at the top of the barrier is called the *transition state.* This barrier, in $3M$-dimensional configuration space, is actually a saddlepoint; dividing the reactants from the products demands the identification of a $(3M-1)$-dimensional transition-state *dividing surface.*

The density of particles at the top of the barrier is smaller than the density at the bottom of the well by a Boltzmann factor $e^{-B/k_B T}$. The rate of the reaction $\aleph$ is thermally-activated, or of *Arrhenius* form:

$$\aleph = \aleph_0 \exp(-B/k_B T).$$

with some prefactor $\aleph_0$ which is proportional to the mass-action formula, i.e. $\aleph_0 \propto [\mathrm{H_2}]^2[\mathrm{N_2}]^2$ for the ammonia reaction.

2.1.26. Supplemental Readings. The following textbooks are recommended reading:

- K. Huang, *Statistical Mechanics*, 2nd edition, Wiley (1987)
- K. Huang, *Lectures on statistical physics and protein folding*, World Scientific (2005)

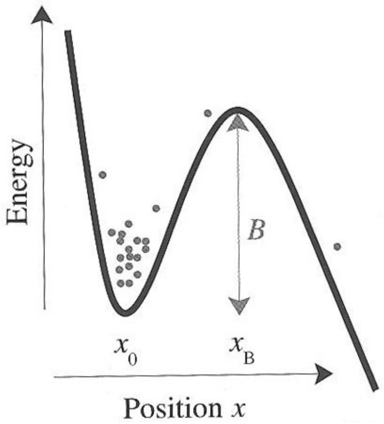

Figure 2.5. Barrier-crossing potential. Energy E as function of some coordinate X of the reaction. The dots schematically represent how many atoms are at each position. The reactants (left) are separated from the products (right) by an energy barrier of height B. One can estimate the rate of the reaction by calculating the number of reactants crossing the top of the barrier per unit time.

- J.P. Sethna, *Statistical Mechanics: Entropy, Order Parameters and Complexity*, Oxford University Press (2006)
- D.A. McQuarrie, *Statistical Mechanics*, 2nd edition, University Science Books (2000)

2.1.27. A short review of thermodynamic principles.

2.1.27.1. *Principle of energy minimum.* We know from the second law of thermodynamics that a system displaced from equilibrium moves towards a new state such that the change in entropy never decreases:

$$dS \geq 0.$$

Eventually it reaches equilibrium and $dS = 0$. Thus, the entropy attains a maximum. According to the first law of thermodynamics, maximizing the entropy is equivalent to minimizing the free energy, F:

$$F(N, V, T) = U - TS(N, V, U),$$

This is an instance of a Legendre transform if we divide both sides by T: the transform takes us from S into F by replacing energy (U) by temperature ($T = 1/k_B\beta$):

$$\mathcal{F}(N, V, T) = \beta U - \mathcal{S}(N, V, U),$$

where $\mathcal{F} = \beta F$ and $\mathcal{S} = S/k_B$. The equivalence of energy minimization with entropy maximization is made possible by the Legendre transformation which preserves the convexity of the functions involved. Thus, going from one set of thermodynamic variables (e.g., N, V, E) to another more convenient one (e.g. N, V, T) preserves the structure.

For a more extensive discussion on the principle of energy minimum in thermostatistics, see the textbook by Callen:

- H.B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2nd edition, Wiley (1985)

2.1.27.2. *Thermal equilibrium.* We learn from undergraduate chemistry that the conditions for thermodynamic equilibrium are as follows:

- For a completely isolated system, $\Delta S = 0$ at equilibrium. [An isolated system, by definition, is a member of the microcanonical ensemble (fixed N, V, E).]
- For a system at constant temperature and volume, $\Delta F = 0$ at equilibrium. [This corresponds to the canonical statistics (fixed N, V, T).]
- For a system at constant temperature and pressure, $\Delta G = 0$ at equilibrium. [Case of the isobaric-isothermal ensemble (fixed N, P, T).]

If we wish to study a chemical reaction for a system under atmospheric conditions, the Gibbs potential (fixed T, P) is appropriate. For a reaction taking place in a vessel at fixed volume, the Helmholtz free energy, A, is more useful.

2.1.27.3. *Summary of Legendre transform relationships between thermodynamic state functions.* All the thermodynamic functions of a system can be derived from a single function, $U(S, V)$. Comparing its differential

$$dU(S,V) = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV,$$

to the first law of thermodynamics

$$dU = TdS - PdV,$$

we obtain definitions of temperature and pressure

$$T = \frac{\partial U}{\partial S} \qquad P = -\frac{\partial U}{\partial V}$$

These two formulas are called *Maxwell relations.* For other types of processes, we use different functions:

- Constant S, V: The internal energy $U(S, V)$

$$\begin{aligned} dU =& TdS - PdV, \\ T = \frac{\partial U}{\partial S} & \qquad P = -\frac{\partial U}{\partial V} \end{aligned}$$

- Constant T, V: Use the (Helmholtz) free energy

$$\begin{aligned} F(T,V) =& U - TS \\ dF =& -SdT - PdV \end{aligned}$$

$$S = -\frac{\partial F}{\partial T} \qquad P = -\frac{\partial F}{\partial V}$$

- Constant T, P: Use the Gibbs potential

$$\begin{aligned} G(P,T) =& F + PV \\ dG =& -SdT + VdP \end{aligned}$$

$$S = -\frac{\partial G}{\partial T} \qquad V = \frac{\partial G}{\partial P}$$

- Constant P, S: Use the enthalpy

$$\begin{aligned} H(P,S) =& U + PV \\ dH =& TdS + VdP \end{aligned}$$

$$T = \frac{\partial H}{\partial S} \qquad V = \frac{\partial H}{\partial P}$$

We may conveniently summarize all these Maxwell relations as shown in Fig. 2.6.

Figure 2.6. Each quantity at the center of a row or column is adjacent to its natural variables. The partial derivative with respect to one of the variables, with the other held fixed, is arrived at by following the diagonal line originating from that variable. Attach a minus sign if you go against the arrow.

Some authors define the "Maxwell relations" as equations that involve second partial derivatives. For example:

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N},$$

which are obtained by differentiating

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$$

with respect to V and differentiating

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

with respect to S, and equating the mixed partial derivatives, i.e.

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} \qquad \to \qquad \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}.$$

See handout by Alberty for details:

- R.A. Alberty, *Use of Legendre transforms in chemical thermodynamics* (IUPAC Technical Report), Pure Appl. Chem., Vol. 73, No. 8, pp. 1349–1380 (2001)

2.1.27.4. *Brief remark on the usual thermodynamic notation for Legendre transforms.* We note that the Legendre transform in thermodynamics is usually presented as follows. We start from the 1st law of thermodynamics

$$dU(S,V) = TdS - PdV$$

and define the Helmholtz free energy as the "Legendre transform"

$$F = U - TS \tag{2.17}$$

Taking d of this expression and substituting the 1st law gives:

$$dF(V,T) = dU - TdS - SdT = (\cancel{TdS} - PdV) - \cancel{TdS} - SdT = -PdV - SdT.$$

Thus, the Legendre transform is made to appear as a relationship between the differentials. By inspection of Eq. (2.17) it appears that it is the energy function, U, that is Legendre-transformed to eliminate the entropy S in favor of the temperature T.

The Legendre transform can be presented in terms of normalized variables. The argument runs as follows.

Solving the 1st law $dU = TdS - PdV$ for dS:

$$dS = \frac{1}{T}(dU + PdV)$$

and divide by k_B, then introducing the normalized variable $\mathcal{S} = S/k_B$,

$$d\mathcal{S} = \beta(dU + PdV).$$

The normalized Helmholtz free energy is the Legendre transform of $\mathcal{S}(E)$

$$\underbrace{\mathcal{F}}_{\beta F} = \sup_E \left[\beta \cdot E - \mathcal{S}(E)\right] \equiv \beta \cdot U - \mathcal{S}(U),$$

where U is the energy E that maximizes $\beta \cdot E - \mathcal{S}(E)$. This formulation makes the structure of the Legendre transformation apparent. Taking the differential of both sides and substituting $d\mathcal{S} = \beta(dU + PdV)$ gives

$$d\mathcal{F} = Ud\beta + \beta dU - d\mathcal{S} = Ud\beta + \cancel{\beta dU} - \beta(\cancel{dU} + PdV)$$

which is ($\mathscr{P} = \beta P$)

$$d\mathcal{F} = Ud\beta - \beta PdV = Ud\beta - \mathscr{P}dV.$$

Note that here it is the entropy function $\mathcal{S}$ that is Legendre-transformed rather than the energy function. This Legendre transform eliminates U in favor of β. This is possible since U is a monotonic function of S and we can always solve for $\mathcal{S}$ in terms of U. This slightly different point of view simply depends on whether one chooses to start with entropy or internal energy. The end result, the Helmholtz free energy, is equivalent.

2.1.28. Chemical reactions.

2.1.28.1. *Euler relation.* Since we are dealing with extensive quantities in thermodynamics, the state functions are homogeneous of degree 1:

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N).$$

Differentiating with respect to λ we get:

$$U(S,V,N) = \left(\frac{\partial U}{\partial(\lambda S)}\right)_{V,N} \frac{\partial(\lambda S)}{\partial\lambda} + \left(\frac{\partial U}{\partial(\lambda V)}\right)_{S,N} \frac{\partial(\lambda V)}{\partial\lambda} + \left(\frac{\partial U}{\partial(\lambda N)}\right)_{V,S} \frac{\partial(\lambda N)}{\partial\lambda}$$

which simplifies to

$$U(S,V,N) = \left(\frac{\partial U}{\partial(\lambda S)}\right)_{V,N} S + \left(\frac{\partial U}{\partial(\lambda V)}\right)_{S,N} V + \left(\frac{\partial U}{\partial(\lambda N)}\right)_{V,S} N$$

Since λ is arbitrary we set $\lambda = 1$,

$$U(S,V,N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} S + \left(\frac{\partial U}{\partial V}\right)_{S,N} V + \left(\frac{\partial U}{\partial N}\right)_{V,S} N$$

Substituting the definitions of T, P and N in terms of partial derivatives, we arrive at

$$U(S,V,N) = TS - PV - \mu N.$$

2.1.28.2. *Gibbs potential is for systems exposed to the atmosphere.* The Gibbs potential is a natural function of the variables $T, P, N_1, N_2, \ldots,$ and is particularly convenient to use in the study of chemical reactions which are performed in systems exposed to the atmosphere, and thereby maintained at constant temperature and pressure.

The Gibbs potential of a multicomponent system is related to the chemical potentials of the individual components, for

$$G(N,P,T) = \underbrace{(U - TS)}_{F(N,V,T)} + PV,$$

(recall that the Gibbs potential is the Legendre transform of the Helmholtz free energy) and inserting the Euler relation

$$U = TS - PV + \mu_1 N_1 + \mu_2 N_2 + \ldots$$

we find

$$G = \mu_1 N_1 + \mu_2 N_2 + \dots$$

2.1.28.3. *Chemical potentials are related to the stoichiometry of the reaction.* Consider the chemical reaction

$$0 \leftrightharpoons \sum \nu_j A_j$$

where ν_j are the stoichiometric coefficients of the reaction and A_j are the various chemical species. (Any chemical reaction can be put into this form.) The change in mole numbers must be proportional to the stoichiometric coefficients,

$$dN_i \propto \nu_i.$$

If the chemical reaction is carried out at constant temperature and pressure (as in an open vessel) the condition of equilibrium then implies

$$\sum_j \nu_j \mu_j = 0.$$

This relationship between the chemical potentials is very important. It is an additional constraint on the number of unknowns that is provided "free of charge" by the stoichiometric coefficients.

For example, in the metabolism of ATP

$$\text{ATP} + \text{H}_2\text{O} \leftrightharpoons \text{ADP} + \text{P}_i, \qquad \Delta G^\circ = -30 \text{ kJ/mol},$$

we can immediately write down the following constraint:

$$\mu_{\text{ATP}} + \mu_{\text{H}_2\text{O}} = \mu_{\text{ADP}} + \mu_{\text{P}_\text{i}}.$$

This type of constraint can be used in the study of chemical equilibria.

The Gibbs potential is more useful when chemical reactions are done in a system exposed to the atmosphere (constant T, P), as is the case for most tabletop chemistry. the reaction was done in a vessel (constant T, V). This setting is more appropriate for gas-phase reactions and Helmholtz free energy (A) is the function to use.

2.1.28.4. *Interpretation of the chemical potential.* In Section 6.1.6 (Equation 2) we have expressed the chemical potential for an ideal gas as the log of the density plus other terms:

$$\mu_i(N_i, V, T) = k_B T \log(\rho_i) + C.$$

A simple interpretation of this is to think of μ as reporting on the local concentration of a particular chemical, since the density, ρ_i, is proportional to the concentration of the ith chemical species, $[A_i]$. If we have a reaction vessel containing an inhomogeneous mixture of chemicals, the chemical potential of the ith species will be a function of position $\mu_i \equiv \mu_i(\mathbf{r})$, and any *gradient in the chemical potentials* will give rise to a flux of particles, i.e. some diffusion equation will act to re-establish homogeneity of the substances.

2.2. The Laws of Thermodynamics and Relationship with Statistical Mechanics

2.2.1. Zeroth law. The "zeroth law of thermodynamics" is the statement that two objects or bodies in thermal contact have equal temperatures at equilibrium. Consider an isolated system comprising a number of subsystems, each with energies E', E'', … and the energies can vary, however, the total energy should remain fixed:

$$E = E' + E'' + \cdots = const.$$

Eventually the system achieves equilibrium by redistributing energy over the subsystems. We assume this equilibrium to be uniquely determined by its total initial energy. We can find the state of the system by maximizing the entropy S with respect to E', E'', … subject to a fixed E. The additivity condition implies that

$$S = S'(E') + S''(E'') + \ldots,$$

where S', S'', … are the entropies of the subsystems, which we assume for simplicity to depend on their energies only. A necessary condition for S to be a maximum at fixed E can be obtained by the method of Lagrange multipliers[16]. It is

$$\frac{dS'}{dE'} = \frac{dS''}{dE''} = \ldots.$$

Accordingly, since we have defined the temperature as $T = (dS/dE)^{-1}$, this condition implies that the temperatures are equal

$$T' = T'' = \ldots.$$

2.2.2. First Law. Consider a slow variation of a thermodynamic system. The slow variation is required so that at every instant, we have a microcanonical ensemble. Consider the entropy function $S(E, V)$ which is associated with this ensemble. The change in entropy is

$$dS(E, V) = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV.$$

The coefficient of dE is related to temperature:

$$\frac{1}{T} = \frac{\partial S(E)}{\partial E}.$$

If we define the pressure by:

$$P \equiv T\left(\frac{\partial S}{\partial V}\right)_E,$$

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[16] For references on the method of Lagrange multipliers, see the textbook by McQuarrie. See also the book by Apostol which provides a very nice geometric picture of the vector calculus:

- T.M. Apostol, *Calculus, Vol II: Multi-Variable Calculus and Linear Algebra with Applications*, 2nd edition, Wiley (1969) the infinitesimal change in entropy is:

$$dS = \frac{1}{T}(dE + PdV),$$

or

$$dE = TdS - PdV. \tag{2.18}$$

This is the first law of thermodynamics. If we solve for E in terms of the variables S and V, this law states that dE is an *exact differential*. The resulting function $U(S, V) = E(S, V)$ is called the *thermodynamic internal energy* of the system.

It is important to realize the following important fact. We started with a *state function* $S(E, V)$, the entropy of the system. Because S is a state function, it can be differentiated. Its differential dS is an exact differential. By solving for dE, when E is a function of S and V, we also get an exact differential.

The first law is often expressed as:

$$dU = \delta Q - \delta W \tag{2.19}$$

is an exact differential. The quantity δQ represents a change in heat while the quantity δW represents work done on the system. By comparing Eqs. (2.18) and (2.19) we find a common expression for the entropy in terms of heat:

$$dS = \frac{\delta Q}{T}.$$

We notice that while δQ is *not* an exact differential, the ratio $\delta Q/T$ is.

2.2.3. Second Law. The second law states that if an *isolated system*[17] undergoes a change in thermodynamic state such that the initial and final states are equilibrium states, the entropy of the final state is not smaller than that of the initial state, i.e.

$$dS \geq 0.$$

For this system, the independent variables are (N, V, E). If the entropy were a function of these variables $S(N, V, E)$, its differential would be:

$$dS(N, V, E) = \frac{\partial S}{\partial N} dN + \frac{\partial S}{\partial V} dV + \frac{\partial S}{\partial E} dE.$$

By definition of an isolated system, N and E cannot change. Only V can change. Now, V cannot decrease without disturbing its isolation, i.e. decreasing V increases the pressure P, which in turn changes the temperature (and energy).

Therefore, increasing V is the only option. An example is the free expansion of a gas when one of the containing walls is suddenly removed. Thus, the second law states that S is a nondecreasing function of V.

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[17] An isolated system is one which cannot interact with its surroundings. Its energy and mass should remain constant. The walls are treated as mirror boundary conditions.

This can also be seen from the definition of entropy:

$$S(E) = k_B \log W(E).$$

As V increases, the number of microstates increases, i.e. W is a nondecreasing function of V. This can be seen from the fact that $W(E)$ is the volume of phase-space corresponding to a total energy $\mathcal{H}(\mathbf{p}, \mathbf{q}) = E$:

$$W(E) = \frac{1}{\delta E} \int_{E<\mathcal{H}(\mathbf{x})<E+\delta E} d\mathbf{x}.$$

If V, the physical dimension of our system, increases this integral which has a positive integrand can only increase.

The simplest way to see this is to consider the example of an ideal gas in a box of volume V. The Hamiltonian $\mathcal{H}(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^{N} \vec{p}_i^{\,2}/2m$ is independent of $\vec{q}$. Therefore, the integral over $\vec{q}$ is proportional to V_N and $W(E)$ scales with V_N. The condition $E < \mathcal{H}(\mathbf{x}) < E + \delta E$ does not pose any restrictions on the integration over q because $\mathcal{H}$ does not depend on $\vec{q}$.

A formulation of the *second law of thermodynamics* asserts that

$$dS = \frac{\delta Q}{T}$$

is an exact differential. In the statistical mechanics, this statement follows by construction: S is a state function and differentiating it gives an exact differential. In mathematical terms, while δQ may be inexact, its multiplication by $1/T$ makes the resulting product exact. $1/T$ is called an *integrating factor.*

2.2.3.1. *Summary of the first two laws.* The first two laws of thermodynamics can be summarized as follows: δW and δQ themselves are not exact differentials, but the combinations $\delta Q - \delta W$ and $\delta Q/T$ are exact. In the statistical approach, dU and dS are exact differentials by construction. The content of the thermodynamic laws, in this view, is the introduction of the idea of heat.

2.2.4. Heat Capacity. THe most important response functions are the heat capacities. They describe the quantity of heat TdS that must be added to a system in order to achieve an increase of the temperature by dT. If these quantities of heat transfer refer to a gram, a mole, or a single particle of the substance in question, they are called specific heats. One still has to distinguish which system variables are kept constant.

The mean energy of a system in thermal equilibrium

$$U \equiv \langle E \rangle = \frac{1}{Z} \sum_i E_i e^{-\beta E_i},$$

can be expressed in terms of the partition function as,

$$U = -\left(\frac{\partial \log Z}{\partial \beta}\right)_V . \tag{2.20}$$

So knowing the partition function as a function of β allows us to find the mean energy. Furthermore, differentiating U with respect to temperature gives the heat capacity at constant volume

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial U}{\partial \beta}\frac{\partial \beta}{\partial T} = k_B\beta^2\left(\frac{\partial^2 \log Z}{\partial \beta^2}\right)_V . \tag{2.21}$$

where

$$\frac{\partial \beta}{\partial T} = \frac{\partial}{\partial T}\frac{1}{k_B T} = -\frac{1}{k_B T^2} = -k_B\beta^2.$$

In a change in which the volume constraint V does not vary, no mechanical work is done on the system. So any change in the energy must be due entirely to a flow of heat,

$$C_V dT = TdS,$$

where S is the entropy as defined in classical statistical thermodynamics. Hence,

$$\boxed{C_V = -\beta\left(\frac{\partial S}{\partial \beta}\right)_V = T\frac{\partial S(T,V,N)}{\partial T} = -T\frac{\partial^2 F(T,V,N)}{\partial T^2}.}$$

The relation $dU = TdS$ tells us that the heat absorbed (TdS) is equal to the change of energy (dU), which also leads us to $C_V = \partial U/\partial T$. Being the second derivative of the free energy with respect to temperature, C_V has to be related to a variance or covariance. To find this relation we consider

$$U(T,V,N) = -\frac{\partial}{\partial \beta}\log Z,$$

and using $\frac{\partial}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial}{\partial \beta}$, we obtain

$$\frac{\partial U(T,V,N)}{\partial T} = \frac{1}{k_B T^2}\frac{\partial^2}{\partial \beta^2}\log Z = \frac{1}{k_B T^2}\left(\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2\right) = \frac{1}{k_B T^2}\left(\langle \mathcal{H}^2\rangle - \langle \mathcal{H}\rangle^2\right). \tag{2.22}$$

Therefore,

$$C_V = \frac{1}{k_B T^2} var(\mathcal{H}(\mathbf{x})).$$

where $\mathbf{x}$ stands for the random vector of positions and momenta. Hence, C_V is proportional to the variance of the energy. Both $U(T,V,N)$ and $var(\mathcal{H}(\mathbf{x}))$ are $O(N)$. We also find that $C_V \geq 0$. For an ideal gas $U = \frac{3}{2}k_B NT$ we obtain

$$C_V = \frac{3}{2}k_B T.$$

When the number of particles and the pressure are kept constant (rather than volume), the heat capacity is

$$\boxed{C_P = T\frac{\partial G(T,P,N)}{\partial T} = -T\frac{\partial^2 G(T,P,N)}{\partial T^2}.}$$

Since

$$dH = TdS + VdP + \mu dN,$$

the absorption of heat at constant pressure (and constant number of particles) results in a change of enthalpt, and C_P can also be expressed in the form

$$C_P = \frac{\partial H(T,P,N)}{\partial T}.$$

Note that we consider there the enthalpy as a function of T, P, N, not of S, P, N. The enthalpy $H(T,P,N)$ can be written as

$$H(T,P,N) = -\frac{\partial}{\partial \beta}\log Y',$$

and with $\frac{\partial}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial}{\partial \beta}$ one thus obtains

$$\frac{\partial H(T,P,N)}{\partial T} = \frac{1}{k_B T^2}\frac{\partial^2}{\partial \beta^2}\log Y'.$$

In analogy with (2.22) one finally gets

$$C_P = \frac{1}{k_B T^2} var\left(\mathcal{H}(\mathbf{x}) + PV\right),$$

where the variance is now determined from the density $\rho(\mathbf{x}, V|T,P,N)$. From this expression for C_P it follows that $C_P \geq 0$. For an ideal gas the enthalpy is

$$H(T,P,N) = U(T,P,N) + PV(T,P,N) = \frac{3}{2}Nk_BT + Nk_BT = \frac{5}{2}NK_BT$$

and therefore

$$C_P = \frac{5}{2}k_B N.$$

Intuitively, one would also expect that $C_P > C_V$. To obtain an increase of temperature at constant pressure additional energy is needed, because some of that energy transferred goes towards increasing the volume ($P - V$ work).

2.2.5. Third law. Substituting from Eq.(2.21) for C_V, dividing both sides by β and integrating with respect to β,

$$\begin{aligned}\int d\beta \left(\frac{\partial S}{\partial \beta}\right)_V &= -\, k_B \int d\beta\, \beta \left(\frac{\partial^2 \log Z}{\partial \beta^2}\right)_V \\ S - \Phi(V) &= -\, k_B\beta\frac{\partial \log Z}{\partial \beta} + k_B \int d\beta\, \frac{\partial \log Z}{\partial \beta} \\ &= -\, k_B\beta\frac{\partial \log Z}{\partial \beta} + k_B \log Z + \Phi'(V)\end{aligned}$$

we get the following expression for the system's entropy:

$$S = -k_B\beta\left(\frac{\partial \log Z}{\partial \beta}\right)_V + k_B \log Z + \Phi''(V),$$

where $\Phi''(V)$ is a function of the constraints alone. The *third law of thermodynamics* requires the entropy of the system to tend to a constant value as $T \to 0$, independently of the constraints. Hence it follows that $\Phi''(V) = 0$ and the entropy is

$$S = -k_B \beta \left(\frac{\partial \log Z}{\partial \beta} \right)_V + k_B \log Z. \tag{2.23}$$

2.2.5.1. *Interpretation of the third law.* This equation has the following interpretation. As we have shown previously, the fluctuations in energy δU of a macroscopic system are usually small. Starting from the definition of partition function as the Laplace transform of the density of states:

$$Z(\beta) = \int_0^\infty dE\, e^{-\beta E} W(E),$$

we can approximate the partition function by neglecting the microstates whose energy lies outside the range $[U, U + \delta U]$:

$$Z \approx \delta U \cdot W(U) e^{-\beta U}, \tag{2.24}$$

where $\delta U \cdot W(U)$ is the number of microstates of the system in the range $[U, U + \delta U]$. Using (2.24) into (2.23) for the entropy, and bearing in mind Eq.(2.20) for U,

$$S = k_B \beta U + k_B \log Z = k_B \beta U + k_B \left(\log \delta U W(U) - \beta U \right), \tag{2.25}$$

we find the Boltzmann definition of entropy:

$$S = k_B \log W + k_B \log \delta U \approx k_B \log W \qquad \text{(since δU is small).}$$

So the classical entropy is a measure of the number of microstates accessible to the system.

2.2.6. Supplemental Readings. The following textbooks are recommended reading:

- M. Toda, R. Kubo, N. Saito, *Statistical physics I*, 2nd edition, Springer (1998)
- D.A. McQuarrie, *Statistical Mechanics*, 2nd edition, University Science Books (2000)
- K. Huang, *Statistical Mechanics*, 2nd edition, Wiley (1987)
- G. Lebon, D. Jou, J. Casas-Vázquez, *Understanding non-equilibrium thermodynamics: foundations, applications, frontiers*, Springer (2008)

2.3. Problems

Problem 78. Show that there is a relation (R is the gas constant)

$$C_p = C_v + R$$

between the isobaric and the isovolumic specific heats per mole of an ideal gas.

Solution. The first law of thermodynamics for an infinitesimal quasi-static process of a mole of gas is

$$\delta Q = dU + pdV.$$

Since the internal energy U of an ideal gas does not depend on the volume, V, we have $dU = C_v(T)dT$ and

$$\delta Q = C_v(T)dT + pdV.$$

The isovolume specific heat $(d'Q/dT)_V$ is in fact C_v. We rewrite this equation as

$$\delta Q = C_v dT + d(pV) - Vdp$$

and substitute $pV = RT$ to obtain

$$\delta Q = (C_v + R)dT - Vdp,$$

or

$$C_p = (\delta Q/dT)_{dp=0} = C_v + R.$$

■

Problem 79. Given the density of air at NTP (normal temperature and pressure, that is, 0°C, 1 atm), ρ=0.00129 g/cm^3, the specific heat at constant pressure c_p=0.238 cal/g deg, and its ratio to the isovolumic specific heat, γ=c_p/c_v=1.41, calculate the work equivalent of heat J. Assume air to be an ideal gas with a volume of 22.4 liters at NTP.

Solution. The gas constant, R, may be obtained in units of joule/mol deg from the ideal gas equation of state $pV = RT$. It can also be obtained in units of cal/mol deg from Mayer's equation $C_p - C_v = R$ (by the previous problem) and if we express that by R', then $J = R/R'$. The normal state (NTP) is an equilibrium state where the temperature, $T = 0°$ C=273 K, and the pressure, $p = 1$ atm=1.013×10^6 dyne/cm^2. The volume of a mole at NTP is $V = 22.4 \times 10^3$ cm^3. Hence:

$$\begin{aligned} R =& pV/T = 1.013 \times 10^6 \times 22.4 \times 10^3/273 \\ =& 8.32 \times 10^7 \text{erg/mol deg} = 8.32 \text{ joule/mol deg} \end{aligned}$$

Since the isobaric specific heat per unit mass is the isobaric heat capacity per mole divided by the mass of a mole of air (average molecular weight), m, which is

$$m = \rho V = 0.00129 \times 22.4 \times 10^3 = 28.9 \text{ g/mol},$$

we have

$$C_p = mc_p = 28.9 \times 0.238 = 6.88 \text{ cal/mol deg}.$$

The isovolumic specific heat per mole $C_v = mc_v = mc_p/\gamma = C_p/\gamma = 6.88/1.41 = 4.88$ cal/mol deg. Therefore we have

$$R' = C_p - C_v = 2.00 \text{ cal/mol deg}$$

and

$$J = R/R' = 8.32/2.00 = 4.16 \text{ joule/cal}.$$

■

Problem 80. Let δq be the heat necessary to change the temperature of a gram of a material by dT keeping the state quantity x constant. For the sake of simplicity, assume that there are only two independent variables, e.g. the specific volume, v, and the temperature, T. Show that the specific heat c_x is given by the equation

$$c_x = \left(\frac{\delta q}{dT}\right)_x = \left(\frac{\partial u}{\partial T}\right)_v + \left\{\left(\frac{\partial u}{\partial v}\right)_T + p\right\}\left(\frac{\partial v}{\partial T}\right)_x$$

where u is the internal energy per unit mass and p is the pressure.

Solution. Since the mass of the system is constant, we need only consider the work done by the pressure. The first law of thermodynamics applied to unit mass is

$$\delta q = du + pdv.$$

The change du in u due to changes dT and dv in T and v is

$$du = (\partial u/\partial T)_v dT + (\partial u/\partial v)_T dv.$$

Substituting this into the equation for δq, we have

$$\delta q = \left(\frac{\partial u}{\partial T}\right)_v dT + \left\{\left(\frac{\partial u}{\partial v}\right)_T + p\right\} dv.$$

Although the parameter x is given as a function of T and v for equilibrium states, it is possible to consider v as a function of T and x taking T and x as the independent variables. Thus if x is kept constant and T is changed, $dv = (\partial v/\partial T)_x dT$. Substituting this into the above equation we obtain the answer. ■

Problem 81. (i) Calculate the heat necessary to heat air which has a volume of 27 m^3 at one atmosphere from 0°C to 20°C at constant volume.
(ii) How much heat is necessary if the initial volume at 0°C is 27 m^3 and the air is heated to 20°C at constant pressure?
(iii) If the air is in an insulated room of 27 m^3 with a small leaking hole connected to the outside at 1 atm, how much heat must be put into the room to raise the temperature slowly from 0°C to 20°C? Refer to problem 2 for the characteristics of air. Consider the specific heat to be constant.

Solution. (i) This is a case of isovolumic heating. The mass M of air which has a volume of 27 m^3 at 0° C and 1 atm is calculated from its density, ρ=0.00129 g/cm^3, as

$$M = 0.00129 \times 27 \times 10^6 = 3.48 \times 10^4 \text{ g}.$$

The isovolumic heat capacity C_v is calculated from the isovolumic specific heat

$$c_v = c_p/\gamma = 0.238/1.41 = 0.169 \text{ cal/g deg},$$

$$C_v = Mc_v = 10.169 \times 3.48 \times 10^4 = 5.88 \times 10^3 \text{ cal/deg.}$$

Considering the heat capacity as constant, the heat Q_v, necessary to raise the temperature T_1 to T_2 is

$$Q_v = \int_{T_1}^{T_2} C_v dT = (T_2 - T_1)C_v = 20 \times 5.88 \times 10^3 = 1.176 \times 10^5 \text{ cal.}$$

(ii) In the case of isobaric heating we use the isobaric heat capacity C_p instead of C_v:

$$C_p = Mc_p = \gamma C_v = 1.41 \times 5.88 \times 10^3 = 8.29 \times 10^3 \text{ cal/deg.}$$

Then the desired heat Q_p is

$$Q_p = (T_2 - T_1)C_p = 20 \times 8.29 \times 10^3 = 1.658 \times 10^5 \text{ cal.}$$

(iii) We may assume that the pressure in the room is maintained at 1 atm since the heating is slow. When the air is heated at constant pressure, p, and constant volume, V, the mass of the air, $M(T)$, in the room at temperature T can be determined from the equation of state $pV = RTM/m$ (m is the average molecular weight of air), or $M(T)T = const.$ If the mass of the air in the room is M_1 when the temperature is T_1, then $M(T) = M_1T_1/T$. Since the air of mass $M(T)$ is being heated at constant pressure, its heat capacity is $M(T)c_p$, so that the heat required to raise the temperature to T_2 is

$$Q = \int_{T_1}^{T_2} M(T)c_p dT = c_p M_1 T_1 \int_{T_1}^{T_2} \frac{dT}{T} = c_p M_1 T_1 \log \frac{T_2}{T_1}.$$

Since T_1=0° C=273 K, T_2 = 20° C=293 K and $C_p = 8.29 \times 10^3$ cal/deg as calculated above, so

$$Q = 8.29 \times 10^3 \times 273 \times \log \frac{293}{273} = 2.26 \times 10^6 \times 0.0706 = 1.596 \times 10^5 \text{ cal.}$$

■

Problem 82. A magnetic body is inserted in a coil and is magnetized by the magnetic field created by a current through the coil. For the sake of simplicity, assume that the field, **H**, and the magnetization, **M**, are uniform throughout the magnetic body. Show that the work done by the electric source in the process of magnetization is

$$A = \int_0^M \mathbf{H} \cdot d\mathbf{M}$$

per unit volume of the magnetic body. Assume that the magnetic body has no deformation by magnetization.

Solution. Let us consider the case where a coil is wound around a sufficiently long cylindrical magnetic body. The magnetic field in a coil with n turns per unit length $H_J = 4\pi nJ/c$ when a current J is passed through the coil. The field H inside the magnetic material is the sum of H_J and the demagnetizing field H_M, which, however, is small if the specimen is a long needle. Therefore, we may assume here $H = H_J$. If the coil is wound over the entire length of the cylinder, whose length is l and cross-sectional area is σ, the flux through the coil is

$$\Phi = \sigma n l B = V n B,$$

where, $V = \sigma l$ is the volume of the magnetic body and $B = H + 4\pi M$ is the flux density in the magnetic body. When the current J is increased, then H and M and accordingly B, also change so that a counter-electromotive force

$$-(1/c)d\Phi/dt = -V(n/c)dB/dt$$

is induced, according to Faraday's induction law. The work which the electric source must do against this counter-electromotive force in a time interval dt as a charge

$$Jdt = \tfrac{1}{4}cH_J dt/\pi n$$

passes through each section of the wire, is

$$\begin{aligned}(1/c)(d\Phi/dt)Jdt =& \tfrac{1}{4}VHdB/\pi = \tfrac{1}{4}V(HdH + 4\pi HdM)/\pi\\ =& d[\tfrac{1}{8}VH^2/\pi] + VHdM.\end{aligned}$$

Of this work, $d[\frac{1}{8}VH^2/\pi]$ is the work which is needed to create a field H irrespective of the presence of the magnetic body. Thus, the work HdM can be identified with the work per unit volume required to increase the magnetization, M, by dM. Hence, $A = \int_0^M HdM$ is the work per unit volume required to increase the magnetization from 0 to M. (If it were possible to fix the final value of magnetization at M, then the work $\frac{1}{8}VH^2/\pi$ would be fed back to the electric source in the process of decreasing H to zero, because then we would have $dB = dH$.) ■

Problem 83. The Hamiltonian of a classical gas of N interacting particles, each of mass m, is

$$\mathcal{H}(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U(q_1, \ldots, q_N).$$

Show that the partition function is the product of two terms, one depending only on the kinetic term and one only on the potential term. Find an expression for the mean kinetic energy of each particle as function of temperature. Some marbles of mass 10 g are being shaken about in a box, with a mean speed of 1 m/s. Find the temperature associated with the motion of the marbles. Why doesn't the box catch fire?

Solution. The partition function is

$$\begin{aligned}Z =& \int dp_1 \ldots dp_N dq_1 \ldots dq_N e^{-\mathcal{H}(\mathbf{p},\mathbf{q})/k_BT}\\ =& \int dp_1 \ldots dp_N e^{-\sum p_i^2/2mk_BT} \int dq_1 \ldots dq_N e^{-U(q_1,\ldots,q_N)/k_BT}\end{aligned}$$

which is in the factorized form. The mean kinetic energy of particle 1 is

$$E = \frac{1}{Z} \int dp\, dq\, (p_1^2/2m) e^{-\mathcal{H}(\mathbf{p},\mathbf{q})/k_B T}$$

The integrals over the q_i and over p_2 to p_N cancel, leaving a Gaussian integral: the result is $E = k_B T d/s$ where d is the number of dimensions.

Treating the marbles as being in thermal equilibrium gives $T \sim 10^{20}$ K. However, only the degrees of freedom associated with the motions of the centers of mass of the marbles are at this temperature. The remaining $\sim N_A$ degrees of freedom per marble are only at room temperature, so what the shaking stops and the energy of motion gets shared out evenly between the modes, the actual temperature rise is only a small fraction of a degree.

The factorization of Z for a classical system means that the kinetic energy term holds no interesting information. Quantum-mechanically Z does not factorize, because the q_i and p_i do not commute. However, we are often concerned with long-distance phenomena, for which classical physics is presumably a good approximation. ■

Problem 84. Let us look at a very simplified model for a collision of molecules undergoing a catalytic reaction. Consider a very small region of space (nm in size) – the collision volume – containing an organic molecule with n carbon-carbon triple bonds. The small volume also contains a dihydrogen and a difluorine molecule and a catalyst which is able to attach an H (or F) atom across any of the unsaturated bonds. When both an H and F atoms are attached across the same carbon-carbon bond, the energy of the system is lowered by κ (this favorable energetic situation is only possible with a catalyst!). The Hamiltonian for this system is $\mathcal{H}(r_1, r_2) = -\kappa\delta_{r_1,r_2}$, where r_1 and r_2 are integers running from 1 to n labelling the positions of the two atoms. Show that the probability of finding the two particles attached across the same carbon-carbon bond is $p = 1/(1 + (n-1)e^{-\beta\kappa})$. The system is thermally isolated, and then n is increased from 2 to 6 without any work being done. What is the new temperature of the system?

Solution. This problem can be reduced to the problem of placing two different balls in n boxes, if we assume that the chemical bonding is done in such a way as to ensure that each carbon bond is sufficiently saturated. δ_{r_1,r_2} is 1 when the balls are in the same box, and 0 otherwise, so its thermal average is the required probability p. This average can be obtained by differentiating Z since δ_{r_1,r_2} appears in $\mathcal{H}$:

$$Z = \sum_{r_1,r_2=1}^{n} e^{\beta\kappa\delta_{r_1,r_2}} = n(n-1+e^{\beta\kappa}); \qquad p = \frac{1}{\beta}\frac{\partial \log Z}{\partial \kappa},$$

which gives the required answer. $-\kappa p$ is the mean energy; since the change in n takes place at constant energy, equating the mean energies for $n = 2$ and $n = 6$ gives

$$T' = \frac{1}{(k_B/\kappa)\log 5 + T^{-1}},$$

this shows a decrease in temperature. ■

Problem 85. At sufficiently low temperatures, the partition function of a system with discrete microstates can be written

$$Z \approx n_0 e^{-\beta E_0} + n_1 e^{-\beta E_1},$$

where E_0 and E_1 are the two lowest energies of the system, and n_0 and n_1 are the number of microstates with each energy. Use this expression for Z to calculate the entropy S using ($\beta = 1/k_B T$)

$$S = -k_B \beta \left(\frac{\partial \log Z}{\partial \beta} \right)_{\{V\}} + k_B \log Z + \Phi(\{V\}),$$

where $\Phi(\{V\})$ is a function of the physical constraints $\{V\}$ of the system (e.g. system's volume), in the limit $T \to 0$, and show that the third law of thermodynamics requires $\Phi(\{V\}) = 0$.

Solution. We have

$$S = k(\log n_0 + \frac{n_1}{n_0} e^{-\beta \Delta E}(1 - \beta \Delta E) + O(e^{-2\beta \Delta E})) + \Phi(\{V\}),$$

where $\Delta E \equiv E_2 - E_1$. When $\beta \to \infty$ this becomes

$$S = k \log n_0 + \Phi(\{V\}).$$

Unless Φ is a constant, the entropy at absolute zero depends on the constraints, which contradicts the third law. ■

Problem 86. Consider a system of N interacting two-state spins, with interactions so strong that the only significant terms in the partition function are those with all the spins pointing in the same direction. Write down the partition function for this system. Calculate the average magnetization per spin – what form does it have in the limit $N \to \infty$?

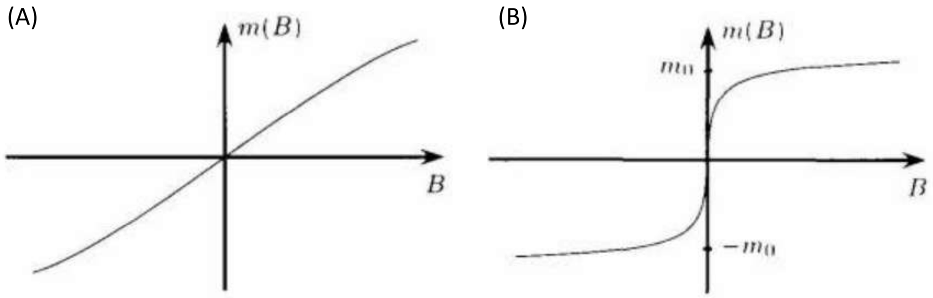
Solution. The partition function of this system in a magnetic field B is

$$Z_N = e^{-\beta N \mu B} + e^{\beta N \mu B} = 2 \cosh(N \beta \mu B)$$

we've taken the zero of the spin interaction energy to be when all spins are aligned. The magnetization per spin is

$$m = \tanh(N \mu B).$$

In the limit $N \to \infty$ this has the form (B) rather than (A) in the figure below:



■

Problem 87. Derive the rotational partition function $r(T)$ for a heteronuclear diatomic molecule (explain all steps of the derivation):

$$r(T) = \sum_{l=0}^{\infty}(2l+1)\exp\left[-\frac{\hbar^2 l(l+1)}{2Ik_BT}\right] = \sum_{l=0}^{\infty}(2l+1)\exp\left[-\frac{\Theta_r}{T}l(l+1)\right]$$

Give the high temperature expansion of $r(T)$ using Euler-Maclaurin's summation formula. Calculate the value of $r(T)$ at $T = 300.4$ K for HCl ($\Theta_r/T = \hbar/2Ik_B = 15.02$ K, where I is the moment of inertia of the molecule) and find the deviation from the classical value of T/Θ_r.

Solution. For a derivation see, e.g., McQuarrie or Bloch. At high temperatures $T \gg \Theta_r$, one can utilize the Euler-Maclaurin's summation formula

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} f(x)dx + \tfrac{1}{2}f(0) - \tfrac{1}{12}f'(0) + \tfrac{1}{720}f'''(0) - \tfrac{1}{30240}f^V(0) + \dots$$

$f(x)$ being analytic for $0 < x < \infty$

Putting $f(x) = (2x+1)\exp(-x(x+1)\sigma)$, with $\sigma = \Theta_r/T$, one has

$$\int_0^{\infty} f(x)dx = \int_0^{\infty}(2x+1)e^{-x(x+1)\sigma}dx = \frac{1}{\sigma}\int_0^{\infty} e^{-\xi}d\xi = \frac{T}{\Theta_r}, \tag{2.26}$$

and

$f(0) = 1, \quad f'(0) = 2-\sigma, \quad f'''(0) = -12\sigma+12\sigma^2-\sigma^3, \quad f^V = 120\sigma^2-180\sigma^3+30\sigma^4-\sigma^5, \dots,$

so that

$$\begin{aligned} r(T) =& \frac{1}{\sigma} + \frac{1}{3} + \frac{\sigma}{15} + \frac{4\sigma^2}{315} + O(\sigma^3) \\ =& \frac{T}{\Theta_r}\left\{1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\Theta_r}{T}\right)^3 + O(\left(\frac{\Theta_r}{T}\right)^4\right\} \end{aligned} \tag{2.27}$$

Equation 2.26 gives the classical partition function.

For HCl one has $\sigma = 1/20$ at 300.4 K. Hence

$$\begin{aligned} r(T)_{classical} &= 20 \\ r(T) &= 20.333\ldots \qquad \text{(up to 2nd term in Eq. 2.27)} \\ r(T) &= 20.33666\ldots \qquad \text{(up to 3rd term in Eq. 2.27)} \\ r(T) &= 20.336698\ldots \qquad \text{(up to 4th term in Eq. 2.27)} \end{aligned}$$

■

Problem 88. Consider an ideal gas molecule AB which undergoes the dissociation reaction $AB \leftrightharpoons A + B$. If n_A, n_B and n_{AB} are the concentrations (the numbers of molecules per unit volume) of each molecule respectively, show that:

$$\frac{n_{AB}}{n_A n_B} = K(T) = \frac{V f_{AB}}{f_A f_B} e^{w_0/kT} = \left[\frac{(m_A + m_B)h^2}{2\pi m_A m_B kT}\right]^{3/2} \frac{j^0_{AB}}{j^0_A j^0_B} e^{w_0/kT}$$

where f_A etc. are the partition functions per molecule, V is the volume of the container and $j^0_A, \ldots$ are the partition functions for the internal degrees of freedom of each molecule. The zero of the energy for each molecule is chosen at the ground state (not including the zero point energy of the vibration) of the respective molecules so that $w_0 = \epsilon^0_A + \epsilon^0_B - \epsilon^0_{AB}$ is the difference in the energy zeros. What does this result tell us about the dissociation reaction?

Note: Your starting point should be to treat gas mixtures as ideal gases. The partition function of a mixture of N_A molecules of type A, N_B of type B, $\ldots$ confined in a box of volume V is given by a product

$$Z_{N_A,N_V,\ldots}(V,T) = \prod_{A,B,\ldots} \left(\frac{2\pi m_A kT}{h^2}\right)^{\frac{3}{2}N_A} \frac{V^{N_A}}{N_A!} (j_A)^{N_A} \equiv \prod_{A,B,\ldots} \frac{f_A^{N_A}}{N_A!}$$

where $f_A, f_B, \ldots$ are the partition functions of molecules $A, B, \ldots$ and $j_A, j_B, \ldots$ are the internal partition functions of each species of molecules, i.e. in the present case,

$$f_A = \left(\frac{2\pi m_A kT}{h^2}\right)^{3/2} V j^0_A e^{\epsilon^0_A/kT}, \qquad \text{etc.}$$

Solution. The partition function of the ideal gas occupying a volume V, which contains N_A, N_B and N_{AB} molecules is given by

$$Z(N_A, N_B, N_{AB}, V, T) = \frac{f_A^{N_A} f_B^{N_B} f_{AB}^{N_A B}}{N_A! N_B! N_{AB}!}.$$

This can also be considered to be proportional to the probability of finding N_A, N_B and N_{AB} molecules in V at temperature T. The equilibrium distribution is the most probable distribution and is determined by maximizing this Z:

$$\log Z(N_A, N_B, N_{AB}) = \sum_{\sigma=A,B,AB} [N_\alpha \log f_\alpha - N_\alpha \log N_\alpha + N_\alpha] = max.$$

This is subject to the constraints:

- the total number of $A = N_A + N_{AB} = const$
- the total number of $B = N_B + N_{AB} = const.$

Therefore one obtains

$$\delta \log Z = \delta N_A \cdot \log(f_A/N_A) + \delta N_B \cdot \log(f_B/N_B) + \log(f_{AB}/N_{AB}) = 0,$$
$$\delta N_A + \delta N_{AB} = 0, \qquad \delta N_B + \delta N_{AB} = 0,$$

so that

$$\delta \log A = [-\log(f_A/N_A) + \log(f_B/N_B) + \log(f_{AB}/N_{AB})]\, \delta N_{AB} = 0,$$

and hence

$$\frac{N_{AB}}{N_A N_B} = \frac{f_{AB}}{f_A f_B}$$

or

$$\frac{n_{AB}}{n_A n_B} = \frac{V f_{AB}}{f_A f_B} = K.$$

Substituting

$$f_A = \left(\frac{2\pi m_A kT}{h^2}\right)^{3/2} V j_A^0 e^{-\epsilon_A^0/kT}$$

etc. and $m_{AB} = m_A + m_B$, one has the final result for K.

Note: if one uses the internal partition function $\prod(1 - e^{-\Theta_v/T})$, which does not include the zero point energy of the vibration, instead we must put $w_0 = \epsilon_A^0 + \epsilon_B^0 - \epsilon_{AB}^0 + \frac{1}{2}\sum(h\nu_A + h\nu_B - h\nu_{AB})$. This is equal to the energy change in this reaction at 0 K. ■

Problem 89. Apply the principle of maximum entropy to show that the Gibbs-Shannon entropy $S = -k_B \sum_i p_i \log p_i$ reduces to the Boltzmann entropy $S = k_B \log W(E)$.

Solution. The Gibbs or Gibbs-Shannon entropy for a probability distribution $\{p_i\}$ is defined by:

$$S = -k_B \sum_i p_i \log p_i.$$

We maximize the expression for S subjected to the constraint $\sum_i p_i = 1$. This is done by using the method of Lagrange multipliers:

$$\delta\left(-k_B \sum_i p_i \log p_i - \lambda \sum_i p_i\right) = 0.$$

Applying the variation operator δ, we get:

$$\sum_i -k_B\left[\delta p_i \cdot \log p_i + p_i \cdot \frac{1}{p_i}\delta p_i\right] - \lambda \delta p_i = 0.$$

factoring δp_i we have

$$\sum_i \left[-k_B(\log p_i + 1) - \lambda\right]\delta p_i = 0.$$

But in the microcanonical ensemble you will recall that the probability distribution consistent with a given energy is given by the principle of equal probabilities. This is consistent with the result $p_i = 1/N$. We know from the microcanonical ensemble that this probability must be related to the phase-space volume according to

$$p_i = \frac{1}{N} = \frac{1}{W(E)}.$$

Therefore, we have

$$S = -k_B \sum_i p_i \log p_i = -k_B N \cdot p_i \log p_i = -k_B N \cdot \frac{1}{N}\log 1/N = k_B \log W(E).$$

Thus, in the thermodynamic equilibrium, the Gibbs-Shannon entropy coincides with the Boltzmann entropy. ■

Problem 90. Velocity autocorrelation function. a) Plot the velocity autocorrelation function for the three cases γs=0, 1 and 5. Show a graph of $\langle v(t)v(s)\rangle M/k_B T$ vs. γt over the range of values $\gamma t \in [0, 10]$.

b) In the notes, we derived analytically the velocity autocorrelation function for a particle moving in 1D. We also learned earlier that mean values, such as $\langle v(t)v(s)\rangle$, can also be calculated probabilistically. In abstract language, it is the sum (integral) of $v_t(\omega)v_s(\omega)$ weighted by the probability of a particular path ω, $dP(\omega)$:

$$\langle v(t)v(s)\rangle = \int_\Omega v_t(\omega)v_s(\omega)dP(\omega)$$

where the integral is over Ω (i.e. the set of all possible paths ω's). Let us solve this integral numerically by simulating the Ornstein-Uhlenbeck process.

The paths can be generated using the following SDE, which defines the increments of the random process $v_t(\omega)$:

$$dv_t(\omega) = -\gamma v_t(\omega)dt + \frac{\Gamma}{M} dW_t(\omega).$$

Take $s = 0$ and $v(0) = 1$. Generate a large number of trajectories ω for $v_t(\omega)$ using this SDE. Remember that dW_t stands for the increment of the Wiener process. By definition, it is Gaussian-distributed, with mean zero and variance dt. You will need to choose a step size dt and discretize the time axis. We shall fix $\gamma = M = k_B = T = 1$ and $\Gamma = \sqrt{2}$.

The discretized equation becomes,

$$v_{t+\Delta t} = v_t - \gamma v_t \Delta t + \frac{\Gamma}{M} \Delta W_t,$$

where $\Delta W_t \sim N(0, \Delta t)$ and $v_0 = 1$.

Write a computer program that iterates this equation from $t = 0$ up to $t = 10$. Plot two of these trajectories. Compute the arithmetic average over all $(n > 1{,}000)$ paths, to get a numerical approximation to the velocity autocorrelation function:

$$\langle v(t)v(s)\rangle \approx \frac{1}{N} \sum_{i=1}^{N} v_t(\omega_i) v_0$$

Plot the autocorrelation function $\langle v(t)v(s)\rangle$ as function of time, from $t = 0$ to $t = 10$. A suggested time step is $\Delta t = 0.01$. Check that this numerical solution is in agreement with the analytical result we have derived in class:

$$\langle v_t v_s\rangle = (k_B T/M) \exp\left[-\gamma|t-s|\right].$$

Solution. Substituting the starting velocity $\langle v_0^2\rangle = 2v_T^2 = 2k_BT/M$ into the expression

$$\langle v(t)v(s)\rangle = \left(\langle v_0^2\rangle - \frac{k_BT}{M}\right) e^{-\gamma(t+s)} + \frac{k_BT}{M} e^{-\gamma|t-s|}.$$

and rearranging the terms gives:

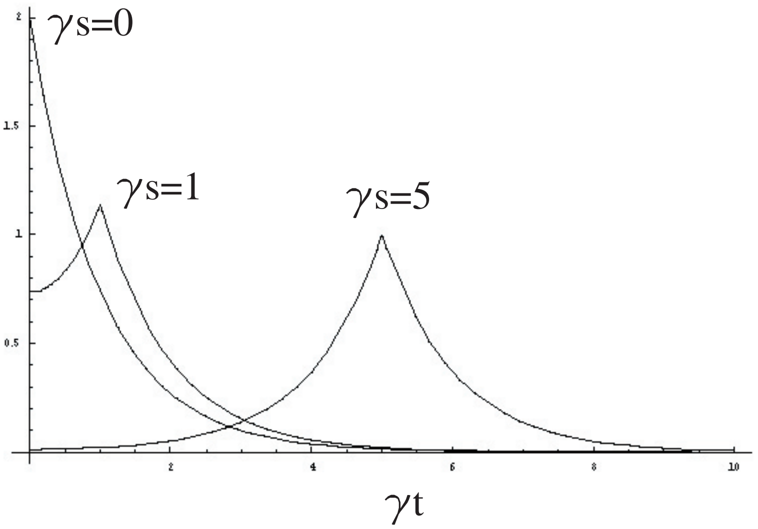
$$\langle v(t)v(s)\rangle \frac{M}{k_BT} = e^{-\gamma(t+s)} + e^{-\gamma|t-s|}.$$

The following command in Mathematica

```
Plot[Exp[-γt] +
      Exp[-Abs[γt]], Exp[-γt - 1] +
      Exp[-Abs[γt - 1]], Exp[-γt - 5] +
      Exp[-Abs[γt - 5]], {γt, 0, 10 }]
```

can be used to produce the following plot: The following Matlab program will work.

```
dt=0.01;
Gamma=sqrt(2); M=1; gamma=1; v0=1;
np=10000; % number of random paths to simulate
```



```
nt=1000; % number of time steps
dWt=sqrt(dt)*randn([np nt]); % generate steps
IVt=v0*ones([np nt]);
for j=2:nt, % integrate SDE
 IVt(:,j)=IVt(:,j-1)*(1-gamma*dt)+(Gamma/M)*dWt(:,j);
end;
EV0Vt=sum(IVt,1)/np; % calc vv autocorrel fn
Path1=IVt(1,:); % extract two paths, 1st
Path2=IVt(2,:); % 2nd
figure;plot(dt*(1:nt),[Path1 ; Path2]); % Plot 2 sample paths
xlabel('time');ylabel('v_t(\omega)');legend('\omega_1','\omega_2');
figure;plot(dt*(1:nt),EV0Vt); % Plot E[v0vt] vs. time
xlabel('time');ylabel('<v_0 v_t>');
```

The results of this simulation are shown in Figure 2.7.

The easiest way to check that the numerical solution is in agreement with the analytical formula is to check that the decay constant of $\langle v_0 v_t\rangle = e^{-\gamma|t|}$ is $\gamma = 1$. The time γ^{-1} corresponds to the point where $\langle v_0 v_t\rangle$ decays to $1/e \approx 0.37$ of its initial value (this can be seen directly from the plot). Also we see that the fall-off is an exponential decay, as it should be. ■

Problem 91. Consider a Brownian particle whose position as function of time is described by the differential equation $dx(t) = v(t)dt$, with $v(t)$ obeying the Ornstein-Uhlenbeck process. Show that the mean particle position is $\langle x(t)\rangle = \frac{v_0}{\gamma}(1 - e^{-\gamma t})$ (assuming an initial

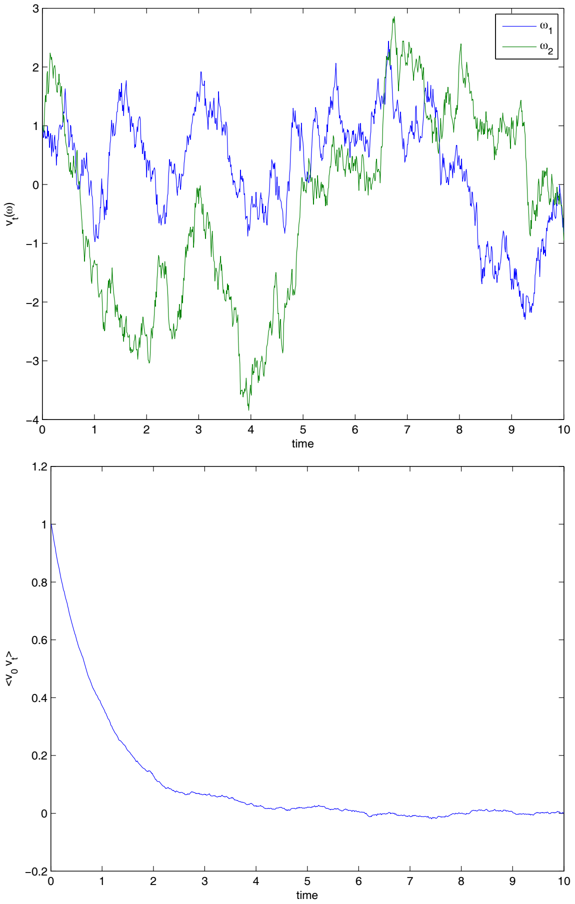


Figure 2.7. The first plots shows two different realizations ω_1, ω_2 of the Itô process. The second plot is the velocity autocorrelation function $\mathbb{E}[v_0 v_t]$. The calculation of expectation value uses 10,000 sample paths.

condition $x(0) = 0$). Show that the mean square displacement is:

$$\langle x^2(t)\rangle = \frac{2k_BT}{M\gamma}t + \frac{v_0^2}{\gamma^2}(1-e^{-\gamma t})^2 - \frac{k_BT}{M\gamma^2}(3-4e^{-\gamma t}+e^{-2\gamma t}).$$

Show that for short times, the Brownian motion captures the ballistic motion of the particle: $\langle x(t)\rangle = v_0 t$ and $\langle x^2(t)\rangle = v_0^2 t^2$. How can a single model for Brownian motion capture both the ballistic motion as well as the diffusion behavior?

Solution. Substituting the expression we found for $v(t)$, the particle position is

$$x(t) = \frac{v_0}{\gamma}(1-e^{-\gamma t}) + \sqrt{2\gamma k_BT}M\int_0^t dt' e^{-\gamma t'}\int_0^{t'} dW(t'')e^{\gamma t''}.$$

Taking the expectation value, the second term vanishes because $\langle dW(t'')\rangle = 0$ and we get $\langle x(t)\rangle = \frac{v_0}{\gamma}(1 - e^{-\gamma t})$.

The calculation goes as follows:

$$\begin{aligned}
\langle x^2(t)\rangle =& \frac{v_0^2}{\gamma^2}(1 - e^{-\gamma t})^2 + \frac{2\gamma k_B T}{M}\int_0^t dt' e^{-\gamma t'}\int_0^t dt'' e^{-\gamma t''}\int_0^{t'} e^{\gamma\tilde{t}'}\int_0^{t''} e^{\gamma\tilde{t}''}\langle dW(\tilde{t}'')dW(\tilde{t}')\rangle,\\
=& \frac{v_0^2}{\gamma^2}(1 - e^{-\gamma t})^2 + \frac{2\gamma k_B T}{M}\int_0^t dt' e^{-\gamma t'}\int_0^t dt'' e^{-\gamma t''}\int_0^{t'\wedge t''} dt''' e^{2\gamma t'''},\\
=& \frac{2\gamma k_B T}{M}t + \frac{v_0^2}{\gamma^2}(1 - e^{-\gamma t})^2 - \frac{\gamma k_B T}{M\gamma^2}(3 - 4e^{-\gamma t} + e^{-2\gamma t}).
\end{aligned}$$

where we have used the covariance of the Wiener process.

The short-time behavior is obtained by expanding $\exp(-t) \approx 1 - t + \ldots$ in the expression found in b)

$$\begin{aligned}
\langle x^2(t)\rangle =& \frac{2\gamma k_B T}{M}t + \frac{v_0^2}{\gamma^2}(1 - e^{-\gamma t})^2 - \frac{\gamma k_B T}{M\gamma^2}(3 - 4e^{-\gamma t} + e^{-2\gamma t})\\
=& \frac{2\gamma k_B T}{M}t + \frac{v_0^2}{\gamma^2}(\gamma t + \mathcal{O}(t^2))^2 - \frac{\gamma k_B T}{M\gamma^2}(2\gamma t + \mathcal{O}(t^2))
\end{aligned}$$

and dropping the terms $\mathcal{O}(t^2)$ we get:

$$\langle x^2(t)\rangle = v_0^2 t^2.$$

Similarly the expression $\langle x(t)\rangle = \frac{v_0}{\gamma}(1 - e^{-\gamma t})$ becomes

$$\langle x(t)\rangle = v_0 t$$

in the limit of short t.

The long-time behavior, of course is that the rms displacement is proportional to $\sqrt{t}$. This is what we expect for diffusional motion. The fact that we observe ballistic motion at short times is because, in the limit of short times, the particle has not collided very many times yet and its trajectory is mostly rectilinear. At longer times, the particle undergoes significant number of collisions, and its net displacement is greatly reduced. ■

Problem 92. Calculate the canonical partition function $Z(\beta) = \int \exp(-\beta H(\mathbf{x}))d\mathbf{x}$ (integration is over all phase space) for the following systems. Then compute the mean energy $U = \langle H\rangle = -\partial \log Z/\partial\beta$, the heat capacity $C_V = \partial U/\partial T$.

a) Particle in a box. A particle of unit mass is confined to a three-dimensional box of side length L. The Hamiltonian function is

$$\mathcal{H}(\mathbf{p}, \mathbf{q}) = \frac{1}{2}(p_x^2 + p_y^2 + p_z^2).$$

b) An apple of unit mass is falling from a tree. Its Hamiltonian is the sum of kinetic and potential energies:

$$\mathcal{H}(z, \dot{z}) = \frac{\dot{z}^2}{2} + gz,$$

where g is the gravitational acceleration constant (-9.8 m/s^2). The canonical coordinates are simply $(z, \dot{z})$ and the phase space is $[0, \infty] \times [-\infty, \infty]$, i.e. the apple is constrained to fall on a table and lie above the table at $z = 0$.

Furthermore, consider the canonical density $\rho = Z^{-1}\exp(-\beta\mathcal{H})$ and integrate over all momenta to find an expression for the probability density for finding the particle in the interval $[z, z + dz]$. Show that this density decays exponentially with altitude z. What is the meaning of this exponential distribution?

c) Linear harmonic oscillator. The state is described by the coordinates $\mathbf{x} = (p, q)$ and the Hamiltonian function is

$$\mathcal{H}(p, q) = \frac{p^2}{2} + \omega^2\frac{q^2}{2}.$$

d) A "lazy" oscillator with Hamiltonian function

$$\mathcal{H}(p, q) = \frac{p^2}{2} + q^4.$$

e) Multiple independent oscillators. The Hamiltonian takes the form:

$$\mathcal{H}(p, q) = \sum_{i=1}^{N}\frac{p_i^2}{2} + \omega_i^2\frac{q_i^2}{2}.$$

Solution. a) Particle in a box. Integration over the position variables gives L^3, and making use of the formula $\int_{\mathbb{R}}\exp(-x^2)dx = \sqrt{\pi}$ gives:

$$Z(\beta) = L^3\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp(-\beta\mathcal{H}(p, q))dp_x dp_y dp_z = L^3\left(\frac{2\pi}{\beta}\right)^{3/2}.$$

From this, it is trivial to differentiate to get the internal energy and the heat capacity.

b) The partition function for the falling apple is:

$$Z(\beta) = \int_0^{\infty}\int_{-\infty}^{\infty}\exp\left(-\beta\left[\frac{\dot{z}^2}{2} + gz\right]\right)dz d\dot{z} = \frac{1}{g\beta}\cdot\sqrt{\frac{2\pi}{\beta}} = g^{-1}(2\pi)^{1/2}\beta^{-3/2}$$

It is trivial to differentiate to get the internal energy and the heat capacity.

Integrating the canonical density we get:

$$Z^{-1}\int_{-\infty}^{\infty}\exp(-\beta\mathcal{H})d\dot{z}\propto\exp(-\beta gz).$$

This exponential distribution says that as z increases it is much less likely to find the apple at that height. At "thermal equilibrium", it is most likely that we will find the apple on the table (at $z=0$). This is a consequence of the action of the gravitational force.

c) Evaluating the Gaussian integrals we find:

$$Z(\beta)=\int\int\exp\left(-\beta\left[\frac{p^2}{2}+\omega^2\frac{q^2}{2}\right]\right)dpdq=\frac{2\pi}{\omega\beta}.$$

It is trivial to differentiate to get the internal energy and the heat capacity.

d) The tricky part is to evaluate the quartic term, which requires the use of the Gamma function $\Gamma(z)=\int_0^\infty r^{z-1}e^{-r}dr$:

$$Z(\beta)=\int\int\exp\left(-\beta\left[\frac{p^2}{2}+q^4\right]\right)dpdq=\sqrt{\frac{2\pi}{\beta}}\cdot 2\Gamma(5/4)\beta^{-1/4},$$

where it is now trivial to differentiate to get the internal energy and the heat capacity. The integral $\int_0^\infty e^{-q^4}dq$ was evaluated with the substitution $r=q^4$, $dq=(1/4)r^{1/4-1}dr$ to give

$$\frac{1}{4}\int_0^\infty e^{-r}e^{1/4-1}dr=\frac{1}{4}\Gamma(1/4)=\Gamma(5/4)$$

with the use of the property $z\Gamma(z)=\Gamma(z+1)$.

e) Since the individual harmonic oscillators are independent, their partition function is simply a product of individual ones. We can use the result from c) to write:

$$Z(\beta)=\prod_{i=1}^{N}Z_i=\prod_{i=1}^{N}\frac{2\pi}{\omega_i\beta}.$$

Once again, it is now trivial to differentiate to get the internal energy and the heat capacity.

■

Chapter 3

Thermodynamics

Thermodynamics provides a framework to account for exchanges (transfers) of energy among different systems or subsets of a given system. Energy transfers can occur in the form of heat exchanges or different types of work. Thermodynamics is a topic that crosses many disciplines (physics, chemistry, engineering, life sciences, etc.). This chapter only provides a brief introduction to this vast topic. To learn more, the reader should consult the more authoritative treatises by Callen [**1**], Kittel [**2**], Moran & Shapiro [**3**], Atkins [**4**], McQuarrie & Simon [**5**], Ben-Amotz [**6**], Sonntag & Borgnakke [**7**] and Honig [**8**].

In thermodynamics the universe is divided into two parts: the system and its surroundings. We must then specify whether or not particles and heat are allowed to exchange between the system and its surroundings (Fig. 3.1).

3.1. Heat vs Work

Energy is the capacity to do work. A change in energy can be thought of as the sum of heat and work (done, say, by the system on its surroundings, or vice-versa). **Heating** is the transfer of energy that makes use of *disorderly molecular motion*. See Fig. 3.2.

Work is the transfer of energy that makes use of *organized motion* (organized, as opposed to random molecular motions). See Fig. 3.3.

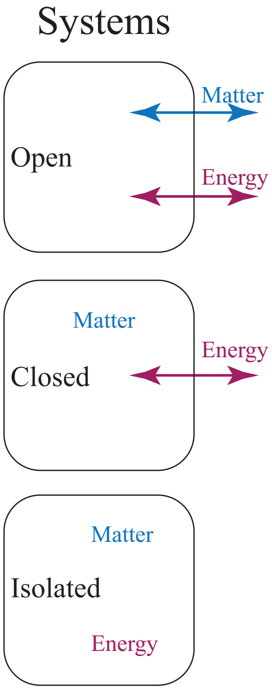


Figure 3.1. If matter can be transferred to the system, it is called **open**, otherwise it is **closed**. An **isolated system** cannot exchange mass or heat with its surroundings. Walls of the system that allow transfer of heat are called **diathermic** whereas those that don't are called **adiabatic**. **Energy** is the capacity of a system to do **work**. Energy can also be transferred as **heat**.

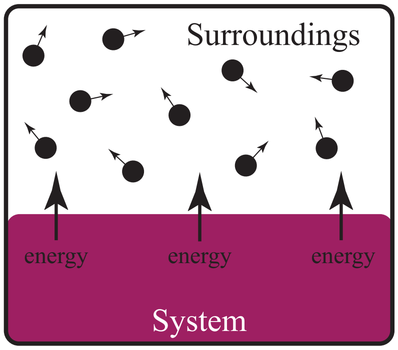


Figure 3.2. When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.

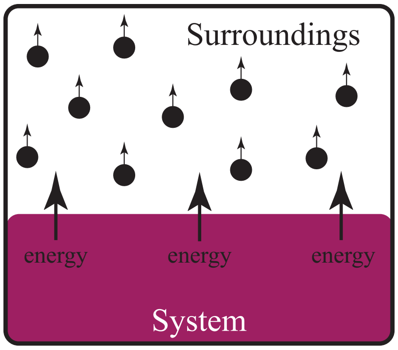


Figure 3.3. When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

An **exothermic process** is one that releases energy as *heat* to the surroundings.[1] All combustion reactions are exothermic. An **endothermic process** is a process in which energy is acquired from its surroundings as heat. An example is vaporization of water.

Heat occurs through random thermal motion. Heat transfer from a hot to a cold body occurs through random thermal motion, so heat should be thought of as a kind of disorderly motion. Suppose a system is in contact with its surroundings and heat flows into the system, the system's energy is increased as a result of the heat transfer. In contrast, work is a transfer of energy, but does not involve disorderly motion. Instead, it involves concerted motion of all particles. For example, a force can be used to lift an object. In this case, all of the molecules move together and in the same direction. This process does not involve disorderly motion.

Universe=System+Surroundings. We should always think of a thermodynamic system together with its surroundings. **Heating** is the energy transfer to the system making use of *thermal motion in the surroundings.* **Work** is the energy transfer to the system resulting from *concerted motion of atoms in the surroundings.*

---

[1] Heat transfer is a process. Heat is not viewed as an entity. It is instead a process: the transfer of energy as a result of temperature difference. Similarly to a diffusion process which is a flux J_i in the i-th chemical species driven by gradients in the chemical potential of that species,

$$J_i(particle\ flux) = -D\frac{\mathrm{d}}{\mathrm{d}x}\mu_i(x) \qquad \text{Fick's law of diffusion}$$

(D is a diffusion coefficient), heat transfer is a flux driven by gradients in temperature

$$q\,(heat\ flux) = -k\frac{\mathrm{d}}{\mathrm{d}x}T(x) \qquad \text{Fourier's law}$$

where k is the coefficient of thermal conductivity (in general, $k = k(T)$ is temperature dependent). At the interface between a hot and a cold body, the temperature gradient is large, causing a transfer of heat from the hot to the cold body. The direction hot → cold is enforced by the minus sign.

3.2. Heat Capacity

Suppose we transfer some amount of heat ΔQ to a system, its temperature will increase by an amount ΔT. If you transfer double the heat $2\Delta Q$, the temperature will increase by double the amount, $2\Delta T$. The proportionality "constant" is the **heat capacity**, $C(T)$, which itself depends on temperature:

$$q \equiv \Delta Q = C(T)\Delta T.$$

In thermodynamics we make the distinction between the heat capacity at constant pressure (C_P) and at constant volume (C_V) using a subscript P or V, respectively. This refers to the kind of experiment used to measure the heat capacity. As we will see later, those two values are different.

The **specific heat capacity**, denoted by a lowercase c, is the heat capacity per unit material.

- **Per unit mass:** $c = C/m$, where m is the mass of the body. SI Units: [J/kg.K]
- **Per mole:** $c = C/n$, where n is the number of moles. This is called the *molar heat capacity.* SI Units: [J/mol.K]

Why should we care about *specific* heat capacity? Because without it, heat capacity is an extensive property, i.e. it depends on the amount of material used. $q = C\Delta T$ says that for a 1°C increase, q will double if the amount of material doubles (because a body twice as large requires twice the amount of heat transfer to cause this 1°C increase), therefore C should double. Because of this dependence, it is impossible to tabulate values of C. Dividing by the amount of material (n or m) renders the heat capacity independent of the amount of material. It is then an intensive property which is intrinsic to the material type, not its quantity.

Another notation you may see for the definition of heat capacity is in terms of infinitesimal quantities:

$$\boxed{C(T) = \frac{\delta q}{\mathrm{d}T},}$$

or the corresponding molar heat capacity

$$c(T) \equiv \frac{1}{n}C(T) = \frac{1}{n}\frac{\delta q}{\mathrm{d}T}.$$

While this notation appears awkward, it is sometimes useful conceptually.

This notation appears to suggest that heat capacity is some type of derivative ($\delta/\mathrm{d}T$) of an extensive parameter (heat flow) with respect to an intensive property (temperature). These are, however, formal definitions. In practice, measured heat capacities are evaluated as derivatives with respect to temperature while holding some other variables constant (P or V). This is done as such, because the measured heat flow will depend on which parameters are held constant. C_V is the most convenient quantity for gases and theoreticians. C_P is the most common tabulated form.

3.2.1. Heat Capacity of a Solid: Dulong-Petit Law. In 1819, Dulong and Petit measured the specific heats[2] of several solids and found that the values for the various materials differed considerably. However, their heat capacity was close to 6 cal/deg.mol (Table 3.1).

Element	Atomic weight	Specific heat (cal/deg.mol)	Heat capacity (cal/deg.mol)
Lithium	6.9	0.92	6.3
Beryllium	9.0	0.39	3.5
Magnesium	24.3	0.25	6.1
Carbon (diamond)	12.0	0.12	1.4
Aluminum	27.0	0.21	5.7
Iron	55.8	0.11	6.1
Silver	107.9	0.056	6.0
Lead	207.2	0.031	6.4
Mercury	200.6	0.033	6.6

Table 3.1. Heat capacities of some solid elements.

Heat capacity arises because of the many different ways (degrees of freedom) in which molecules can absorb energy. The Law of Dulong and Petit is:

Law of Dulong and Petit. The molar specific heats of most solids at room temperature and above are nearly the same value. (This value is $3R \approx 25$ J/-mol/K.)

We note that the Dulong-Petit heat capacity is independent of temperature (in the high-T limit only). See Fig. 3.4.

Units of heat transfer. The connection between heat transfer (SI units: Joule) and temperature change (units: Kelvin) should not be so unfamiliar to you at this point. We have seen in the case of gases that the average kinetic energy per molecule, $K \equiv \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT$, established a connection between temperature and energy. Thus, a change in the kinetic energy ΔK is proportional to a change in temperature ΔT. The two quantities (energy and temperature) were related by the Boltzmann constant. k_B and C have the same SI units (J/K).

---

[2] Specific heat is the number of calories (or Joules) required to raise one gram (or kilogram) of material one degree celsius. The term *heat capacity* often refers to the heat required to raise *one mole* of material one degree celsius.

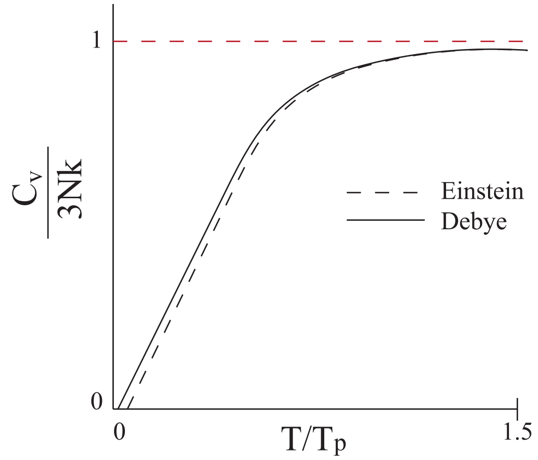


Figure 3.4. The dimensionless heat capacity divided by three, as a function of temperature as predicted by the Debye and Einstein models. The horizontal axis is the temperature divided by the Debye temperature. The dimensionless heat capacity is zero at absolute zero, and rises to a value of three as the temperature becomes much larger than the Debye temperature. The red line corresponds to the classical limit of the Dulong-Petit law.

3.2.2. Heat Capacity of Ideal Gas. Consider an ideal monatomic gas held at constant volume V. The internal energy of an ideal monatomic gas is purely kinetic. There is no potential energy. From

$$K \equiv \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT$$

or $(3/2)RT$ for 1 mole, we can easily derive the heat capacity of an ideal gas by considering the change in temperature that accompanies an infinitesimal change in internal energy, which for an ideal gas is just the kinetic energy ($U = K$).

The heat capacity is obtained by taking the derivative of energy with respect to temperature. For 1 mole of substance, the heat capacity is,

$$\boxed{c_V = \frac{3}{2}R \quad \text{ideal gas}}$$

Here, c_V denotes the specific (molar) heat capacity at constant volume. (The volume is constant because the gas is contained in a volume V.)

It can be shown that at constant pressure, the heat capacity of the ideal gas is:

$$\boxed{c_P = \frac{5}{2}R. \quad \text{ideal gas}}$$

3.2.3. Internal Energy. The internal energy of a system, U, is the sum of total kinetic and potential energy of the molecules in the system. Potential energy *includes the energy* *stored in the chemical bonds.* The internal energy is a **state function**, meaning that it depends only on the state of the system, not on the history or path taken to reach this state.

For a state function, we can express *changes* in the state function in terms of the final state minus the initial state, $\Delta U = U_f - U_i$, without any mention of the intermediate states taken to reach the final state from the initial state.

Internal energy is an **extensive property** of the system (i.e. if we double the size of the system, its internal energy doubles). The SI units of U are Joule (J). However, the internal energy per mole, U/n, is an **intensive property** of the system. The SI units of U/n are J/mol.

The change in internal energy U will contain terms which can be classified as heat transfer or work:

$$\text{change in } U = (heat) + (work)$$

In general, we do not need to enumerate all contributions to the energy because thermodynamics is only concerned about *changes* in the energy (e.g. ΔU or $\mathrm{d}U$), in which case, only the terms that are involved in the change are needed.

In thermodynamics we are interested in $\mathrm{d}U$, the total differential of the function U. $\mathrm{d}U$ is the sum of "infinitesimal" heat transfer, δQ, and "infinitesimal" work done on the system δW:

$\mathrm{d}U$ is the sum of infinitesimal heat transfer and work

The change in internal energy is:

$$\mathrm{d}U = \delta Q + \delta W$$

The total change in heat and work is obtained by integrating the infinitesimal expressions, $\Delta Q = \int \delta Q$ and $\Delta W = \int \delta W$. For ΔU, we have:

$$\boxed{\Delta U = \int \mathrm{d}U = \int \delta Q + \int \delta W = \Delta Q + \Delta W.}$$

Some books write q for heat transfer. Here, we write ΔQ to emphasize that it is a change. We will see later that the first law of thermodynamics states that U is a state function, or equivalently, that dU is an exact differential. This implies that $\Delta U = \int_i^f \mathrm{d}U = U_f - U_i$ only depends on the state of the system (hence the name "state function"), not on the history of changes it undergoes between i and f.

3.2.4. Compression Work (Hydrostatic Pressure Work). Suppose that we compress a gas using a piston by applying an external force (pressure), as shown in Fig. 3.5.

The *system* is the gas inside the chamber. The *surroundings* is everything else external to it. The external pressure P_{ext} originates from the surroundings. The pressure is force per

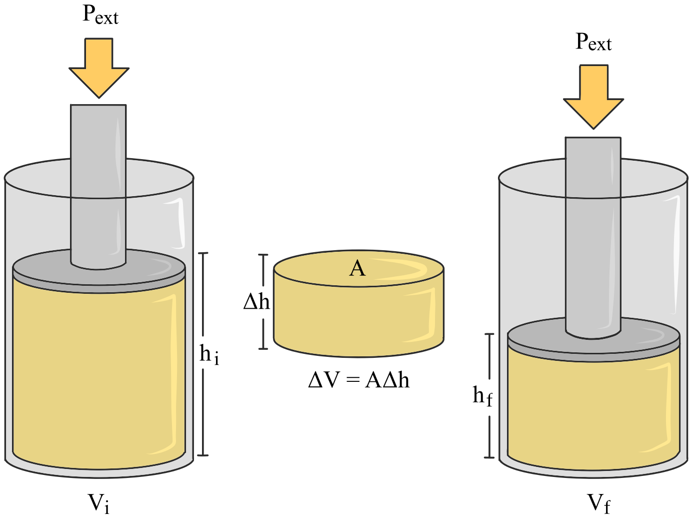


Figure 3.5. Work accomplished when compressing a gas using a piston.

unit area:

$$P_{ext} = \frac{F_{ext}}{A}$$

3.2.5. Work Done *by the Surroundings* **to the System is $-P_{ext}\Delta V$.** We also know that mechanical work, ΔW, is obtained by integrating the force over distance (let z denote the vertical direction which corresponds to the direction of the displacement Δh):

$$\Delta W = \int_{z_i}^{z_f} P_{ext}\, A\, \mathrm{d}z = \int_{V_i}^{V_f} P_{ext}\, \mathrm{d}V.$$

As a matter of convention in chemistry we put a negative sign to denote work done on the system by the surroundings. Engineers use the opposite convention (work done *by* the system). For example, if a gas is compressed (work done on the system), $\Delta V < 0$, leading to positive values of W in the definition below:

Compression work

$$\Delta W = -\int_{V_i}^{V_f} P_{ext}\, \mathrm{d}V \quad \text{or} \quad \delta W = -P_{ext}\, \mathrm{d}V$$

If P_{ext} remains constant during this change (as would be the case if the surroundings were atmospheric pressure, which remains essentially constant), we can pull it out of the integral and the work done on the system is the product of the external pressure and the change in the volume of the gas:

$$\Delta W = -P_{ext}\, \Delta V.$$

In general, depending on what you consider to be the surroundings, P_{ext} may not necessarily be constant, in which case you need to use $\delta W = -P_{ext}\,\mathrm{d}V$ and integrate $\Delta W = \int \delta W$ along the path of the change.

3.2.6. RECALL: Work = Force × Distance. In classical mechanics, we learn that force times distance is the mechanical form, i.e.

$$work = \int_i^f \vec{F} \cdot \mathrm{d}\vec{x},$$

where i and f denote the initial and final points, respectively. If the force is in the x direction, $\vec{F} = F\hat{x}$, we have

$$work = \int_i^f F\mathrm{d}x.$$

The integral is taken along some path with initial point i and final point f. The result is generally path-dependent, unless $F\mathrm{d}x$ is the derivative of some function (say) g, i.e. $F\mathrm{d}x = \mathrm{d}g$, in which case it only depends on the initial and final points since $\int_i^f \mathrm{d}g = g(f) - g(i)$ (fundamental theorem of calculus).

If F is constant along the path, then the work is simply $F(x_f - x_i) = F\Delta x$.

Now let's return to the example from the previous section, where a gas is compressed by a piston. Starting from $P_{ext} = F_{ext}/A$, substituting $A = \Delta V/\Delta h$ yields $P_{ext} = F_{ext}\Delta h/\Delta V$. Thus, $P_{ext}\Delta V = F_{ext}\Delta h$. For infinitesimal changes, $P_{ext}\mathrm{d}V = F_{ext}\mathrm{d}h$. Since the work done by the surroundings on the system is $-P_{ext}\mathrm{d}V$,

$$-\mathrm{d}w = P_{ext}\mathrm{d}V = F_{ext}\mathrm{d}h \qquad P_{ext}\frac{\mathrm{d}V}{\mathrm{d}h} = F_{ext}.$$

The external force (force exerted on the system by its surroundings) is seen to be related to the spatial derivative of the work $F_{ext} = -\frac{\mathrm{d}w}{\mathrm{d}h}$. If h is the x direction:

$$F_{ext} = -\frac{\mathrm{d}w}{\mathrm{d}x}.$$

This is a general principle. The force is generally obtained by taking minus the gradient (spatial derivative) of the (potential) energy:

$$\boxed{F_{ext} = -\frac{\mathrm{d}U}{\mathrm{d}x}.}$$

(The kinetic energy does not appear because it rarely depends on position.)

3.3. Expansion $(P - V)$ Work

In chemistry, $P - V$ work is important because it describes the behavior of gases and the work arising from a change in volume. This includes the work done by a gas as it expands and pushes against the atmosphere. Chemical reactions generate gases. The $P - V$ work here is the work that must be done to make room for the gas it has produced. $P-V$ work also describes compression (negative changes in volume).

3.3.1. Free Expansion. Suppose that a gas is allowed to expand in a vacuum. Since there is zero opposing force, $P_{ext}=0$ and the work is zero $\Delta W=0$.

3.3.2. Expansion Against Constant Pressure. Suppose that a gas inside a piston expands, and the piston is pressing against the atmosphere. The latter corresponds to a constant pressure P_{ext}. Thus, it is constant and we can take it outside the integral:

$$\Delta W=-\int_{V_i}^{V_f} P_{ext}\mathrm{d}V=-P_{ext}\int_{V_i}^{V_f}\mathrm{d}V=-P_{ext}(V_f-V_i)=-P_{ext}\Delta V.$$

3.3.3. Reversible Process. *Reversible* processes are important because they represent the most efficient processes. They are idealizations (no process in nature can be perfectly reversible) which enable us to do useful calculations. A process is fully reversible if both system and surroundings will return exactly to their initial states if the process is run in reverse. Less efficient processes do not have this property, and so are referred to as *irreversible*. A process is said to be *reversible* if it remains arbitrarily close to equilibrium with its surroundings at all times.

When a system is **arbitrarily close** to equilibrium with its surroundings, we mean close in the sense of infinitesimals. If T, P, μ are the temperature, pressure and chemical potential of the *system* and $T_{ext}, P_{ext}, \mu_{ext}$ are those of the surroundings, then arbitrarily close means that they are close in the sense of infinitesimals:

$$\begin{aligned}T_{ext}=&T+\mathrm{d}T\\P_{ext}=&P+\mathrm{d}P\\\mu_{ext}=&\mu+\mathrm{d}\mu\end{aligned}$$

According to the rules of calculus, we can handle expressions containing infinitesimals such as $\mathrm{d}T$, $\mathrm{d}P$ and $\mathrm{d}\mu$. However, second-order quantities such as $(\mathrm{d}T)^2$ or $(\mathrm{d}T)(\mathrm{d}P)$ should be neglected because the square of an infinitesimally small quantity is so small that it is effectively zero.[3]

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[3] From calculus, we know that

$$\mathrm{d}f=\frac{\mathrm{d}f}{\mathrm{d}x}\mathrm{d}x. \qquad (1)$$

However, it is also the case that:

$$\mathrm{d}f(x)=f(x+\mathrm{d}x)-f(x).$$

Taylor-expanding the first term,

$$\mathrm{d}f=\left[\cancel{f(x)}+(\mathrm{d}x)\frac{\mathrm{d}f}{\mathrm{d}x}+\frac{(\mathrm{d}x)^2}{2}\frac{\mathrm{d}^2f}{\mathrm{d}x^2}+O((\mathrm{d}x)^3)\right]-\cancel{f(x)} \qquad (2)$$

But for (1) and (2) to be equal we are “forced” to drop terms of order $(\mathrm{d}x)^2$ or higher. Thus, when handling differential expressions we keep terms of order $O(\mathrm{d}x)$ only. The higher order infinitesimal terms are negligible (too small).

3.3.4. Reversible Compression. If the mechanical compression work done by the surroundings on a system

$$\delta W = -P_{ext}\mathrm{d}V$$

is reversible, this means we can write $P_{ext} = P + \mathrm{d}P$,

$$\delta W = -(P + \mathrm{d}P)\mathrm{d}V.$$

Noting that the product of infinitesimals $\mathrm{d}P\mathrm{d}V$ is much smaller than the term $P\mathrm{d}V$, we neglect $\mathrm{d}P\mathrm{d}V$:

$$\delta W = -P\mathrm{d}V.$$

The reversible work done on the system is then:

$$\Delta W^{rev} = \int \delta W = -\int_{V_i}^{V_f} (P + \mathrm{d}P)\mathrm{d}V = -\int_{V_i}^{V_f} P\mathrm{d}V.$$

It seems that we have accomplished by little because there is little difference between the work $\delta W = -P_{ext}\mathrm{d}V$ and $\delta W = -P\mathrm{d}V$. On the contrary, the difference is significant because this allows us to replace P_{ext} by P. In many experiments P is known, because the gas mixture is known, and obtained from the equation of state, whereas P_{ext} is often unknown (e.g., the surroundings may be out of your control).

Indeed, when computing the work done on the gas, $-\int F\,\mathrm{d}s = -\int P_{ext}\,\mathrm{d}V$, the force F must be the gravitational force acting downward on all of the mass supported by the gas at pressure P. This mass includes that of the piston, the piston rod, the pan, any weight placed on the piston (to compress the gas), and the atmosphere above the piston. In the case of a reversible process this force F is never more than minutely out of balance with the force exerted upward on the piston face by the gas and given by the product of pressure and piston area. Thus, for all practical purposes, $F = PA$ for the reversible process. The volume change of the gas (system) is $\mathrm{d}V = A\,\mathrm{d}s$; thus $\mathrm{d}s = \mathrm{d}V/A$ and the work done on the gas is

$$\Delta W = -\int F\mathrm{d}s = -\int PA\frac{\mathrm{d}V}{A} = -\int P\mathrm{d}V.$$

Therefore, if we can substitute PA for F, we can calculate the work from knowledge of the system without knowing anything about what happens in the surroundings. This substitution is possible only for reversible processes where the forces are never more than differentially out of balance (e.g. $P_{ext} = P + \mathrm{d}P$).

For irreversible processes this substitution is not possible because we may not have thermal equilibrium. For example, suppose that gas expansion takes place: when a finite weight is removed from the piston in the processes described, the forces of gravity acting downward is overbalanced by the gas pressure acting upward by a finite amount (i.e. $P_{ext} = P - \Delta P$, where ΔP is not an infinitesimal), and F does not equal PA again until a new equilibrium position of the piston is reached. (Similarly, for gas compression we have $P_{ext} = P + \Delta P$, and the internal gas pressure is overcome by the external pressure from the weight pressing downward.) Thus PA cannot be substituted in the integral $\int F\,\mathrm{d}s$, and it is not possible to calculate the work from a knowledge of the properties of the system (the gas). The integral $\int F\,\mathrm{d}s$ is given by $\int P\,\mathrm{d}V$ only when the process is reversible; that is,

$$\Delta W^{rev} = -\int_{V_1}^{V_2} P\,\mathrm{d}V$$

This work for an expansion process is the maximum work which the system can produce.

3.3.5. Why are Reversible Processes Important? The reversible process is unique, and important in thermodynamics, because it represents the *limit* of what is possible in the real world. We cannot imagine anything better than a reversible process. Such processes lend themselves to exact mathematical analysis, which is not the case for other processes. In thermodynamics, our choice is often to do calculations for reversible processes, or to do no calculations at all. The reasons for this is that reversible processes are those for which the forces causing change are almost exactly in balance. Thus the states through which the system passes during a reversible process are for all practical purposes equilibrium states, or more precisely are never removed more than differentially from equilibrium states (e.g. $P_{ext} = P + \mathrm{d}P$).

3.3.6. Example: (Reversible Compression of an Ideal Gas). To illustrate the application of this result, let's look at a specific example. The easiest case is an isothermal compression ($T = const$) for an ideal gas ($P = nRT/V$):

$$\Delta W^{rev} = -\int_{V_1}^{V_2} P\,\mathrm{d}V = -\int_{V_1}^{V_2} \frac{nRT}{V}\mathrm{d}V = -nRT\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = nRT\log(V_1/V_2).$$

3.3.7. Example: (Reversible Compression of VDW Gas). A slightly more complicated example is the van der Waals gas. Suppose that n moles of gas is expanded from V_1 to V_2 reversibly and isothermally. Calculate ΔW for a Van der Waals gas.
Solution:

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$\begin{aligned}\Delta W^{rev} &= -\int_{V_1}^{V_2} P\,\mathrm{d}V = -\int_{V_1}^{V_2} \frac{nRT}{V-nb}\mathrm{d}V + \int_{V_1}^{V_2} \frac{n^2 a}{V^2}\mathrm{d}V \\ &= -\,nRT\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V-nb} + n^2 a\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V^2} \\ &= -\,nRT\log\frac{V_2 - nb}{V_1 - nb} + n^2 a\left(\frac{1}{V_1} - \frac{1}{V_2}\right).\end{aligned}$$

3.3.8. Example: (w/ numbers) Calculate the work done when 50 g of iron reacts with hydrochloric acid to produce $FeCl_2(aq)$ and hydrogen in (a) a closed vessel of fixed volume, (b) an open beaker at 25°C.

Solution: For (a) the volume cannot change, so the expansion work done is zero ($\Delta W = 0$). For (b) the gas pushes against the atmosphere, $\Delta W = -P_{ext}\Delta V$. After production of gas, the volume changed by $\Delta V = V_f - V_i \approx V_f = nRT/P_{ext}$ (the initial volume is so small compared to V_f that it can be neglected), where n is the amount of H_2 produced. Therefore,

$$\Delta W = -P_{ext}\Delta V = -P_{ext}\frac{nRT}{P_{ext}} = -nRT.$$

Because the reaction is $Fe(s)+2HCl(aq) \rightarrow FeCl_2(aq)+H_2(g)$, we know that 1 mol H_2 is generated when 1 mol Fe is consumed, and n can be taken as the amount of Fe atoms that react. The molar mass of Fe is 55.85 g/mol. Then,

$$\Delta W \approx -\frac{50\text{ g}}{55.85\text{ g/mol}} \times (8.3145\text{ J/K.mol}) \times (298\text{ K}) \approx -2.2\text{ kJ}.$$

3.3.9. Why the Infinitesimals? In the previous sections we have been writing down the work in terms of infinitesimal changes δW. The total work is obtained by integrating:

$$\Delta W = \int \delta W.$$

where δW represents infinitesimal work. For example, the $P - V$ work term is

$$\delta W = -P_{ext}\,\mathrm{d}V$$

or

$$\delta W = -P\,\mathrm{d}V$$

in the case of reversible $P - V$ work.

You may ask, why are we working with infinitesimal expressions? This is because the intensive quantity (e.g., the pressure) may change along the path of integration. To get the total work ΔW, we may need to express the intensive quantity in terms of the extensive quantity. This can be done using an equation of state, as we did in the above examples for the reversible compression of an ideal and VDW gas. The exact dependence of this intensive quantity is problem-dependent.

Working with infinitesimal expressions reminds us that integration is the process where infinitesimals are added along the path of integration. These infinitesimals are not necessarily constant along the path.

3.4. Other Types of Work

Apart from P-V work (compressive mechanical work), $\delta W = -P_{ext}\,\mathrm{d}V$, there exists several different other types of work corresponding to the various laws of physics available. Let us look at some examples.

3.4.1. Work Done by Gravity. Suppose we lift an object of mass m from the surface of the earth ($z = 0$) to a height ($z = h$). The gravitational force $F = mg$, where m is mass and g is the gravitational acceleration, leads to a term of the form $\Delta W = \int_0^h F.\mathrm{d}z = mgh$.

Thus, elevating a body of mass m to a height h from the ground requires an amount of work mgh. The SI units of g are $\mathrm{m/s^2}$.

3.4.2. Work Done by a Spring. The linear restoring force $F = kx$ (Hooke's law), where k is the spring constant and x is the extension of the spring from its rest position, leads to a term of the form $\Delta W = \int F.\mathrm{d}x = \int kx\mathrm{d}x = \frac{1}{2}kx^2$.

3.4.3. Electrostatic Work. Suppose that we add an electric charge to a system of charged particles. The charged particles distribution is described by an electric potential ϕ or electromotive force, $\mathcal{E}$. The charge added is $\mathrm{d}q$. The work is $\delta W = \mathcal{E}\mathrm{d}q$ or $\delta W = \phi\mathrm{d}q$, depending on the notation used ($\mathcal{E}$ vs ϕ). $\mathcal{E}$ vs ϕ are the same thing; different books use different notations. The units of $\mathcal{E}$ and ϕ are volt (V), whereas those of $\mathrm{d}q$ are Coulomb (C).

3.4.4. Work Done by an Electric Field. Suppose that we have an electric field $\vec{E}$ and an object with an electric dipole moment $\vec{p}$. If this object is re-oriented in the presence of the electric field, work is required according to $\delta W = \vec{E}\cdot\mathrm{d}\vec{p}$. The units of $\vec{E}$ are V/m whereas those of $\vec{p}$ are C·m, since a dipole $\vec{p} = q\vec{d}$ consists of two point charges $+q$ and $-q$, separated by a displacement vector $\vec{d}$. We recall from electrostatics that $\vec{E} = -\nabla\phi$, so you can see how these units also agree with the previous work $\delta W = \phi\mathrm{d}q$ (the units ∇ are 1/m).

3.4.5. Work Done by a Magnetic Field. Suppose that we have a magnetic field $\vec{B}$ and an object with a magnetic dipole moment $\vec{m}$. If this object is re-oriented in the presence of the magnetic field, work is required according to $\delta W = \vec{B}\cdot\mathrm{d}\vec{m}$. The units of $\vec{B}$ are Tesla (T) whereas those of $\vec{m}$ are $\mathrm{J/T=A.m^2}$ (amperes-meter square), since a magnetic dipole $\vec{m} = I\vec{A}$ can be described as a current I flowing around a loop whose area is A (area is a vector pointing normal to the surface).

3.4.6. Adding Molecules to a System. It requires work to add a molecule to a system. The energetic cost is given by the chemical potential:

$$\mu_i \equiv \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_j \neq i} \approx \frac{\Delta U}{\Delta N_i}$$

where the subscript $S, V, N_j \neq i$ indicates that other variables are being held constant. μ_i is the energy required to add 1 particle to the system (the resistance to adding particles). It costs energy to add particles because at equilibrium the particle must have energy comparable to the average energy. The associated work is:

$$\delta W = \mu_i \mathrm{d}N_i.$$

In chemistry, we normally work with molar quantities:

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j \neq i}, \qquad \delta W = \mu_i \mathrm{d}n_i.$$

The units of μ_i are the same (joules) except that the amount of energy involved is that which involves adding a mole of substance to the system.

3.4.7. The Infinitesimal Work Terms Follow a General Pattern.

We note that all types of works are of the form:

$$\delta W = (\text{intensive quantity}) \times \mathrm{d}(\text{extensive quantity}).$$

In the above examples, our **intensive** and **extensive** quantities were:

Intensive variable	Corresp. **Extensive** variable	Type of work
P (pressure)	V (volume)	mechanical (e.g. $P-V$) work: when a system goes from high pressure P_{ext} to lower pressure while changing its volume V. The energy changes by $-P_{ext}\mathrm{d}V$.
ϕ (electrostatic potential) or $\mathcal{E}$ (electromotive force)	q (electric charge)	electrical (e.g. electromotive force, emf): when a system goes from high emf $\mathcal{E}$ to low emf by transferring electric charges q between the two electrodes. The energy changes by $\mathcal{E}.\mathrm{d}q$.
$\vec{E}$ (electric field)	$\vec{p}$ (electric dipole moment)	electrical polarization work: the force is defined by the surroundings' electric field strength and the "displacement" is change of the polarization of the medium (the sum of the electric dipole moments of the molecules).
$\vec{B}$ (magnetic field)	$\vec{m}$ (magnetic dipole moment)	magnetic work: here the force is defined by the surroundings' magnetic field strength and the "displacement" is the change of total magnetic dipole moment.
mg (gravitational force)	h (displacement)	gravitational work: the force is defined by the surroundings' gravitational field and the generalized displacement is change of the spatial distribution of the matter within the system. For example, the work involved when a point particle of mass m is dropped from height h_2 to h_1 is $mg(h_2 - h_1)$.
kx (spring force)	x (displacement)	(same as above)
μ (chemical potential)	N (number of molecules) or n (number of moles)	chemical: a system can go from high chemical potential μ_i to low potential by transferring particles n_i. The energy change by $\mu_i \mathrm{d}n_i$.
T	S	thermal: a system equilibrates by going from high T to low T while transferring a quantity known as entropy S. If T depends on position, heat will flow from regions of high T to regions of low T. The energy of the system changes by $T\mathrm{d}S$.

3.5. Laws of Thermodynamics

3.5.1. Classical thermodynamics describes systems close to equilibrium. The laws of thermodynamics describe the behavior of systems which are in thermal equilibrium or approaching thermal equilibrium. *An equilibrium system is defined as one whose macroscopically observable properties do not change with time.*

Equilibrium implies the macroscopic properties are spatially homogeneous, i.e. there are no gradients (spatial derivatives) in the properties. For, if gradients were present, forces (fluxes) would be set into motion to restore the system to equilibrium conditions, eliminating the gradients.

Thermodynamics is capable of describing changes away from equilibrium, but only provided we are not too far from equilibrium. For example, it can predict the direction of a chemical reaction, heat flow or mass flux.

However, if the system is far from equilibrium, equilibrium thermodynamics will not predict its detailed behavior except to indicate the direction of change. What it does not do is provide information about the microscopic properties of the system. For that, we need *statistical mechanics.*

3.5.2. The Four Classical Laws. There are four classical laws of thermodynamics. The first and second laws introduce state functions, U and S. The zeroth law introduces the existence of temperature T, whereas the second law establishes the absolute temperature scale. The third law is statement regarding the properties of systems in equilibrium at absolute zero temperature.

Zeroth Law (Maxwell 1871, Carathéodory 1909)	If two systems are in thermal equilibrium with a third system, then they are in equilibrium with each other. In fact, there is a single system property (called temperature) that serves to indicate whether systems are in thermal equilibrium. Note: this law postulates the existence of a thermometer.
First Law (Hess 1841, Clausius & Rankine 1850)	There is a system property (i.e. state function) called energy, U, that is conserved, but can take several different forms that can interconvert. Note: this law postulates the existence of a state function, U.
Second Law (Clausius 1854, Kelvin 1851, Carathéodory 1909, Carnot 1824)	There is a system property (i.e. state function), S, called entropy that, if the system is isolated from its environment, either increases or (in principle) remains constant during thermodynamic processes. Mathematically, $\mathrm{d}S_{univ} \geq 0$, where S_{univ} is the entropy of the isolated system. Note: S_{univ} can be taken to be the whole universe (system plus surroundings) because the universe is an isolated system. Note: this law postulates the existence of a state function, the entropy.
Third Law (Nernst 1912)	The entropy of a system is a universal constant (set to zero, for a perfect crystal) at the absolute zero of temperature.[4] Note: $S(T \to 0) = 0$ for a perfect crystal. The third law was first conjectured by Walther Nernst in 1912 and proved in 2017 by Lluis Masanes and Jonathan Oppenheim.[5]

3.6. Zeroth Law

The **Zeroth Law** of thermodynamics states that **thermal equilibrium is an equivalence relation:** *If A is in equilibrium with B and B is in equilibrium with C then A is in equilibrium with C.* What is an equivalence relation? A binary relation $\sim$ on the set $X = \{A, B, C, \dots\}$ is an *equivalence relation* if and only if it is reflexive, symmetric and transitive, i.e. for all A, B, C in X:

- $A \sim A$ (reflexivity)
- if $A \sim B$ then $B \sim A$ (symmetry)
- if $A \sim B$ and $B \sim C$ then $A \sim C$ (transitivity)

Here, $A \sim B$ denotes "A is in thermodynamic equilibrium with B". X denotes the set of all possible thermodynamical systems. In spite of its apparent simplicity, the zeroth law has the important consequence that it establishes any number of possible empirical temperature scales. Each thermodynamic system can be labeled with a temperature, similar to a real number system (systems with the same temperature are considered equivalent). The existence of an absolute temperature scale is then a consequence of the Second Law, which

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[4] The entropy of degenerate systems tends to a nonzero value when $T \to 0$. This is why the Third Law is formulated in terms of "the entropy of a perfect crystal". For perfect crystals, the ground state is non-degenerate.

[5] Masanes and Oppenheim, A general derivation and quantification of the third law of thermodynamics, *Nature Comm.* **8**, 14538 (2017) `https://www.nature.com/articles/ncomms14538`

establishes the existence of the entropy. Other physical meanings of the zeroth law include: "All heat is of the same kind" (Maxwell) and "All diathermal walls are equivalent".

3.7. First Law

The importance of *changes* is embedded in the statement of the First Law of thermodynamics,

First Law of Thermodynamics Statement 1: There is a system property (i.e. state function) called energy that is conserved, but can take several different forms that can interconvert.
Statement 2:

$$\mathrm{d}U = \delta Q + \delta W \quad \text{is an exact differential.}$$

dU is the sum of"infinitesimal" heat transfer (from the surroundings to the system), δQ, and "infinitesimal" work done on the system δW by the surroundings. Here, $\Delta Q = q = \int \delta Q$ and $\Delta W = \int \delta W$. Many textbooks write q for heat transfer.

3.7.1. U is a state function, meaning it is path independent.

If dU is an exact differential, its integral is independent of path, $\Delta U = \int_i^f \mathrm{d}U = U_f - U_i$ (according to the fundamental theorem of calculus), and only depends on the initial and final points. This is the definition of a state function.

First Law of Thermodynamics (in integral form)

$$\Delta U = \Delta Q + \Delta W \quad \text{is independent of path.}$$

A function U which is independent of path is called a *state function* in the language of thermodynamics. This is because it only depends on the state of the system, not on the path taken to arrive at the final state.

In other books (e.g. Oxtoby [**9**], p.529) you may encounter a slightly different notation ($q = \Delta Q$, $w = \Delta W$) which writes $\Delta U = q + w$. These definitions are equivalent. A state function implies that the change ΔU can be written as the difference of final and initial states, $U_f - U_i$. Thus, internal energy is a state function. This is the same as saying that dU is an exact differential, which implies that $\Delta U = \int_{U_i}^{U_f} \mathrm{d}U = U_f - U_i$. Obviously, this is independent of path (it only depends on initial and final states).

3.7.2. First Law is a Statement on Conservation of Energy.

In this section we show that the First Law can be interpreted as a statement of conservation of energy.

Conservation of energy and energy transfer to the system or its surroundings. In any process, the heat added to the system is removed from the surroundings ($q = -q_{ext}$). The work done on the system is the work done by the surroundings ($w = -w_{ext}$). Adding these two and invoking the first law,

$$\Delta U = -\Delta U_{ext}.$$

The total energy changes in the universe (system plus surroundings) is always zero in any process:

$$\Delta U_{univ} = \Delta U + \Delta U_{ext} = 0.$$

Thus, energy is conserved (even in the presence of heat exchange and dissipation). It can only be *exchanged* between the system and its surroundings. **Note:** We will drop the notation *sys* to denote the system. By default, quantities without a subscript refer to the system.

The statement $\Delta U_{univ} = 0$ ("The energy of the universe is constant") is another formulation of the First Law.

3.7.3. Summary of First Law: $\mathrm{d}U = \delta$(heat) + δ(work).

The change in the internal energy for a *closed system*, by any process, is defined by the change in *external variables*:

$$\mathrm{d}U = \delta Q + \delta W.$$

Since heat, Q, and work, W, are not state functions, many alternative paths can result in a given change $\mathrm{d}U$. One may choose a reversible path where $\delta Q = T\mathrm{d}S$ and $\delta W = -P\mathrm{d}V$, and thus $\mathrm{d}U$ can be expressed by internal variables:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V.$$

Here, the change in the internal energy is expressed by state functions only. The change in a state function is independent of the path and this last equation is valid, *regardless of which path the change in internal energy was brought about.* For a closed system, U is a function of S and V; thus $\mathrm{d}U$ is a total *differential of internal variables.*

For an open system, the internal energy is, in addition, a function of the amount of matter, i.e. U is a function of $S, V, \{n_i\}$, where n_i is the amount (moles) of component i. The change in internal energy, expressed as the total differential of internal variables, will then be

$$\mathrm{d}U(S, V, \{n_i\}) = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i$$

where

$$\mu_i = (\partial U/\partial n_i)_{S,V,n_{j\neq i}}$$

is the chemical potential of component i. The summation is over all components. This latter expression for the differential $\mathrm{d}U$ contains only state functions. $\mathrm{d}U$ is a total differential of internal variables and the equation is generally valid for an open system. Chemical potentials have no absolute values, and the value of dU for an open system can only be given with respect to a reference state.

3.7.4. Choice of System vs Surroundings. The differential dU used in the statement of the first law, d$U = \delta(\text{heat}) + \delta(\text{work})$, can refer to the system, its surroundings or the whole universe. It's up to us to decide what we call the system and its surroundings. For example, when writing d$U = \delta Q - P_{ext}$dV, we could be referring to the circular region below, or its surroundings. See Fig. 3.6.

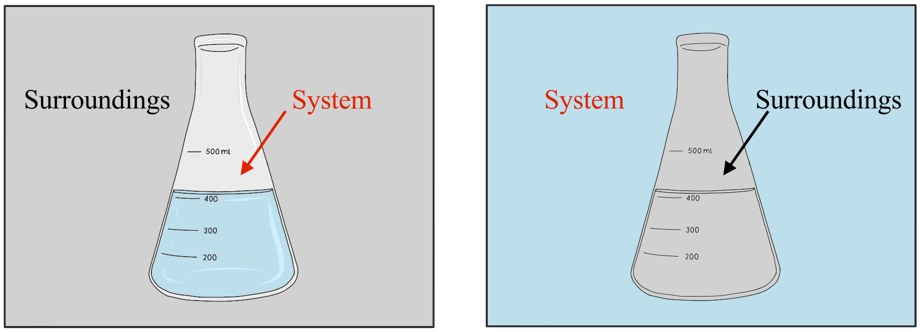

Figure 3.6. The universe is divided into a system and its surroundings. This division is largely arbitrary and a matter of convenience.

On the left, we have a system and its surroundings. The union of these two is the universe. On the right, we have the inverted situation: the system what used to be the surroundings, and the surroundings is what used to be the system. This inverted configuration is also possible. On the left, dU refers to the circular region, δQ is the heat transferred into it, dV refers to its volume change, P_{ext} refers to the external pressure acting on it from the surroundings. On the right, dU refers to the change in internal energy of the grey region, dV refers to the change in volume of the grey region and P_{ext} refers to the pressure exerted on the grey region by the colored region.

3.8. Second Law

There is an *extensive* thermodynamic state function called **entropy**, S, which can be used to indicate the direction in which systems may spontaneously evolve. S also dictates the maximum amount of work that can be obtained from a given chemical transformation or maximum efficiency for extracting work out of a heat engine.

To operate at maximum efficiency, a process must be fully *reversible*. Clausius defined change in entropy of a system[6] dS in terms of the quantity of heat δQ^{rev} that is *reversibly*

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[6] In the definition of entropy, d$S = \delta Q^{rev}/T$, the $1/T$ factor is an integrating factor. This integrating factor is analogous to integrating factors in the theory of differential equations, which are used to transform the differential equation into an exact differential equation. The reversible heat transfer, δQ^{rev}, by itself is not an exact differential. However, when multiplied by $1/T$, it is. Another way to say this is that while dS is exact differential, the product

added to the system at a given temperature T:

Thermodynamic definition of entropy: (of a system)

$$\mathrm{d}S \equiv \frac{\delta Q^{rev}}{T}.$$

$\mathrm{d}S$: infinitesimal entropy change of the *system*.
δQ^{rev}: heat added *reversibly* to the system.

Note: A process for which $\mathrm{d}S = 0$ is called *isentropic*. A process for which $\delta Q = 0$ is called *adiabatic*. The two notions are equivalent when the process is reversible ($\delta Q = \delta Q^{rev} = T\mathrm{d}S$).

This implies that to find the entropy change in the system, we need to find a reversible path and integrate. (In practice, a reversible path is one that involves slow changes.) It will yield a state function which depends on initial and final point:

$$\Delta S = \int_i^f \mathrm{d}S = S_f - S_i = \int_i^f \frac{\delta Q^{rev}}{T}.$$

The equality on the right hand side applies for a *reversible* process, in which case, $\mathrm{d}S = \delta Q^{rev}/T$.

The problem is further simplified if the process is *isothermal*, in which case temperature is a constant and can be taken out of the integral:

$$\boxed{\Delta S = \frac{1}{T}\int_i^f \delta Q^{rev} \equiv \frac{\Delta Q^{rev}}{T}, \text{ where } \Delta Q^{rev} \equiv \int_i^f \delta Q^{rev}.}$$

The total entropy is

$$\mathrm{d}S_{univ} = \underbrace{\mathrm{d}S}_{\substack{\text{entropy change}\\ \text{in system}}} + \underbrace{\mathrm{d}S_{ext}}_{\substack{\text{entropy change}\\ \text{in surroundings}}}.$$

The second law states that the total entropy change (of the universe) must be nonnegative:

$T\mathrm{d}S$ is no longer exact. An example discussed in class is the exact differential $\mathrm{d}f = y\mathrm{d}x + x\mathrm{d}y$ (which we verified was exact using Euler's test). When multiplying by another function, $\mathrm{d}f$ may no longer be exact. For example, $\omega = y\mathrm{d}f = y^2\mathrm{d}x + xy\mathrm{d}y$ is no longer an exact differential even though $\mathrm{d}f$ was exact.

Second Law of Thermodynamics (Clausius inequality):
The entropy of the universe is a nondecreasing function of time:

$$\boxed{\mathrm{d}S_{univ} = \mathrm{d}(S + S_{ext}) = \mathrm{d}S + \mathrm{d}S_{ext} \geq 0.}$$

where

$$S_{univ} = S + S_{ext}.$$

The equality holds at thermal equilibrium (when processes become reversible). This statement applies to an isolated system ("the entropy of an isolated system is nondecreasing"), not only the universe. The universe, of course, is an isolated system. We often use the terms "universe" and "isolated" (system) interchangeably.

3.8.1. Classical Statement of the Second Law. Clausius defined change $\mathrm{d}S$ in entropy of a system S in terms of the quantity of heat δQ^{rev} that is *reversibly* added to the system at a given temperature T:

Thermodynamic definition of entropy:
The addition of heat to a system changes its entropy by an amount:

$$\mathrm{d}S \equiv \frac{\delta Q^{rev}}{T}.$$

Note: S refers to the entropy of the system, not its surroundings. $\mathrm{d}S$ is a total differential which can be positive, zero or negative (since heat can be added or removed from the system). δQ^{rev} by itself is not exact, but when multiplied by $1/T$ it becomes exact.

Consider a system with entropy S and its surroundings at entropy S_{ext}. Let $S_{univ} = S + S_{ext}$.

Second Law of Thermodynamics (Clausius inequality): $\mathrm{d}S_{univ}$ is an exact differential which is non-negative:

$$\mathrm{d}S_{univ} = \mathrm{d}S + \mathrm{d}S_{ext} \geq 0.$$

This is the statement that entropy of the universe is a nondecreasing function of time. The equality holds at thermal equilibrium (when processes become reversible). This statement applies to an isolated system ("the entropy of an isolated system is nondecreasing"). The universe, of course, is an isolated system.

The equality on the right hand side applies for a *reversible* process, in which case, $\mathrm{d}S = \delta Q^{rev}/T$.

Heat added to the surroundings is opposite in sign to the heat added to the system

$$\delta Q^{rev}_{ext} = -\delta Q^{rev}.$$

Thus, for a reversible process ($\mathrm{d}S = \delta Q^{rev}/T$),

$$\mathrm{d}S_{univ} = \mathrm{d}S + \mathrm{d}S_{ext} = \frac{\delta Q^{rev}}{T} + \frac{\delta Q^{rev}_{ext}}{T} = \frac{\delta Q^{rev}}{T} - \frac{\delta Q^{rev}}{T} = 0.$$

This is the case $\mathrm{d}S_{univ} = 0$ (reversible process). The remaining case is $\mathrm{d}S_{univ} > 0$ (irreversible process). In a general process, the heat exchanged between the system and surroundings may be irreversible. The difference (excess) between heat transferred irreversibly and reversibly gives the increase in entropy:

$$\mathrm{d}S_{univ} = \mathrm{d}S + \mathrm{d}S_{ext} = \underbrace{\frac{\delta Q^{rev}}{T}}_{\mathrm{d}S \equiv \frac{\delta Q^{rev}}{T}} - \frac{\delta Q}{T} \geq 0,$$

which leads to the following form of the Clausius inequality:

$$\boxed{\delta Q^{rev} \geq \delta Q,}$$

where δQ is the amount of heat absorbed by the system from its surroundings (in a process that can be irreversible), whereas δQ^{rev} is the heat added to the system in a reversible process. The equality holds in the reversible case.

Note: there are many different formulations of the Clausius inequality. See, for example:
`http://www.eoht.info/page/Clausius+inequality`
For a general irreversible process, we then have the change in entropy *of the system*:

$$\Delta S = \int_A^B \mathrm{d}S = S_B - S_A = \int_A^B \underbrace{\frac{\delta Q^{rev}}{T}}_{\mathrm{d}S \equiv \frac{\delta Q^{rev}}{T}} \geq \int_A^B \frac{\delta Q}{T}.$$

For any cyclic process (process which begins and ends at the same state)

$$S_B - S_A = 0$$

so that

$$\int_A^B \frac{\delta Q^{rev}}{T} \equiv \oint \frac{\delta Q^{rev}}{T} = 0.$$

Therefore,

$$\boxed{\oint \frac{\delta Q}{T} \leq 0.} \quad \text{Clausius' theorem (1854)}$$

The symbol $\oint$ denotes that the process is carried out along a path that is cyclic (end point = start point).

It is helpful to learn more about the Carnot engine (see, e.g., Oxtoby [**9**], Section 13.4, “Carnot cycles, efficiency and entropy”), where this integral is carried out along paths of constant T and S.

3.8.2. Isentropic vs Adiabatic Process. From the thermodynamic definition of entropy $\mathrm{d}S \equiv \frac{\delta Q^{rev}}{T}$, we have that the heat transferred to the system in a reversible process is $\delta Q^{rev} = T\mathrm{d}S$. A process for which $\mathrm{d}S = 0$ is called *isentropic*. A process for which $\delta Q = 0$ is called *adiabatic*. The two notions are equivalent when the process is reversible ($\delta Q = \delta Q^{rev} = T\mathrm{d}S$).

3.8.3. Reversible Process, Fundamental Equation of Thermodynamics. For a reversible process the heat transferred is $\delta Q^{rev} \equiv T\mathrm{d}S$. The infinitesimal change in energy is then

$$\boxed{\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i}$$

This equation is so important that it is called the *fundamental equation of thermodynamics*. It is valid for a reversible process. For the case of $P - V$ work only,

$$\mathrm{d}U \equiv \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V = T\mathrm{d}S - P\mathrm{d}V$$

is plotted in Fig. 3.7.

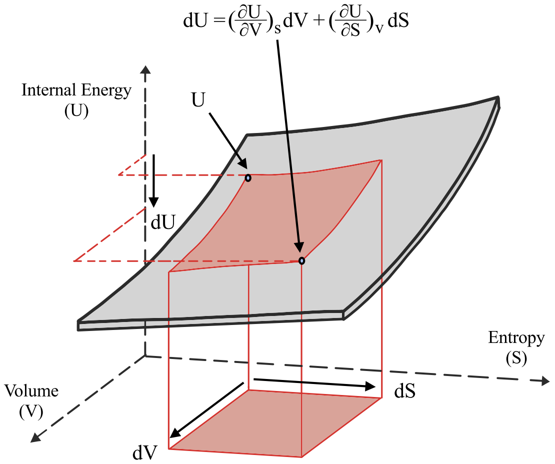

Figure 3.7. An overall change in U, which is denoted $\mathrm{d}U$, arises when both V and S are allowed to change. If second-order infinitesimals are ignored, the overall change is the sum of changes for each variable separately.

3.8.4. Inequality for First Law, Irreversible Process. For a general process we have $\delta Q \leq T\mathrm{d}S$, according to the Clausius inequality

$$\delta Q^{rev} \geq \delta Q.$$

Therefore, the Clausius inequality implies that

$$\boxed{\mathrm{d}U \le T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i.} \quad \text{(First Law)}$$

On the left hand side, $\mathrm{d}U$ refers to a general (not necessarily reversible) process. This inequality is true for a general process.

Note: we have not changed the First Law, which is still "$\mathrm{d}U = \delta Q + \delta W$ is an exact differential". All we have done is express $\mathrm{d}U$ as an inequality because $\delta Q \le \delta Q^{rev} = T\mathrm{d}S$.

The equality $\delta Q^{rev} = T\mathrm{d}S$, of course, follows from the thermodynamic *definition* of entropy $\mathrm{d}S = \delta Q^{rev}/T$.

3.8.5. Proof of Second Law. A proof of the Second Law can be found in the articles [**10, 11**]. By examining the second law in the context of a finite system evolving over a short time period, the authors show from first principles that random fluctuations in the behavior of a non-equilibrium system can appear to violate the second law of thermodynamics over isolated periods of time, and that these local violations become more probable exponentially as we decrease either the size of the system or the time over which we measure the entropy. The mathematical form of this result is known as the fluctuation theorem. Remarkable, at the same time that the fluctuation theorem shows that the total entropy can decrease over very short periods of time in small systems, it also shows that in the limit of long times and macroscopic systems the entropy must increase, providing a mathematical proof of the second law.

3.9. Third Law

According to the **Third Law** of thermodynamics (Nernst), we can find the absolute entropy of a perfect crystal:

$$\lim_{T\to 0} S = 0.$$

Combining $\mathrm{d}S = \frac{\delta Q}{T}$, with $\delta Q = C_V \mathrm{d}T$ (heating at constant volume),

$$S(T) = S_0 + \int_0^T \frac{C_V(T)}{T}\mathrm{d}T.$$

S_0 is the entropy at absolute zero. An analogous formula exists at constant pressure:

$$S(T) = S_0 + \int_0^T \frac{C_P(T)}{T}\mathrm{d}T.$$

Note that since the heat capacity is always positive, the entropy increases with increasing temperature.

If S_0 is known, the absolute entropy $S(T)$ can be obtained at any temperature T through measurements of the heat capacity versus temperature from 0 up to T.

Invoking the third law, $S_0 = 0$, and

$$S(T) = \int_0^T \frac{C_V(T)}{T} \mathrm{d}T.$$

The plausibility of the Third Law can be appreciated from the Boltzmann entropy:

$$S = k_B \log \Omega,$$

which is zero ($S = 0$), because at $T = 0\ K$ the system is in its unique ground state, i.e. there is only 1 ground state configuration.[7]

3.9.1. Absolute Zero. The third law is equivalent to the statement that "It is impossible by any procedure, no matter how idealized, to reduce the temperature of any system to zero temperature in a finite number of finite operations" (Guggenheim, 1967).

3.9.2. Proof of Third Law. A proof of the Third Law can be found in [**12**].

3.9.3. Common Thermodynamic Potentials. In classical thermodynamics, we often use thermodynamics potentials, such as U, H, A and G, depending on the experimental situation. They are all energies, and serve the same purpose of calculating *changes* in the energy of the system. Except that which one we should use depends on the experimental conditions. U depends on $S, V, \{N_i\}$. This may not be a convenient representation to use in many situations, because it may be difficult to keep S and V constant. It may be easier, for example, to keep T and P constant instead, as is the case for many chemistry experiments. In which case, we prefer to use G, the Gibbs free energy.

3.9.4. Internal Energy. The change in internal energy is

$$\boxed{\mathrm{d}U(S, V, \{N_i\}) = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i}$$

if there is more than one chemical species. The differential form $\mathrm{d}U$ is exact, according to the First Law.

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[7] (Optional) For those familiar with the Gibbs-Shannon entropy,

$$S = -k_B \sum_i p_i \log p_i,$$

this situation corresponds to $p_0 = 1$ (where 0 denotes the ground state) and $p_{i \neq 0} = 0$. But this implies that $S = 0$. Even if the ground state is degenerate, their probability would be $p_i = 1/N$ for each of these eigenstates of the ground state. Then, $S = -k_B \sum_{i=1}^{N} \frac{1}{N} \log \frac{1}{N} = k_B \log N$, where N denotes the number of states (not the number of particles). Suppose that the degeneracy is as large as Avogadro's number ($n = 6 \times 10^{23}$), $k_B = 1.38 \times 10^{-23}$, so $S = (1.38 \times 10^{-23}) \log(6 \times 10^{23}) \approx (1.38 \times 10^{-23}) \cdot 55 \approx 10^{-21}$ J/K/mol, which is vanishingly small (well below a measurable value of S).

Note: The Third Law is formulated in terms of "the entropy of a perfect crystal". This is because in a perfect crystal the ground state is unique and non-degenerate. When the ground state is degenerate, the entropy tends to a nonzero value when $T \to 0$.

3.9.5. Enthalpy. The enthalpy is defined as:

$$H(S, P, \{N_i\}) = U + PV.$$

Differentiating:

$$\mathrm{d}H(S, P, \{N_i\}) = \mathrm{d}U + (P\mathrm{d}V + V\mathrm{d}P) = (T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i) + (P\mathrm{d}V + V\mathrm{d}P).$$

This gives:

$$\boxed{\mathrm{d}H(S, P, \{N_i\}) = T\mathrm{d}S + V\mathrm{d}P + \sum_i \mu_i \mathrm{d}N_i.}$$

The enthalpy is useful for processes carried out at constant entropy and pressure, such as chemical reactions. Constant pressure because the reaction is often exposed to atmospheric pressure. The entropy is constant if there is no heat transferred to the system, since $\delta Q^{rev} = T\mathrm{d}S = 0$ (for a reversible process).

A calorimeter is a device that measures the heat flow during a process. They are the chief diagnostic tool in thermodynamics. Many calorimeters operate with the sample at fixed volume. We can design a calorimeter to maintain a constant temperature (using a suitable temperature control system, such as water bath or heating mantle) and constant pressure (by exposure to the atmosphere). Keeping certain variables fixed is important because it isolates the ones of interest. During a process, the enthalpy change is:

$$\Delta H = \int \mathrm{d}H = \int (T\mathrm{d}S + V\mathrm{d}P).$$

If the pressure is fixed during a process ($\mathrm{d}P = 0$), then the enthalpy change is equal to the heat transferred:

$$(\Delta H)_P = \int T\mathrm{d}S = \int \delta Q = \Delta Q.$$

The enthalpy was *invented* to make this relationship true.

3.9.6. Helmholtz Free Energy. The Helmholtz free energy is denoted as A or F, depending on the textbook. It is defined as:

$$A(T, V, \{N_i\}) = F = U - TS.$$

Applying the same ideas as above, you can verify that

$$\boxed{\mathrm{d}A(T, V, \{N_i\}) = -S\mathrm{d}T - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i}$$

The differential form dA is also exact because it was obtained by differentiating A. The Helmholtz free energy is useful for processes carried out at constant temperature and volume (e.g., such as solids, whose volumes don't change).

Note: here, F denotes Helmholtz free energy, not force. In the section below, we will use F to denote force. While F is widely used in the literature to denote Helmholtz free energy, we will use A in these notes to avoid confusing the Helmholtz potential with the force F.

The definition $A = U - TS$ shows that A is determined by a balance between internal energy and entropy. At low temperatures, the energy dominates. At high temperatures, the entropy dominates.

3.9.7. Gibbs Free Energy. The Gibbs Free energy is defined as:

$$G(T, P, \{N_i\}) = U + PV - TS.$$

Similarly,

$$\boxed{\mathrm{d}G(T, P, \{N_i\}) = -S\mathrm{d}T + V\mathrm{d}P + \sum_i \mu_i \mathrm{d}N_i}$$

The differential form $\mathrm{d}G$ is exact because it was obtained by differentiating G. The Gibbs free energy is useful in chemistry for processes carried out at constant temperature and pressure. Notice that $H = U + PV$ and $G = U + PV - TS$ are related by $G = H - TS$.

By integrating $\mathrm{d}G$ at constant temperature ($\mathrm{d}T = 0$) we have the famous formula:[8]

$$\boxed{\Delta G = \Delta H - T\Delta S.}$$

Notice that at constant T, P ($\mathrm{d}T = 0$, $\mathrm{d}P = 0$), the Gibbs free energy is simply a measure of the energy exchanged through chemical transformation:

$$\mathrm{d}G(T, P, \{N_i\}) = \sum_i \mu_i \mathrm{d}N_i. \quad \text{(constant } T, P\text{)}$$

The Gibbs energy was *invented* with this experimental situation in mind. Many chemistry experiments are carried out at constant T, P.

By its construction, $G = H - TS$, the Gibbs free energy describes the balance between enthalpy and entropy (enthalpy dominates at low temperatures; entropy dominates at high temperatures). In a system held at constant P, T, the Gibbs energy will be at a minimum. The system can exchange energy with the surroundings by volume changes and heat transfer. Equilibrium is the state at which the entropy of the system plus surroundings is at a maximum. However, for the system itself, at constant P, T, N, equilibrium occurs when G is at a minimum.

3.9.8. Landau Potential (Grand potential). The grand potential is a quantity used in statistical mechanics, especially for irreversible processes in open systems. The grand

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[8] Take $G = H - TS$ and differentiate to get $\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T = \mathrm{d}H - T\mathrm{d}S$ (since $\mathrm{d}T = 0$). Integrating gives $\Delta G = \Delta H - T\Delta S$, where $\Delta G = \int \mathrm{d}G$, $\Delta H = \int \mathrm{d}H$ and $\Delta S = \int \mathrm{d}S$.

potential is the characteristic state function for the grand canonical ensemble.

$$\Omega(T, V, \{\mu_i\}) = U - TS - \sum_i \mu_i N_i$$

$$\mathrm{d}\Omega(T, V, \{\mu_i\}) = -P\mathrm{d}V - S\mathrm{d}T - \sum_i N_i \mathrm{d}\mu_i$$

3.9.9. Meaning of Free Energy. The term "free energy" refers to any thermodynamic potential that has T as its independent variable instead of S. We know that the entropy of an isolated system can never decrease, however, an isolated system is of little experimental interest. We consider instead a system connected to a much larger system (heat bath) whose properties do not change significantly. For example, a bath may be chosen with T, P constant. Chemical reactions are rarely studied under conditions of constant entropy or constant energy. Usually, the chemist carries out reactions at constant temperature and pressure (T, P), or constant volume and temperature (V, T).

Examples of "free energies" include the Gibbs free energy, $G \equiv G(T, P, \{N_i\})$, and the Helmholtz free energy, $A \equiv A(T, V, \{N_i\})$. Per this definition, the Landau potential is also a type of free energy, since $\Omega \equiv \Omega(T, V, \{\mu_i\})$. On the other hand, H and U are not free energies, since they depend on S not T.

The free energies include:

$$\begin{aligned} A(T, V, \{N_i\}) &= U - TS, \\ G(T, P, \{N_i\}) &= H - TS, \\ \Omega(T, V, \{\mu_i\}) &= A - \sum_i \mu_i N_i. \end{aligned}$$

The thermodynamic potentials that are not free energies include: $U(S, V, \{N_i\})$, $S(U, V, \{N_i\})$, $H(S, P, \{N_i\}) = U + PV$.

3.9.9.1. *Meaning of Free Energy.* First law, $\mathrm{d}U = \delta Q + \delta W$ and second law, $\mathrm{d}S \geq \delta Q/T$, combined: $T\mathrm{d}S \geq \mathrm{d}U - \delta W$. (When changes are slow[9], and the process is reversible, the equality holds, $T\mathrm{d}S = \mathrm{d}U - \delta W$.) Thus, $\delta W \geq \mathrm{d}U - T\mathrm{d}S$. Since $A = U - TS$, at constant temperature, $\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S$, we have that $\delta W \geq \mathrm{d}A$ or $\Delta W \geq \Delta A$. In a reversible process, the equality holds and the total work done is equal to the free energy change. For an irreversible process, the work done on the system by its surroundings is always greater than the increase in free energy. An equivalent formulation is obtained: *the work done by the system to the surroundings is always less than or equal to the* **decrease** *in its free energy.* Thus, the free energy of a system determines the maximum amount of work that the system can do.

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[9] This relation holds for closed systems (closed to particle exchange). When particles can transfer, $T\mathrm{d}S = \mathrm{d}U - \delta W - \mu\mathrm{d}N$.

3.9.10. Any ("Create-Your-Own") Potential. There are situations where other choices of thermodynamic variables may be more convenient than the ones given above. For example, consider the following potential:

$$\Phi(S,P,\{\mu_i\}) = U + PV - \sum_i \mu_i N_i$$

$$\mathrm{d}\Phi(S,P,\{\mu_i\}) = T\mathrm{d}S + V\mathrm{d}P - \sum_i N_i \mathrm{d}\mu_i$$

$\mathrm{d}\Phi$ has the units of work. In classical mechanics infinitesimal work is of the form $F\mathrm{d}x$.[10] Suppose that the variables S, P and μ_i are all spatially-dependent, i.e. $S = S(x)$ [or $S = S(\vec{x})$ in 3D]. Dividing through by $\mathrm{d}x$ gives the force:[11]

$$\boxed{F = \frac{\mathrm{d}\Phi}{\mathrm{d}x} = \underbrace{T\frac{\mathrm{d}S}{\mathrm{d}x}}_{\text{entropic}} + \underbrace{V\frac{\mathrm{d}P}{\mathrm{d}x}}_{\text{mechanical}} \underbrace{-\sum_i N_i \frac{\mathrm{d}\mu_i}{\mathrm{d}x}}_{\text{chemical}}}$$

where $T\frac{\mathrm{d}S}{\mathrm{d}x}$ is interpreted as an *entropic force.*[12]

$$\boxed{F_{entropic} = T\frac{\mathrm{d}S}{\mathrm{d}x}.}$$

The three terms are:

- $T\frac{\mathrm{d}S}{\mathrm{d}x}$ is the entropic force. Entropic force is an emergent force that reflects a system's tendency to reach equilibrium by increasing entropy (in accordance to the Second Law).
- $V\frac{\mathrm{d}P}{\mathrm{d}x}$ is the force of $P-V$ work originating from a pressure gradient (spatially non-uniform pressure). Pressure gradients drive flow.
- $N_i\frac{\mathrm{d}\mu_i}{\mathrm{d}x}$ is the force corresponding to the chemical work.

3.9.11. Entropy Representation, Fundamental Equation. It is sometimes convenient to treat S (rather than U) as the dependent variable, so that $S(U,V,N_i)$ leads to the following *entropy representation* of the fundamental equation

$$\mathrm{d}S(U,V,N_i) = \left(\frac{\partial S}{\partial U}\right)_{V,N_i}\mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{U,N_i}\mathrm{d}V + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_j\neq N_i}\mathrm{d}N_i.$$

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[10] (Optional) $\vec{F}\cdot\mathrm{d}\vec{x}$ in 3D.

[11] We are not really dividing through by $\mathrm{d}x$ but rather invoking the chain rule, i.e. since $S = S(x)$, $\mathrm{d}S(x) = S'(x)\mathrm{d}x = \frac{\mathrm{d}S}{\mathrm{d}x}\mathrm{d}x$.

[12] (Optional) In 3D, the analogous expression is:

$$\vec{F}\cdot\mathrm{d}\vec{x} = \nabla\Phi\cdot\mathrm{d}\vec{x} = T\nabla S\cdot\mathrm{d}\vec{x} + V\nabla P\cdot\mathrm{d}\vec{x} - \sum_i N_i\nabla\mu_i\cdot\mathrm{d}\vec{x}.$$

where $\nabla S = \frac{\partial S}{\partial x}\hat{x} + \frac{\partial S}{\partial y}\hat{y} + \frac{\partial S}{\partial z}\hat{z}$ is the gradient of S, $\nabla S\cdot\mathrm{d}\vec{x}$ is the dot product of ∇S and $\mathrm{d}\vec{x} = \mathrm{d}x\,\hat{x} + \mathrm{d}y\,\hat{y} + \mathrm{d}z\,\hat{z}$, i.e. $\nabla S\cdot\mathrm{d}\vec{x} = \frac{\partial S}{\partial x}\mathrm{d}x + \frac{\partial S}{\partial y}\mathrm{d}y + \frac{\partial S}{\partial z}\mathrm{d}z$, etc.

Which can be read out from the Fundamental equation by isolating dS:

Entropy Representation of the Fundamental Equation:

$$\mathrm{d}S(U,V,N_i) = \left(\frac{1}{T}\right)\mathrm{d}U + \left(\frac{P}{T}\right)\mathrm{d}V - \sum_i \left(\frac{\mu_i}{T}\right)\mathrm{d}N_i.$$

(reversible process, $P = P_{ext}$)

Matching the coefficients we get:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N_i}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N_i}, \quad \frac{\mu_i}{T} = -\left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_j \neq N_i}.$$

The entropy representation gives a natural decomposition of the entropy as the sum of two terms: heat (dU/T) + work (here, PV + chemical term). When d$V = 0$, we are left with heat transfer dU/T plus chemical terms. The chemical term can describe transport of chemical species in and out of the system, or it can describe spontaneous (irreversible) chemical transformations within the system. The heat term can be positive, zero or negative. It can describe reversible or irreversible heat transfer. Spontaneous chemical reactions are irreversible and lead to "entropy production". The latter is nonnegative (≥ 0).

3.9.12. Gibbs Free Energy, Criteria for Spontaneity. The criterion for spontaneity is given by the Second Law (d$S_{univ} \geq 0$):

Spontaneity Criterion (Entropy, d$S_{univ} \geq 0$**):**

d$S_{univ} > 0$	spontaneous (irreversible)
d$S_{univ} = 0$	reversible
d$S_{univ} < 0$	not spontaneous ("forbidden")

In terms of the Gibbs energy $G = H - TS$, this becomes (fixed T and P):

Spontaneity Criterion (Gibbs energy, d$G_{univ} \leq 0$**):**

d$G_{univ} < 0$	spontaneous (irreversible)
d$G_{univ} = 0$	reversible
d$G_{univ} > 0$	not spontaneous ("forbidden")

Thus, maximizing the entropy of the universe is equivalent to minimizing the Gibbs energy. Note that spontaneity does not imply that the reaction will necessarily occur at a detectable rate.

3.9.13. Free Energy in Statistical Thermodynamics. The concept of free energy in statistical thermodynamics is pivotal for understanding the conditions under which a thermodynamic system can perform work. The term "free energy" refers to thermodynamic potentials where the temperature T is held constant. The two main types of free energy are the Helmholtz free energy, F, and the Gibbs free energy, G, which are defined for systems at constant volume and constant pressure, respectively.

The Helmholtz free energy is given by:

$$F = U - TS \tag{3.1}$$

where U is the internal energy, T is the absolute temperature, and S is the entropy. Minimization of the Helmholtz free energy corresponds to the system reaching equilibrium at constant volume and temperature.

The Gibbs free energy, more common in chemical processes, is defined as:

$$G = H - TS \tag{3.2}$$

where H is the enthalpy of the system. The change in Gibbs free energy, ΔG, is a crucial criterion for spontaneity under constant pressure and temperature conditions. A process is spontaneous if ΔG is negative, non-spontaneous if ΔG is positive, and at equilibrium if ΔG is zero.

The spontaneity of a process is not solely determined by the change in enthalpy ΔH, as it does not account for the entropy change of the system. The free energy change combines both enthalpic and entropic factors, providing a complete thermodynamic criterion for spontaneity:

$$\Delta G = \Delta H - T\Delta S \tag{3.3}$$

This equation implies that even if a process is exothermic ($\Delta H < 0$), it may not be spontaneous if the entropy decreases sufficiently ($\Delta S < 0$) such that $T\Delta S$ is greater than ΔH. Conversely, endothermic processes ($\Delta H > 0$) can be spontaneous if they are accompanied by a significant increase in entropy ($\Delta S > 0$).

The equilibrium condition, $dG = 0$, signifies that the system has reached a state where no further spontaneous change is possible, encompassing both enthalpy and entropy changes. While $dH = 0$ and $dF = 0$ also indicate equilibrium states for their respective constant pressure and constant volume conditions, $dG = 0$ is the most comprehensive condition for equilibrium in terms of free energy, applicable to a broad range of chemical and physical processes.

3.9.14. Differences between Enthalpic and Thermodynamic Equilibria. Enthalpy, denoted by H, serves as a comprehensive measure of the total heat content within a system, expressed mathematically as the sum of the system's internal energy U and the product of its pressure P and volume V: $H = U + PV$. An isenthalpic process, implied by a differential change of zero in enthalpy ($dH = 0$), indicates that the system neither absorbs nor releases heat under constant pressure conditions.

However, the absence of heat exchange alone does not necessarily confer a state of thermodynamic equilibrium. Equilibrium, in a broader thermodynamic context, requires the minimization of a potential function that accounts for both energy and entropy factors—such as the Gibbs or Helmholtz free energy—depending on the system constraints.

Isothermal and Isobaric Conditions: Under constant temperature and pressure, a process or reaction that proceeds without a net heat exchange with its surroundings ($\Delta H = 0$) is considered isenthalpic. Nevertheless, this constraint does not guarantee the maximization of entropy, a requisite for thermodynamic equilibrium.

Throttling Process: In a throttling process, a fluid's expansion from a region of high pressure to one of lower pressure occurs adiabatically and without external work, maintaining constant enthalpy. This process underpins certain refrigeration cycles, although it may not achieve thermodynamic equilibrium.

Chemical Reactions: A chemical reaction that manifests no change in enthalpy at constant pressure and temperature is enthalpy-neutral. However, this condition does not imply thermodynamic equilibrium, as the system may be driven away from equilibrium by changes in entropy.

The concept of thermodynamic equilibrium encompasses a state of minimal free energy, not merely an isenthalpic condition. For example, a system may experience no change in heat content ($\Delta H = 0$) yet not be spontaneous if the process involves an entropy decrease ($\Delta S < 0$) that is not compensated by temperature or other contributing factors. Mathematically, the spontaneity of a process at constant temperature and pressure is determined by the Gibbs free energy change (ΔG), given by $\Delta G = \Delta H - T\Delta S$. A process is spontaneous only if ΔG is negative, implying that an isenthalpic process ($\Delta H = 0$) lacking a sufficient entropy increase ($\Delta S > 0$) to offset the $T\Delta S$ term will not spontaneously proceed toward equilibrium.

3.9.15. Thermodynamic Equilibrium and Potential Functions. Thermodynamic equilibrium is a state where macroscopic changes are absent, and the system's properties are unvarying in time. It is a condition that is not merely characterized by constant energy, such as enthalpy, but by a balance between energy and entropy, ensuring the system is at maximum entropy allowed by the constraints.

Two fundamental potential functions are considered in the analysis of thermodynamic equilibrium: Gibbs free energy (G) and Helmholtz free energy (F). These potentials are minimized at equilibrium under specific conditions.

- **Gibbs Free Energy (G):** This potential is minimized for a system at constant pressure (P) and temperature (T). The differential form of Gibbs free energy is given by:

$$dG = dH - TdS - SdT$$

At equilibrium and constant temperature ($dT = 0$), the above relation simplifies to:

$$dG = dH - TdS$$

where dH represents a differential change in enthalpy, T the temperature, and dS the differential change in entropy. A system is in thermodynamic equilibrium when dG is at a minimum, which implies that any spontaneous process at constant T and P will proceed until this minimum is reached.

- **Helmholtz Free Energy (F)**: This potential is minimized for systems at constant volume (V) and temperature (T). The differential form is:

  $$dF = dU - TdS - SdT$$

  With $dT = 0$ at constant temperature, it simplifies to:

  $$dF = dU - TdS$$

  Here, dU is the differential change in internal energy. At equilibrium, dF is at its minimum, indicating that any spontaneous change at constant T and V will proceed towards this state.

The second law of thermodynamics dictates these conditions by stating that the entropy (S) of an isolated system will tend to increase over time, reaching a maximum at equilibrium. The Gibbs and Helmholtz free energies incorporate both the system's internal energy and the entropy term, weighted by temperature. Their minimization ensures that the system is in a state where no additional "useful" work can be extracted, and the entropy is maximized within the system's constraints, which is indicative of true thermodynamic equilibrium.

3.9.16. Euler Relation. Since U is extensive and is also a function of extensive variables S, V, N_i, if these variables are all multiplied by λ, then U will also change by the same factor:

$$U(\lambda S, \lambda V, \{\lambda N_i\}) = \lambda U(S, V, N_i). \qquad (*)$$

Differentiating both sides with respect to λ gives:

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\lambda U(S, V, N_i) = U(S, V, N_i).$$

and

$$\begin{aligned}\left.\frac{\mathrm{d}}{\mathrm{d}\lambda}\right|_{\lambda=1} U(\lambda S, \lambda V, \{\lambda N_i\}) =& \frac{\partial U}{\partial S}\cdot\frac{\mathrm{d}(\lambda S)}{\mathrm{d}\lambda} + \frac{\partial U}{\partial V}\cdot\frac{\mathrm{d}(\lambda V)}{\mathrm{d}\lambda} + \sum_i \frac{\partial U}{\partial N_i}\cdot\frac{\mathrm{d}(\lambda N_i)}{\mathrm{d}\lambda}\\ =& \frac{\partial U}{\partial S}\cdot S + \frac{\partial U}{\partial V}\cdot V + \sum_i \frac{\partial U}{\partial N_i}\cdot N_i\end{aligned}$$

by the chain rule. Here, $\frac{\mathrm{d}}{\mathrm{d}\lambda}\big|_{\lambda=1}$ denotes the derivative with respect to λ evaluated at the point $\lambda = 1$. The partial derivatives $\frac{\partial U}{\partial S}$, $\frac{\partial U}{\partial V}$ and $\frac{\partial U}{\partial N_i}$ are all evaluated at $\lambda = 1$.

Thus, U obeys

$$U = \underbrace{\left(\frac{\partial U}{\partial S}\right)}_{T} S + \underbrace{\left(\frac{\partial U}{\partial V}\right)}_{-P} V + \sum_i \underbrace{\left(\frac{\partial U}{\partial N_i}\right)}_{\mu_i} N_i.$$

Recall[13] that $T \equiv (\partial U/\partial S)$, $P \equiv -(\partial U/\partial V)$, $\mu_i \equiv (\partial U/\partial N_i)$. Then, we get the Euler relation:

$$\boxed{U = TS - PV + \sum_i \mu_i N_i,}$$

which can also be expressed in the *entropy representation* as:

$$\boxed{S = \frac{U}{T} + \frac{PV}{T} - \sum_i \frac{\mu_i N_i}{T}.}$$

3.9.17. Gibbs-Duhem Relation. Differentiating the Euler relation (reversible process, $P = P_{ext}$):[14]

$$U = TS - PV + \sum_i \mu_i N_i,$$

we obtain

$$\mathrm{d}U = T\mathrm{d}S + S\mathrm{d}T - P\mathrm{d}V - V\mathrm{d}P + \sum_i \mu_i \mathrm{d}N_i + \sum_i N_i \mathrm{d}\mu_i.$$

Comparing with the First Law:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i,$$

we see that for both to be correct we must have:

$$\boxed{S\mathrm{d}T - V\mathrm{d}P + \sum_i N_i \mathrm{d}\mu_i = 0. \qquad \text{(Gibbs-Duhem)}}$$

Note: Writing the heat term as $T\mathrm{d}S$ implicitly assumes reversibility of the process. Therefore, we wrote P instead of P_{ext}. The Gibbs-Duhem equation shows that three intensive variables are not independent; if we know two of them, the value of the third can be determined from the Gibbs-Duhem equation.

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[13] From $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N$ we get $T = \partial_S U$, $P = -\partial_V U$ and $\mu = \partial_N U$.

[14] Reversibility is assumed because the expression for $\mathrm{d}U$ (First Law) makes use of $\delta Q = T\mathrm{d}S$, which is true for a reversible process. For an irreversible process we have $\delta Q \leq T\mathrm{d}S$. (See Clausius inequality below.) Incidentally, you can see that this Clausius inequality also implies that $\mathrm{d}U \leq T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i$.

3.9.18. Application: (Chemical Potential of Ideal Gas). Write down Gibbs-Duhem[15] for a single component system:[16]

$$\mathrm{d}\mu = \left(\frac{V}{N}\right)\mathrm{d}P - \left(\frac{S}{N}\right)\mathrm{d}T.$$

If we assume that the temperature is constant ($\mathrm{d}T = 0$) and integrate:

$$\int \mathrm{d}\mu = \mu(T,P) - \mu^\circ(T,P) = \int_{P_0}^{P}\left(\frac{V}{N}\right)\mathrm{d}P.$$

Substituting $V/N = k_BT/P$ from the ideal gas law:

$$\begin{aligned}\mu(T,P) =&\mu^\circ(T,P) + k_BT\log\left(\frac{P}{P_0}\right) = \mu^\circ + k_BT\log\left(\frac{\rho}{\rho_0}\right)\\ =&\mu^\circ + k_BT\log\left(\frac{[c]}{[c]_0}\right)\end{aligned} \tag{3.4}$$

where $\rho = N/V$ and $[c] = n/V = \rho/N_A$.

3.10. Multi-Component Gas

Suppose we have a mixture of gases. Such an expression holds for each component:

$$\mu_i(T,P) = \mu_i^\circ(T,P) + k_BT\log\left(\frac{P_i}{P_0}\right)$$

For ideal gases, Dalton's law holds, $P_i = X_iP$, where P is the total pressure and X_i is the mole fraction of component i. P_0 is a reference pressure, often taken to be 1 atm. Substituting Dalton's law and collecting the terms independent of composition into the square bracket:

$$\mu_i(T,P) = \underbrace{[\mu_i^\circ(T,P) + k_BT\log(P/P_0)]}_{\mu_i^*} + k_BT\log X_i$$

Some textbooks call the square bracket μ_i^*. Regardless of notation, this offset/baseline term corresponds to the chemical potential of the *pure substance* under some reference conditions (P,T). P_0 can be regarded as the unit of pressure used. When $X_i = 1$ (pure substance of type i), the log term is zero and only the square bracket remains. What should this square bracket represent? It is the chemical potential of the pure substance. If our pure substance were an ideal gas, $U = \frac{3}{2}Nk_BT$. Taking the derivative with respect to N gives $\frac{3}{2}k_BT$, which is the energy cost of adding a molecule to a gas at temperature T.

3.10.1. Gibbs Free Energy (Integrated Form, using Euler's Formula).

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[15] An easy trick to remember this equation is to start from the First Law for a reversible chemical process, $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i$, and reverse the roles of the intensive and extensive variables, then set $\mathrm{d}U = 0$.

[16] Gibbs-Duhem assumes reversibility because its derivation involved a $T\mathrm{d}S$ term; hence we may write $P = P_{ext}$.

Definition of Gibbs energy. The Gibbs energy is defined as[17]

$$G(P,T,\{N_i\}) = \underbrace{U + PV}_{H} - TS,$$

where the transformation from U swaps the roles of V in favor of P and S in favor of T. In chemistry it is common to work at constant T and P. With $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i$ (for a reversible process, $\delta Q = T\mathrm{d}S$),

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_i \mu_i \mathrm{d}N_i.$$

Constant T, P. At constant T, P ($\mathrm{d}T = 0$, $\mathrm{d}P = 0$)

$$\mathrm{d}G = \sum_i \mu_i \mathrm{d}N_i.$$

3.10.1.1. *Integrated Form.* Combining $G = U - TS + PV$ with the Euler formula[18] $U = TS - PV + \sum_i \mu_i N_i$

$$\boxed{G = \sum_i \mu_i N_i.}$$

Thus, the *Gibbs free energy is equal to the sum of all the chemical potentials of the molecules in any system,* regardless of any assumptions of constant T or P. (Here we did not impose any restrictions such as constant temperature or pressure[19].)

3.10.1.2. *Single-Component, Ideal Gas.* For a single component[20], $G = \mu N$ and substituting Eq. (3.4) yields:

$$G = G^\circ + k_B T N \log\left(\frac{P}{P_0}\right) = G^\circ + k_B T N \log\left(\frac{\rho}{\rho_0}\right) = G^\circ + k_B T N \log\left(\frac{[c]}{[c]_0}\right).$$

or in terms of *molar Gibbs energy* G/n,

$$\boxed{\frac{G}{n} = \mu^\circ + RT\log\left(\frac{P}{P_0}\right) = \mu^\circ + RT\log\left(\frac{\rho}{\rho_0}\right) = \mu^\circ + RT\log\left(\frac{[c]}{[c]_0}\right).}$$

3.10.2. At Equilibrium, $\mathrm{d}G = 0$**.** For a chemical reaction (usually, T, P are constant), $\mathrm{d}G = \sum_i \mu_i \mathrm{d}N_i$. The second law states that $\mathrm{d}G = 0$ at equilibrium. Thus, $\sum_i \mu_i \mathrm{d}N_i = 0$.

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[17] Note: we have assumed reversibility because of the presence of the $T\mathrm{d}S$ term. In this case, we write P in place of P_{ext}.

[18] An easy way to remember the Euler formula is to start with the First Law for a reversible chemical process, $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i$, and remove the 'd' in the differentials.

[19] The only two elements that were used to derive this formula were the definition of the Gibbs energy and the Euler relation. The latter was derived using the extensively property of the thermodynamic variables. Thus, the result was obtained without assuming constant P or T.

[20] We often write P, ρ and $[c]$ instead of P/P_0, ρ/ρ_0 and $[c]/[c]_0$, where P, ρ and $[c]$ are expressed in units of P_0, ρ_0 and $[c]_0$, respectively.

Or, in integrated form,

$$\Delta G = \int_{react.}^{prod.} \mathrm{d}G = G(prod.) - G(react.) = \sum_i \mu_i \int \mathrm{d}N_i = \sum_i \mu_i \Delta N_i.$$

The equilibrium condition is therefore equivalent to $\sum_i \mu_i \Delta N_i = 0$. However, ΔN_i (and also $\mathrm{d}N_i$) is proportional to the stoichiometric coefficient ν_i. Thus, the equilibrium condition is $\sum_i \mu_i \nu_i = 0$.

There is a sign convention that we must follow for the stoichiometric coefficients: the products are positive, the reactants are negative. Let's look at a simple example:

$$aA + bB \rightleftharpoons cC + dD$$

is written in the more general form

$$0 = \sum_i \nu_i A_i,$$

where A_i denotes the i-th chemical species and ν_i is the associated stoichiometric coefficient (taken negative for a reactant species or positive for a product species) in the balanced chemical equation.

For example, with the reaction $aA + bB \rightleftharpoons cC + dD$, we have that $\nu_1 = -a$, $\nu_2 = -b$, $\nu_3 = c$, $\nu_4 = d$ and $A_1 = A$, $A_2 = B$, $A_3 = C$ and $A_4 = D$.

3.10.3. Chemical Potential, Activity. Activities are used as a way to account for non-idealities of solutions. Chemical potentials can be written in terms of activities (a_i), as follows:

$$\mu_i = \mu_i^\circ + RT \log a_i.$$

This can be taken as the definition of activity:

$$a_i \equiv \exp\left(\frac{\mu_i - \mu_i^\circ}{RT}\right).$$

The equilibrium condition $\sum_i \mu_i \nu_i = 0$ becomes

$$\boxed{0 = \sum_i \mu_i^\circ \nu_i + RT \sum_i \nu_i \log a_i.}$$

The values μ_i° can be found tabulated for different (pure) chemical species i and some standard conditions.

3.10.4. Gibbs Free Energy of Reaction. To recap what we have done, we just calculated ΔG of the reaction, by integrating dG from reactants to products. Some textbooks use a subscript “rxn” to emphasize this:

$$\Delta G_{rxn} = \int_{react.}^{prod.} \mathrm{d}G = G(prod.) - G(react.)$$

$$= \sum_i \mu_i \nu_i = \underbrace{\sum_i \mu_i^\circ \nu_i}_{\Delta G^\circ_{rxn}} + RT \sum_i \nu_i \log a_i.$$

At equilibrium $\Delta G_{rxn} = 0$. (Obviously, this is only valid at constant T, P.)

3.10.5. Standard Gibbs Free Energy of Reaction. The first term is a collection of constants describing an energy change going from reactants to products:

$$\sum_i \mu_i^\circ \nu_i = G^\circ_{prod.} - G^\circ_{react.} = \Delta G^\circ_{rxn}$$

which depends only on the properties of the unmixed species. The quantity ΔG°_{rxn} is known as the *standard Gibbs free energy* of the reaction. Its value can be obtained from tables.

The second term is rewritten as

$$RT \sum_i \nu_i \log a_i = RT \sum_i \log a_i^{\nu_i} = RT \log \left[\prod_i a_i^{\nu_i} \right].$$

Then we have, at equilibrium,

$$\boxed{\Delta G^\circ_{rxn} + RT \log \left[\prod_i a_i^{\nu_i} \right] = 0.}$$

The quantity in the brackets can be identified as the *reactant quotient*, Q, the ratio of product and reactant activities, each raised to its stoichiometric power. For example, for the symbolic reaction:

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \prod_i a_i^{\nu_i} = \frac{products}{reactants} = \frac{a_C^c a_D^d}{a_A^a a_B^b}.$$

3.10.6. Reaction Constant. At equilibrium ΔG°_{rxn} and T are constants, $Q = K$ and we have the central equation of chemical equilibrium theory:

$$\boxed{\Delta G^\circ_{rxn} = -RT \log K}$$

where $K = \frac{a_C^c a_D^d}{a_A^a a_B^b}$ (activities are equilibrium values). Your book uses the notation $K_C = \frac{[C]^c_{eq}[D]^d_{eq}}{[A]^a_{eq}[B]^b_{eq}}$ when dealing with solutions. Here, the concentrations are equilibrium values.

Note that $a_i \propto [A_i] = n_i/V$ and the proportionality constants have been absorbed into the definition of K_C. Similarly, for gaseous mixtures, $a_i \propto P_i$ and $K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$.

3.10.7. What is the Meaning of the Standard Gibbs Free Energy? We saw in the previous lecture that chemical reactions can be written in the general form, $\sum_i \nu_i A_i = 0$, where A_i denotes the i-th chemical species and ν_i is the associated stoichiometric coefficient (taken negative for a reactant species or positive for a product species) in the balanced chemical equation. For example, with the reaction $aA + bB \rightleftharpoons cC + dD$, we have that $\nu_1 = -a$, $\nu_2 = -b$, $\nu_3 = c$, $\nu_4 = d$ and $A_1 = A$, $A_2 = B$, $A_3 = C$ and $A_4 = D$. At chemical equilibrium we have that $\mathrm{d}G = 0$ (constant T, P), where $\mathrm{d}G = \sum_i \mu_i \mathrm{d}n_i$. Integrating from reactants to products gives

$$\Delta G_{rxn} = G(prod.) - G(react.) = \sum_i \mu_i \nu_i,$$

since

$$\int_{react.}^{prod.} \mathrm{d}n_i = \Delta n_i = \nu_i$$

(with the above sign convention). Thus, $\sum_i \mu_i \nu_i = 0$. Finally, we note that the combination of $G = U - TS + PV$ and the Euler formula, $U = TS - PV + \sum_i \mu_i n_i$, leads to $G = \sum_i \mu_i n_i$, which, for a single component, implies that $G_i/n_i = \mu_i$ (μ_i, the chemical potential, is also the molar Gibbs energy). We have seen that substitution of the ideal gas expression for μ_i into $\sum_i \mu_i \nu_i = 0$ leads to $\Delta G_{rxn} = \Delta G^0_{rxn} + RT \log Q$, where $\Delta G^0_{rxn} = \sum_i \mu_i^\circ \nu_i$. It is important to note that ΔG_{rxn} and ΔG°_{rxn} are two different things.

ΔG°_{rxn} is computed as follows:

$$\boxed{\Delta G^\circ_{rxn} = \sum_i \nu_i (\Delta G^\circ_f)_i,}$$

where ν_i are the stoichiometric coefficients of species i in the reaction (products are positive, reactants are negative) and ΔG°_f are standard Gibbs energies of formation (i denotes the i-th chemical species in the reaction). These values are found in tables. The symbol ° attached to ΔG_{rxn} means "standard" Gibbs energy, which has a single value for a particular reaction at a given temperature and pressure. We can obtain the value of ΔG°_{rxn} from tables (such as Appendix D of Oxtoby [**9**]). It corresponds to the free energy change for a process that never really happens: the *complete transformation* of pure reactants into pure products at a constant pressure of 1 atm (or whatever the reference conditions happen to be; but usually 1 atm). In the case of the reaction:

$$\mathrm{C}(s, graphite) + 2\mathrm{O}_2(g) \to \mathrm{CO}_2(g),$$

ΔG°_{rxn} is the free energy change for the complete transformation of pure graphite and O_2 into pure CO_2 at a constant pressure of 1 atm.

In contrast to ΔG°_{rxn}, which is a *constant* for a given reaction, ΔG_{rxn} varies continuously as the composition changes, finally reaching zero at equilibrium. ΔG_{rxn} is the "distance" (in free energy) from the equilibrium state of a given reaction. The two are related by:

$$\boxed{\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT \log Q,}$$

where Q is the reaction quotient, which would be, for a reaction

$$aA + bB \to cD + dD$$

$Q = P^c_C P^d_D/(P^a_A P^b_B)$ or $Q = [C]^c[D]^d/([A]^a[B]^b)$. At equilibrium we have $\Delta G_{rxn} = 0$ and the above equation gives $\Delta G^0_{rxn} = -RT \log K$ (because $Q = K$ at equilibrium).

The change in standard Gibbs free energy *for the above reaction* is the sum of standard Gibbs energies of formation:

$$\boxed{\Delta G^\circ_{rxn} = c(\Delta G^\circ_f)_C + d(\Delta G^\circ_f)_D - a(\Delta G^\circ_f)_A - b(\Delta G^\circ_f)_B.}$$

The equation, $\Delta G^0_{rxn} = -RT \log K$, is important because it relates the equilibrium composition of a chemical reaction system to measurable physical properties of the reactants and products. If you know the entropies (S°) and the enthalpies (ΔH°_f) of formation of a set of substances, you can predict (since $\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$ at constant temperature) the equilibrium constant of any reaction involving these substances without the need to know anything about the mechanism of the reaction. We may find tables of ΔG°_f, S° and ΔH°_f for different substances in chemistry handbooks (e.g., [**13**]) or textbooks (e.g., [**9**]).

The standard enthalpy of formation or standard heat of formation of a compound is the change of enthalpy during the formation of 1 mole of the substance from its constituent elements, with all substances in their standard states, and at a pressure of 1 atm. There is no standard temperature. It is usually denoted ΔH°_f. The superscript ° on this symbol indicates that the process has occurred under standard conditions at the specified temperature (usually 25°C).

The standard Gibbs free energy of formation of a compound is the change of Gibbs free energy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard states (the most stable form of the element at 1 atm of pressure and the specified temperature, usually 25°C).

3.10.8. Where to Find Values for ΔH°_f, ΔG°_f and S°. Values of ΔH°_f, S° and ΔG°_f can be found tabulated in most chemistry textbooks (usually, in appendices), and on the internet. In chemistry books, we do not find ΔG°_{rxn} values for all possible chemical reactions, because it would be impossible to list all possible chemical reactions (there are too many of them). Instead, we will find tables of the energy of formation of various compounds, which may be involved in your reaction. Textbooks often denote these energies of formation as ΔG°_f.

Standard enthalpies of formation can be found at
`https://en.wikipedia.org/wiki/Standard_enthalpy_of_formation`

Standard Gibbs free energies of formation can be found at
`https://en.wikipedia.org/wiki/`
`Standard_Gibbs_free_energy_of_formation`

Appendix D of Oxtoby [**9**], entitled "Standard Chemical Thermodynamic Properties", contains tabulated values for enthalpies, entropies and Gibbs energies of formation. Please note that Oxtoby [**9**] writes S° and not ΔS_f°. This is because the Third Law guarantees the existence of an absolute entropy scale. So what is being tabulated here is the absolute entropy S° for each substance. On the other hand, there exists no absolute scale for ΔH_f° and ΔG_f°, hence the Δ notation.

Table 3.2 is an excerpt from page 1 of the Appendix D of Oxtoby [**9**]. Oxtoby [**9**] prefaces the table as follows: "This table lists standard enthalpies of formation ΔH_f°, standard third-law entropies S°, standard free energies of formation ΔG_f°, and molar heat capacities at constant pressure, c_P, for a variety of substances, all at 25°C (298.15 K) and 1 atm. [...] Note that the solution-phase entropies are not absolute entropies but are measured relative to the arbitrary standard $S^\circ(\mathrm{H}^+(aq)) = 0$. Consequently, some of them (as well as some of the heat capacities) are negative."

Table 3.2. Excerpt from Appendix D of Oxtoby [**9**].

Substance	$\Delta H_f^\circ(25^\circ\mathrm{C})$	$S^\circ(25^\circ\mathrm{C})$	$\Delta G_f^\circ(25^\circ\mathrm{C})$	$c_P(25^\circ\mathrm{C})$
units	kJ/mol	J/K/mol	kJ/mol	J/K/mol
$\mathrm{H}(g)$	217.96	114.60	203.26	20.78
$\mathrm{H_2}(g)$	0	130.57	0	28.82
$\mathrm{H^+}(aq)$	0	0	0	0
$\mathrm{H_3O^+}(aq)$	-285.83	69.91	-237.18	75.29
$\mathrm{Li}(s)$	0	29.12	0	24.77
$\mathrm{Li}(g)$	159.37	138.66	126.69	20.79
$\mathrm{Li^+}(aq)$	-278.49	13.4	-293.31	68.6
$\mathrm{LiH}(s)$	-90.54	20.01	-68.37	27.87
$\mathrm{Li_2O}(s)$	-597.94	37.57	-561.20	54.10
$\mathrm{LiF}(s)$	-615.97	35.65	-587.73	41.59
$\mathrm{LiCl}(s)$	-408.61	59.33	-384.39	47.99
$\mathrm{LiBr}(s)$	-351.21	74.27	-342.00	—
$\mathrm{LiI}(s)$	-270.41	86.78	-270.29	51.04
$\mathrm{Na}(s)$	0	51.21	0	28.24
$\mathrm{Na}(g)$	107.32	153.60	76.79	20.79
$\mathrm{Na^+}(aq)$	-240.12	59.0	-261.90	46.4
$\mathrm{Na_2O}(s)$	-414.22	75.06	-375.48	69.12
$\mathrm{NaOH}(s)$	-425.61	64.46	-379.53	59.54

NaF(s)	-573.65	51.46	-543.51	48.86
NaCl(s)	-411.15	72.13	-384.15	50.50

3.10.9. The Standard States. When writing ΔG_f°, the ° indicates that all components (reactants and products) are in their standard states. This concept of standard states is especially important in the case of the free energy. For most practical purposes, the following definitions are used

(see `https://en.wikipedia.org/wiki/Standard_enthalpy_of_formation`)

- Gases: 1 atm partial pressure (i.e., the hypothetical state it would have assuming it obeyed the ideal gas equation at a pressure of 1 atm).
- Pure liquids: for a solute present in an ideal solution, a concentration of exactly 1 M at a pressure of 1 atm.
- Solutes: an effective concentration of 1 mol/L. ("Effective" concentrations approach real concentrations as the latter approach zero; for practical purposes, these can be considered identical at real concentrations smaller than about 10^{-4} molar.)
- Solids: for a pure substance or a solvent in a condensed state (a liquid or a solid), the standard state is the pure liquid or solid under a pressure of 1 atm.
- For an element: the form in which the element is most stable under 1 atm of pressure. One exception is phosphorus, for which the most stable form at 1 atm is black phosphorus, but white phosphorus is chosen as the standard reference state for zero enthalpy of formation.
- All elements in their standard states (oxygen gas, hydrogen gas, nitrogen gas, solid carbon in the form of graphite, etc.) have a standard enthalpy of formation (ΔH°) of zero, as there is no change involved in their formation.
- There is no "standard temperature" in thermodynamics, but one often uses 25°. (Thermodynamic standard state is different from STP used in gas law calculations.)
- Some texts will use 1 atm as the reference pressure; others may use 1 bar.

3.10.10. Example Calculation. Find the standard Gibbs energy change for the reaction

$$\mathrm{CaCO_3}(s) \to \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

where the following values of standard Gibbs energies of formation are found from tables: $\mathrm{CaCO_3}(s)$: -1128 kJ/mol, $\mathrm{CaO}(s)$: -603.5 kJ/mol, $\mathrm{CO_2}(g)$: -137.2 kJ/mol.

Solution: Substitute these values into the equation for ΔG°_{rxn}, we find:

$$\Delta G^\circ_{rxn} = (-603.5 - 137.2) - (-1128) \text{ kJ/mol} = +387.3 \text{ kJ/mol}.$$

A positive value for ΔG°_{rxn} means that the process is not spontaneous (under standard conditions), i.e. solid calcium carbonate will not form solid calcium oxide and $\mathrm{CO_2}$ at 1 atm at 25°. Note: This reaction is carried out on a large scale to manufacture cement, so obviously the process can be spontaneous under different conditions.

Recall the relationship between K and ΔG°_{rxn}:

$$K = \exp\left(-\frac{\Delta G^\circ_{rxn}}{RT}\right).$$

Here, since ΔG°_{rxn} is positive, $K < 1$, meaning the equilibrium favors the reactants, meaning that $\mathrm{CaCO_3}$ wants to remain in its solid form.

The practical importance of the Gibbs energy is that it allows us to make predictions based on the properties (ΔG°_{rxn} values) of the reactants and products themselves, eliminating the need for experiment.

3.10.11. Heat Transfer at Constant Volume and Pressure. For a closed system ($\mathrm{d}N_i = 0$) under constant volume,

$$\mathrm{d}U = \delta Q - \underbrace{P_{ext}\,\mathrm{d}V}_{\mathrm{d}V=0} = \delta Q_V = C_V(T)\mathrm{d}T,$$

which implies that

$$\boxed{C_V(T) = \left(\frac{\partial U}{\partial T}\right)_V}$$

If the temperature dependence of C_V over some temperature range of interest is negligible, $C_V(T) = C_V$, the expression for $\mathrm{d}U$ can be integrated to give:

$$\Delta U = C_V \Delta T.$$

For a closed system at constant pressure,

$$\mathrm{d}H = \delta Q + \underbrace{V\mathrm{d}P_{ext}}_{\mathrm{d}P_{ext}=0} = \delta Q_P = C_P(T)\mathrm{d}T,$$

which implies that

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P.}$$

If C_P is independent of temperature we can integrate $\mathrm{d}H$ to get:

$$\Delta H = C_P \Delta T.$$

3.10.12. Relationship Between Specific Heats. Take the derivative of

$$H = U + PV \qquad \text{(definition of enthalpy)}$$

with respect to temperature:

$$\underbrace{\frac{\partial H}{\partial T}}_{C_P} = \frac{\partial(U+PV)}{\partial T} = \underbrace{\frac{\partial U}{\partial T}}_{C_V} + \frac{\partial(PV)}{\partial T}$$

$$\boxed{C_P = C_V + \frac{\partial(PV)}{\partial T}.}$$

For an ideal gas, $PV = nRT$, so the second term equals nR, and we obtain:

$$C_P = C_V + nR.$$

Dividing through by n we get a relationship between the specific heats:

$$\boxed{c_P = c_V + R.} \quad \text{(Mayer's relation)}$$

A look at the term $\frac{\partial(PV)}{\partial T}$ reveals that it is always positive because as temperature increases, PV also increases. Thus, $C_P > C_V$.

The situation is illustrated in Fig. 3.7.

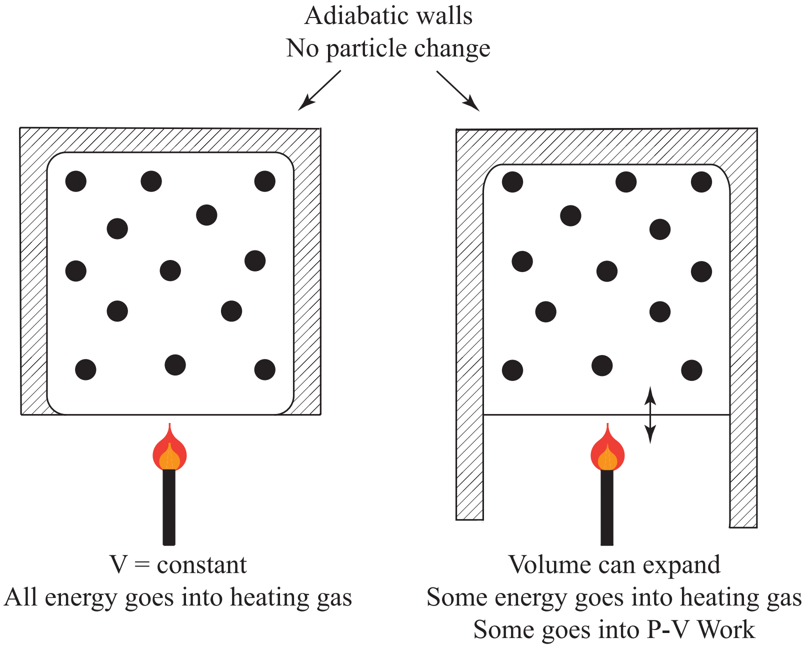

Figure 3.8. Difference between heating at constant pressure vs volume.

Thus,

$$\left(\frac{\partial U}{\partial T}\right)_V \equiv \boxed{C_V < C_P} \equiv \left(\frac{\partial H}{\partial T}\right)_P.$$

The enthalpy accounts for energy transfer to the environment through the expansion of the system.

3.10.13. Latent Heat. Latent heats are associated with phase transitions, such as the melting of solids or vaporization of liquids and solids. It is the heat absorbed or released by a thermodynamic system as it undergoes a phase transition.

At the microscopic level, this heat serves to break or form bonds. Such heats are also called heat of fusion (melting), heat of vaporization, etc. There are entropy changes associated with such phase transitions, namely, the entropy of fusion, entropy of vaporization, etc. Entropy changes because there is a spatial rearrangement of the molecules in the system (e.g. from ordered crystal to disorder in a liquid). See Fig. 3.9.

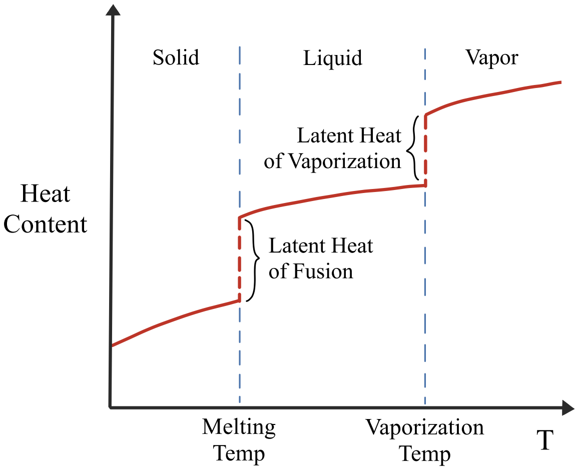

Figure 3.9. Difference between heating at constant pressure vs volume.

For a reversible process,

$$\mathrm{d}S = \frac{\delta Q^{rev}}{T}$$

Consider a small temperature interval $[T_C - \epsilon, T_C + \epsilon]$ centered on T_C (critical temperature), with ϵ so small that the temperature is essentially constant. The system undergoes a phase transition at T_C. The latent heat associated with this transition is

$$\delta Q_{lat} = T_C\,\mathrm{d}S_{lat}, \quad \text{or} \quad \Delta Q_{lat} = T_C\,\Delta S_{lat},$$

where ΔS_{lat} is called the *entropy of fusion or vaporization*, if the process is one of melting or evaporation, respectively.

We can also express it in terms of the enthalpy change $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P$ at constant pressure ($\mathrm{d}P = 0$) gives

$$\Delta S = \int_{T_C-\epsilon}^{T_C+\epsilon} \frac{\mathrm{d}H}{T}$$

across the phase transition (see Fig. 3.10).

and

$$\boxed{\Delta S_{lat} = \frac{\Delta H_{lat}}{T_C},}$$

where T_C is the phase transition temperature (critical temperature) and ΔH_{lat} is the latent heat. Since we assumed constant P, ΔH_{lat} is the same as ΔQ_{lat}. This formula gives the entropy change ΔS_{lat} corresponding to latent heat ΔH_{lat} of a phase transition at constant P.

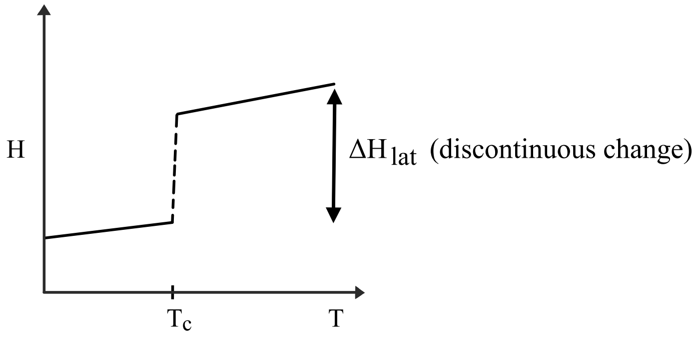

Figure 3.10. Latent heat.

Remarks:

- ΔS_{lat} and ΔH_{lat} represent discontinuous changes between two phases of the same substance occurring at the transition temperature T_C.
- Latent heats are tabulated as *specific latent heats*, L, which is an intensive property: $L \equiv \Delta Q_{lat}/m$, where m is the mass of the substance. The common units are kJ/kg.

3.10.14. Application of First and Second Laws: Equilibrium Establishes a Common Temperature. Suppose that A denotes the system and B denotes the surroundings (see Fig. 3.11) and that A and B are separated by a thermally conductive wall. Assume that the volumes of A and B do not change. The combined system is the *universe* and it is isolated. Because entropy is an *extensive* property, S_A and S_B added yields the entropy of the universe:

$$S = S_A + S_B.$$

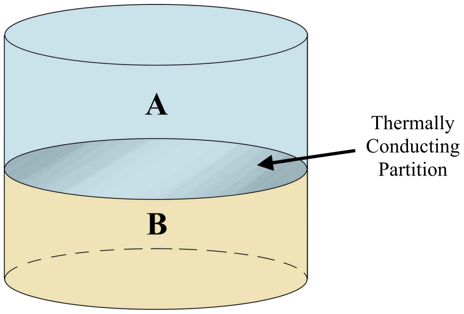

Figure 3.11. Two closed, constant-volume, sub-systems are separated by a thermally conducting partition. The second law requires that at thermal equilibrium the temperatures of the two subsystems will necessarily become equal ($T_A = T_B$).

First, we rewrite the fundamental equation

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i$$

in the entropy representation:

$$\mathrm{d}S = \left(\frac{1}{T}\right)\mathrm{d}U + \left(\frac{P}{T}\right)\mathrm{d}V - \sum_i \left(\frac{\mu_i}{T}\right)\mathrm{d}n_i.$$

The entropy of the isolated system ("universe") is the sum of entropies of A and B, $S = S_A + S_B$ (entropy is additive). Then, we invoke the fundamental equation in the entropy representation (with $\mathrm{d}V = 0$ and $\mathrm{d}N_i = 0$),

$$\mathrm{d}S = \mathrm{d}S_A + \mathrm{d}S_B = \left(\frac{1}{T_A}\right)\mathrm{d}U_A + \left(\frac{1}{T_B}\right)\mathrm{d}U_B$$

where we have invoked the First Law twice, once for S_A and once for S_B. Since energy is conserved ($A + B$ is an isolated system) $\mathrm{d}U_A = -\mathrm{d}U_B$:

$$\mathrm{d}S = \left[\left(\frac{1}{T_A}\right) - \left(\frac{1}{T_B}\right)\right]\mathrm{d}U_A.$$

Since V_A, V_B, N_A, N_B are all constant, there can be no mechanical or chemical work exchanged between the system and its surroundings and so $\mathrm{d}U_A = \delta Q$.

$$\mathrm{d}S = \left[\left(\frac{1}{T_A}\right) - \left(\frac{1}{T_B}\right)\right]\delta Q \tag{3.5}$$

where δQ is the heat transferred to the system (or to the surroundings if $\delta Q < 0$). At thermal equilibrium, entropy of the system is maximized $\mathrm{d}S = 0$. So a nonzero infinitesimal heat exchange $\delta Q \neq 0$ implies that the temperatures of A and B must be equal:

$$\boxed{T_A = T_B.} \quad (A \text{ and } B \text{ in thermal equilibrium})$$

Note: Suppose that T_A (the system) is higher than T_B. Then we expect heat to flow from the system into the surroundings. The second law $\mathrm{d}S \geq 0$ and Eq. (3.5) imply that $\mathrm{d}U_A = \delta Q < 0$ and indeed heat flows out of the system. So the Second Law correctly predicts the direction of the heat exchange.

3.10.15. When is Heat Transfer Reversible? We have previously seen that reversibility is defined as a process for which the surroundings have intensive variables that are arbitrarily close to those of the system, i.e. $P = P_{ext} + \mathrm{d}T$, $P = P_{ext} + \mathrm{d}P$, $\mu = \mu_{ext} + \mathrm{d}\mu$. We've also seen that $\mathrm{d}S = 0$ when a process is reversible. Let us check that these two conditions imply each other. Using the notation from the previous section, we would expect that if T_A is vastly different than T_B, the process would not be reversible. Let $T_B = T$ and $T_A = T - \mathrm{d}T$ so that the process is truly reversible. Then,

$$\mathrm{d}S = \left[\left(\frac{1}{T - \mathrm{d}T}\right) - \left(\frac{1}{T}\right)\right]\delta Q$$

Factoring out $1/T$ and invoking the geometric series, $1/(1-r) = 1 + r + r^2 + \dots$ with $r = dT/T$, we have:

$$\mathrm{d}S = \left[\left(1 + \frac{\mathrm{d}T}{T} + \frac{\mathrm{d}T^2}{T^2} + \dots\right) - 1\right]\frac{\delta Q}{T} \approx \frac{\delta Q \mathrm{d}T}{T^2} \approx 0,$$

since $\delta Q \mathrm{d}T$ is an infinitesimal of the second order. Thus, the entropy change $\mathrm{d}S$ is zero when the process is reversible.

3.10.16. Can we Have Isothermal Heat Transfer? Isothermal means $\mathrm{d}T = 0$ or $T = constant$. From $\mathrm{d}S = \delta Q^{rev}/T$, a heat transfer δQ^{rev} to the system corresponds to a change in its energy in the amount of $T\mathrm{d}S$. Thus, it describes a change in entropy, i.e. given $\Delta Q^{rev} > 0$, we must have $\Delta S > 0$. This can happen, for example, during the course of a phase transition. Some amount of heat (latent heat) is transferred to the system at constant temperature while the entropy changes.

3.10.17. Application of First and Second Laws: Chemical Equilibria. In a similar way, we can use the Second Law to predict that at thermal equilibrium the chemical potentials of the reactant and product species should be equal to each other. Consider a chemical a system in which one chemical component (A) may react to form another component (B). For example, A and B could be the gauche and trans conformational isomers of n-butane, or they could be the native and denatured states of a protein. See Fig. 3.12.

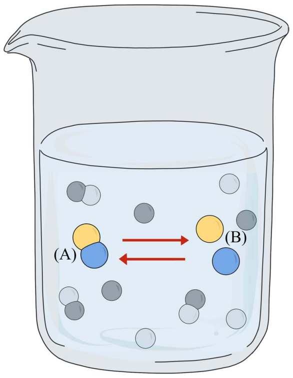

Figure 3.12. A closed, insulated, constant-volume, system contains molecules that can inter-convert between two different chemical states (A and B). The second law requires that the chemical potentials of the two compounds must become equal ($A = B$) at equilibrium.

We will also assume that the container which holds the system is insulated and sealed (so neither heat nor matter can enter or leave), and that the volume of the container is constant. Thus, no work or heat exchange can take place between the system and its surroundings (so it is isolated).

Now imagine that we initially put some amounts of A and B into the system which are not equal to their equilibrium concentrations. The entropy representation of the fundamental equation implies that the total entropy change is

$$\mathrm{d}S(U,V,N_i) = \left(\frac{1}{T}\right)\mathrm{d}U + \left(\frac{P}{T}\right)\mathrm{d}V - \sum_i \left(\frac{\mu_i}{T}\right)\mathrm{d}N_i,$$

and since energy and volume are constant $\mathrm{d}U = \mathrm{d}V = 0$,

$$\mathrm{d}S = -\left(\frac{\mu_A}{T_A}\right)\mathrm{d}N_A - \left(\frac{\mu_B}{T_B}\right)\mathrm{d}N_B.$$

At thermal equilibrium $T_A = T_B = T$. Moreover, stoichiometric balance requires that $\mathrm{d}N_B = -\mathrm{d}N_A$,

$$\mathrm{d}S = -\left[\left(\frac{\mu_A}{T}\right) - \left(\frac{\mu_B}{T}\right)\right]\mathrm{d}N_A.$$

At equilibrium $\mathrm{d}S = 0$ and (provided $\mathrm{d}N_A \neq 0$),

$$\mu_A = \mu_B.$$

Away from equilibrium $\mathrm{d}S > 0$, so if $\mu_A > \mu_B$ then we must have $\mathrm{d}N_A < 0$ (reactants are consumed), as would be expected. Thus, the Second Law correctly predicts the direction of change in a chemical reaction.

3.10.18. Generalization to Arbitrary Reactions. The above result may be extended to chemical reactions involving more complex stoichiometry,

$$\sum_{i=1}^{n_R} a_i A_i \rightleftharpoons \sum_{i=1}^{n_P} b_i B_i$$

where a_i and b_i are stoichiometric coefficients for the reactant A_i and product B_i species, respectively. n_R is the number of reactants. n_P is the number of products.

The chemical reaction can be written as an equation, where $\{A_i\}$ denote the set of all reactants and products, $\{\nu_i\}$, the set of stoichiometric coefficients with the convention that ν_i are positive numbers for the reactants ($\nu_i = a_i$) and negative numbers for the products ($\nu_i = -b_i$),

$$\sum_{i=1}^{n_S} \nu_i A_i = 0,$$

with $n_S = n_R + n_P$.

For any such reaction one may use the following equation to express the relationship between the chemical potentials of the reacting species at equilibrium:

Chemical Equilibrium:

$$\sum_{i=1}^{n_S} \nu_i \mu_i = 0 \qquad \text{at equilibrium.}$$

This result follows from the same analysis as in the previous section. There, we would also have that at thermal equilibrium, all temperatures are the same, $T_i = T$ for all i.

The $\mathrm{d}N_i$ are parametrized by a new variable t, i.e. so that $\mathrm{d}N_i(t) = N_i'(t)\mathrm{d}t$, where $t \in [0, 1]$ is a variable that denotes the "extent of the reaction". Then $t = 0$ the reaction begins and when $t = 1$, it ends. $N_i'(t)$ is the speed at which species i is produced or depleted; it is proportional to the stoichiometric coefficient ν_i, so we write $N_i'(t) = \alpha\nu_i$, where α is a constant.[21]

Under those conditions, the chemical term in $\mathrm{d}S$ reads:

$$\mathrm{d}S = -\left[\sum_{i=1}^{n_S}\left(\frac{\mu_i}{T_i}\right)\alpha\nu_i\right]\mathrm{d}t = -\frac{\alpha}{T}\left[\sum_{i=1}^{n_S}\mu_i\nu_i\right]\mathrm{d}t.$$

At equilibrium, $\mathrm{d}S = 0$ (provided $\mathrm{d}t \neq 0$), from which it follows that the coefficient of $\mathrm{d}t$ must vanish, i.e. $\sum_{i=1}^{n_S}\nu_i\mu_i = 0$.

3.10.19. Application of First and Second Laws: Phase Equilibrium. Consider a system composed of two sub-systems whose boundary allows the exchange of molecules, as well as heat and mechanical work. For example, one sub-system could be a vapor phase A and the other a liquid phase B, as shown in Fig. 3.13. In such a situation, we may again invoke the Second Law to obtain general relations between all of the intensive variables of the two sub-systems at equilibrium.

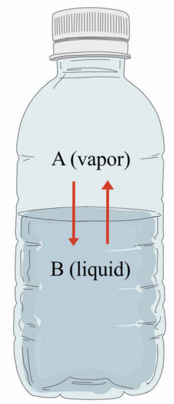

Figure 3.13. A closed, insulated, constant-volume, system contains two phases (A and B). The second law requires that at equilibrium the temperature, pressure and chemical potentials of the two phases will necessarily become equal ($T_A = T_B$, $P_A = P_B$ and $\mu_A = \mu_B$).

---

[21] If t is time, then $\mathrm{d}N_i$ denotes the change in number of molecules of species i whereas $N_i'(t)\mathrm{d}t$ denotes the rate of change in N_i times $\mathrm{d}t$.

For simplicity we will assume there is only one chemical component in the system (such as water). We assume that the number of water molecules in the vapor phase is N_A and in the liquid phase is N_B.

Note that when molecules are exchanged between the two phases the volumes V_A and V_B, as well as the energies U_A and U_B, of each phase will also change. We further assume that both phases are enclosed by a sealed and insulated container of fixed total volume (so the entire system is isolated from its surroundings).

When we apply the fundamental equation to each phase we obtain the following expressions.

$$\begin{aligned}\mathrm{d}S_A &= \left(\frac{1}{T_A}\right)\mathrm{d}U_A + \left(\frac{P_A}{T_A}\right)\mathrm{d}V_A - \left(\frac{\mu_A}{T_A}\right)\mathrm{d}N_A\\ \mathrm{d}S_B &= \left(\frac{1}{T_B}\right)\mathrm{d}U_B + \left(\frac{P_B}{T_B}\right)\mathrm{d}V_B - \left(\frac{\mu_B}{T_B}\right)\mathrm{d}N_B.\end{aligned}$$

The entropy change of the entire system is again $\mathrm{d}S = \mathrm{d}S_A + \mathrm{d}S_B$. Since the total energy, volume and number of molecules are all conserved, we may equate $\mathrm{d}U_A = -\mathrm{d}U_B = \mathrm{d}U$, $\mathrm{d}V_A = -\mathrm{d}V_B = \mathrm{d}V$, and $\mathrm{d}N_A = -\mathrm{d}N_B = \mathrm{d}N$. Thus, an infinitesimal entropy change of the whole system, resulting from the transfer of some molecules between phase A and phase B, may be expressed as follows.

$$\mathrm{d}S = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\mathrm{d}U + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)\mathrm{d}V - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right)\mathrm{d}N.$$

At equilibrium $\mathrm{d}S = 0$ when $\mathrm{d}U \neq 0$ and $\mathrm{d}V \neq 0$ and $\mathrm{d}N \neq 0$, so all three quantities in parentheses must equal to zero. Thus implies that all three of the following intensive variables of the two phases must be equal at equilibrium:

$$\boxed{T_A = T_B, \qquad P_A = P_B, \qquad \mu_A = \mu_B.}$$

In fact, you can check that

$$\boxed{T_A = T_B + \mathrm{d}T, \qquad P_A = P_B + \mathrm{d}P, \qquad \mu_A = \mu_B + \mathrm{d}\mu,}$$

leads to equilibrium ($\mathrm{d}S = 0$).

In any two phase equilibrium all of the intensive variables of the two phases – temperatures, pressures and chemical potentials – must be in perfect balance with each other.

If the system contained more than one chemical species then similar expressions would hold for each chemical species. Moreover, if the system contained molecules that can chemically react with each other, then $\sum_i \nu_i \mu_i = 0$ would impose an additional equilibrium condition which must hold for any such reactive species.

3.10.20. Application of Chemical Potential, Various Equilibria.

Gibbs energy of mixing. Suppose that we have two perfect gases, A and B, in two containers, in the amounts n_A and n_B, respectively. Both are at temperature T and pressure P. The chemical potentials of the two gases have their "pure" values,

$$\mu = \mu^\circ + RT\log(P/P_0)$$

where μ° is the *standard chemical potential*, the chemical potential of the pure gas at 1 bar. See Fig. 3.14.

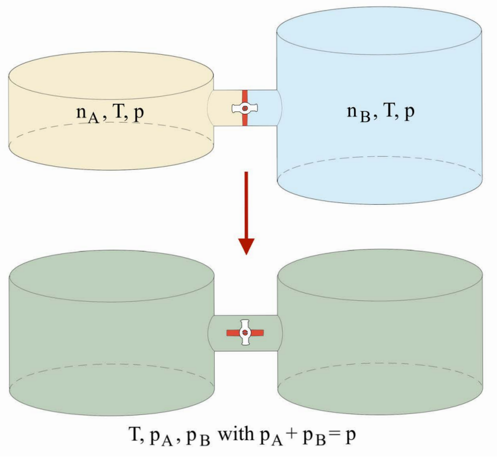

Figure 3.14. Arrangement for calculating the thermodynamic functions of mixing of two perfect gases.

Taking P_0 to be 1 bar and writing P instead of P/P_0, the Gibbs energy of the total system is (before mixing):

$$G_i = n_A\mu_A + n_B\mu_B = n_A(\mu_A^\circ + RT\log P) + n_B(\mu_B^\circ + RT\log P).$$

After mixing, the partial pressures are P_A and P_B ($P_A + P_B = P$). The total Gibbs energy changes to:

$$G_f = n_A(\mu_A^\circ + RT\log P_A) + n_B(\mu_B^\circ + RT\log P_B)$$

The difference, $G_f - G_i$, the Gibbs energy of mixing, ΔG_{mix}, is therefore

$$\Delta G = G_f - G_i = n_ART\log(P_A/P) + n_BRT\log(P_B/P).$$

Replacing n_A by X_An, where n is the total number of moles of A and B, and using Dalton's law, $P_A = X_A \cdot P$, we have:

$$\boxed{\Delta G_{mix} = nRT(X_A\log X_A + X_B\log X_B).}$$

Because $0 \leq X_A, X_B \leq 1$, the logs are negative and $\Delta G_{mix} < 0$. Thus, perfect gases mix spontaneously in all proportions. And from $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P$, $S = -(\partial G/\partial T)$, the entropy of mixing is:

$$\Delta S_{mix} = -nR\{X_A\log X_A + X_B\log X_B\}.$$

Note: since $\Delta G = \Delta H - T\Delta S$, it follows that $\Delta H_{mix} = 0$. This is expected for a system in which there are no interactions between the molecules forming the gaseous mixture. It follows that the driving force for mixing comes from the increase in entropy of the system because the entropy of the surroundings is unchanged.

3.10.20.1. *Example: (Gibbs energy of mixing).* A container is divided into two equal compartments (Fig. 3.15). One contains 3.0 mol H_2(g) at 25°C. The other contains 1.0 mol N_2(g) at 25°C. Calculate the Gibbs energy of mixing when the partition is removed. Assume perfect behavior.

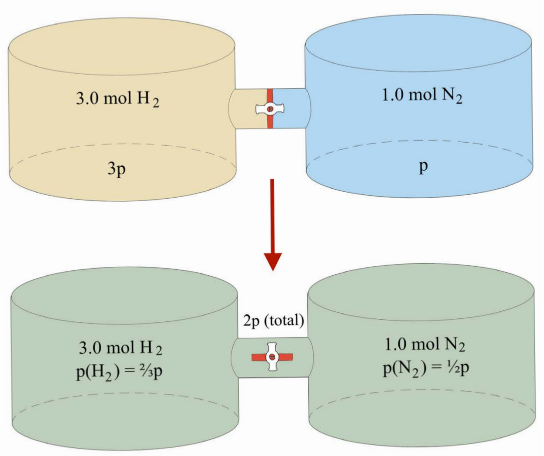

Figure 3.15. The initial and final states considered in the calculation of the Gibbs energy of mixing of gases at different initial pressures.

Solution: The formula from the previous section cannot be used directly because the initial gas pressures are different. Given that the pressure of nitrogen is P and the pressure of hydrogen is $3P$, the initial Gibbs energy is

$$G_i = (3.0\text{ mol})\{\mu^\circ(\mathrm{H_2}) + RT\log 3P\} + (1.0\text{ mol})\{\mu^\circ(\mathrm{N_2}) + RT\log P\}$$

When the partition is removed and each gas occupies twice the original volume, the partial pressure of nitrogen falls to $\frac{1}{2}P$ and that of hydrogen falls to $\frac{3}{2}P$. Therefore, the Gibbs energy changes to

$$G_f = (3.0\text{ mol})\{\mu^\circ(\mathrm{H_2}) + RT\log \tfrac{3}{2}P\} + (1.0\text{ mol})\{\mu^\circ(\mathrm{N_2}) + RT\log \tfrac{1}{2}P\}$$

Taking the difference gives the Gibbs energy of mixing:

$$\begin{aligned}\Delta G_{mix} = G_f - G_i =&(3.0\text{ mol})RT\log\left(\frac{\frac{3}{2}P}{3P}\right) + (1.0\text{ mol})RT\log\left(\frac{\frac{1}{2}P}{P}\right)\\ =&-(3.0\text{ mol})RT\log 2 - (1.0\text{ mol})RT\log 2\\ =&-(4.0\text{ mol})RT\log 2 = -6.9\text{ kJ}\end{aligned}$$

Here, $\Delta G_{mix} < 0$, however, the negative sign does not necessarily indicate spontaneity. $dG < 0$ indicates spontaneity only at constant temperature and pressure. (Here, the pressure dropped from $4P$ to $2P$ when opening the partition.)

Problem. Suppose that 2.0 mol H_2 at 2.0 atm and 25°C and 4.0 mol N_2 at 3.0 atm and 25°C are mixed at constant volume. Calculate ΔG_{mix}. What would be the value of ΔG_{mix} had the pressures been identical initially? [-9.7 kJ, -9.5 kJ]

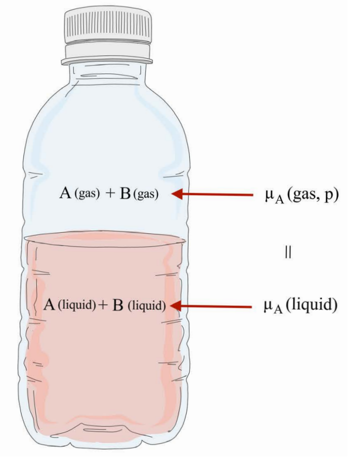

Figure 3.16. At equilibrium, the chemical potential of the gaseous form of a substance A is equal to the chemical potential of its condensed phase. The equality is preserved if a solute is also present. Because the chemical potential of A in the vapor depends on its partial vapor pressure, it follows that the chemical potential of liquid A can be related to its partial vapor pressure.

3.10.21. Ideal Solutions & Raoult's Law. Suppose we have an ideal solution made up of two components, A and B (Fig. 3.16). Let us denote with a * the quantities relating to pure substances. Let $\mu_A^*(l)$ denote the chemical potential of pure A (liquid). Vapor pressure of the pure liquid is P_A^*. Chemical potential in the vapor is $\mu_A^\circ + RT\log P_A^*$. These two chemical potentials are equal at equilibrium:

$$\underbrace{\mu_A^*(l)}_{liquid} = \underbrace{\mu_A^\circ + RT\log P_A^*.}_{gas} \qquad \text{(pure A)}$$

If another substance, a solute, is also present in the liquid, the chemical potential of A in the liquid is changed to $\mu_A(l)$ and its vapor pressure is changed to P_A. The vapor and solvent are still in equilibrium, so we can write

$$\mu_A(l) = \mu_A^\circ + RT\log P_A. \qquad \text{(add some B)}$$

Next, we combine these two equations to eliminate the standard chemical potential of the gas. To do so, we solve for μ_A° in both equations an equate the two results to obtain

$$\mu_A(l) = \mu_A^*(l) - RT\log P_A^* + RT\log P_A = \mu_A^*(l) + RT\log(P_A/P_A^*).$$

Substituting Raoult's law, $P_A = X_A \cdot P_A^*$, we get:

$$\boxed{\mu_A(l) = \mu_A^*(l) + RT\log X_A.}$$

This important equation can be used as the definition of an ideal solution (so that it implies Raoult's law rather than stemming from it) and is better, because it does not assume that the vapor is a perfect gas.

3.10.22. Liquid Mixtures: Ideal Solutions. Suppose that we mix two liquids A and B. Before mixing, we have:

$$G_i = n_A\mu_A^* + n_B\mu_B^*.$$

When they are mixed, the individual chemical potentials are modified, and the total Gibbs energy is,

$$G_f = n_A\{\mu_A^* + RT\log X_A\} + n_B\{\mu_B^* + RT\log X_B\}.$$

Consequently, the Gibbs energy of mixing, $G_f - G_i$ is

$$\Delta G_{mix} = nRT\{X_A\log X_A + X_B\log X_B\}.$$

And from $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P$, $S = -(\partial G/\partial T)$, the entropy of mixing is:

$$\Delta S_{mix} = -nR\{X_A\log X_A + X_B\log X_B\}.$$

3.10.23. Elevation of Boiling Point. The vapor pressure of a pure liquid represents a balance between the increase in disorder arising from vaporization and the decrease in disorder of the surroundings. See Figs. 3.17 and 3.18.

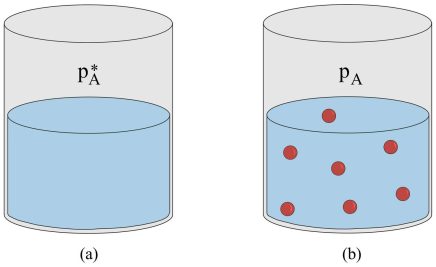

Figure 3.17. (a) Liquid is represented by the blue space. (b) When solute (red circles) is present, the disorder of the condensed phase is increased, and there is decreased tendency to acquire the disorder of the vapor.

The heterogeneous equilibrium of interest when considering boiling is between the solvent vapor and the solvent in solution at 1 atm. We denote the solvent by A and the solute by B. The equilibrium is established at a temperature for which

$$\mu_A^*(g) = \mu_A^*(l) + RT\log X_A.$$

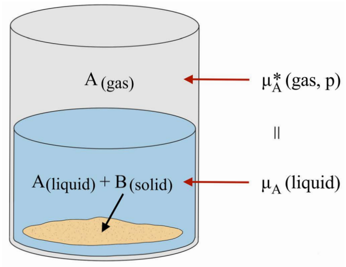

Figure 3.18. The heterogeneous equilibrium involved in the calculation of the elevation of boiling point is between A in the pure vapor and A in the mixture, A being the solvent and B an non-volatile solute.

(The pressure of 1 atm is the same throughout and is not written explicitly.) This equation implies[22] that the presence of a solute at a mole fraction X_B causes an increase in normal boiling point from T^* to $T^* + \Delta T$, where

$$\Delta T = K \cdot X_B, \qquad K = \frac{RT^{*2}}{\Delta_{vap} H}.$$

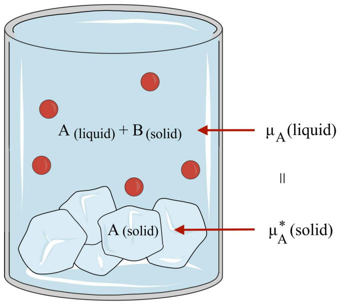

Figure 3.19. Heterogeneous equilibrium involved in the calculation of the lowering of freezing point is between A in the pure solid and A in the mixture, A being the solvent and B a solute that is insoluble in solid A.

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[22] From Atkins [**4**]: Rearranging the equation to $\log X_A = \frac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \frac{\Delta_{vap} G}{RT}$, where $\Delta_{vap} G$ is the Gibbs energy of vaporization of the pure solvent (A). Differentiating both sides with respect to T gives: $\frac{\mathrm{d} \log X_A}{\mathrm{d}T} = \frac{1}{R} \frac{\mathrm{d}(\Delta_{vap} G/T)}{\mathrm{d}T} = -\frac{\Delta_{vap} H}{RT^2}$, where use was made of the Gibbs-Helmholtz equation, $(\partial(G/T)/\partial T)_P = -H/T^2$. Multiplying both sides by $\mathrm{d}T$ and integrating from $X_A = 1$ (boiling point $T = T^*$ of pure solvent) to X_A (boiling point T), $\int_0^{\log X_A} \mathrm{d} \log X_A = -\frac{1}{R} \int_{T^*}^{T} \frac{\Delta_{vap} H}{T^2} \mathrm{d}T$. The left hand side integrates to $\log X_A = \log(1 - X_B)$. For constant enthalpy of vaporization, $\log(1 - X_B) = -\frac{\Delta_{vap} H}{R} \int_{T^*}^{T} \frac{1}{T^2} \mathrm{d}T$, and therefore, $\log(1 - X_B) = \frac{\Delta_{vap} H}{R} \left(\frac{1}{T} - \frac{1}{T^*}\right)$. We now suppose that the amount of solute present is so small that $X_B \ll 1$. We can write $\log(1 - X_B) \approx -X_B$ and obtain $X_B = \frac{\Delta_{vap} H}{R} \left(\frac{1}{T^*} - \frac{1}{T}\right)$. Finally, because $T \approx T^*$, it follows that $\frac{1}{T^*} - \frac{1}{T} = \frac{T - T^*}{TT^*} \approx \frac{\Delta T}{T^{*2}}$, with $\Delta T = T - T^*$. PROOF of Gibbs-Helmholtz: on one hand, $-S = (\partial G/\partial T)_P = (G - H)/T$, on the other hand, $\left(\frac{\partial (G/T)}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P + G \frac{\mathrm{d}(1/T)}{\mathrm{d}T} = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = \frac{1}{T} \left\{ \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T} \right\}$. In the curly bracket, we substitute $\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T} = \frac{G - H}{T} - \frac{G}{T} = -\frac{H}{T}$. Gibbs-Helmholtz follows.

3.10.24. Depression of Freezing Point. The heterogeneous equilibrium now of interest is between pure solid solvent A and the solution with solute present at a mole fraction X_B (Fig. 3.19). At the freezing point, the chemical potentials of A in the two phases are equal:

$$\mu_A^*(s) = \mu_A^*(l) + RT \log X_A$$

The calculation is the same as in the previous section, and the result is

$$\Delta T = K' \cdot X_B, \qquad K' = \frac{RT^{*2}}{\Delta_{fus} H},$$

where ΔT is the freezing point depression, $T^* - T$, and $\Delta_{fus} H$ is the enthalpy of fusion of the solvent. Larger depressions are observed in solvents with low enthalpies of fusion at high melting points. When the solution is dilute, the mole fraction is proportional to the molality of the solute, b, and it is common to write the last equation as

$$\Delta T = K_f \cdot b.$$

where K_f is the empirical freezing-point constant.

3.10.25. Solubility. When a solid solute is left in contact with a solvent, it dissolves until the solution is saturated. Saturation is a state of equilibrium, with the undissolved solute in equilibrium with the dissolved solute. Therefore, in a saturated solution the chemical potential of the pure solid solute, $\mu_B^*(s)$, and the chemical potential of B in solution, μ_B, are equal (Fig. 3.20).

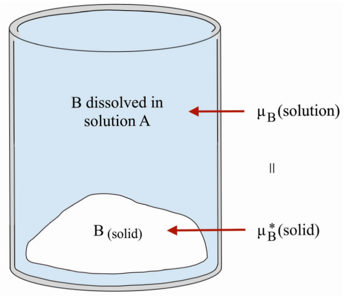

Figure 3.20. Heterogeneous equilibrium involved in the calculation of the solubility is between pure solid B and B in the mixture.

Because the latter is $\mu_B = \mu_B^*(l) + RT \log X_B$, we can write

$$\mu_B^*(s) = \mu_B^*(l) + RT \log X_B.$$

This expression is the same as the starting expression in the last section, except that the quantities refer to the solute B, not the solvent A. It leads to:

$$\log X_B = \frac{\Delta_{fus} H}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right).$$

3.10.26. Example: (Ion transport Across Cell Membrane). There are ions (e.g. Na^+, Ca^{2+}, K^+, etc.) found in the intra and extra-cellular spaces at different concentrations. Cell membrane proteins participate in the transport of such ions. As an example, let us analyze the chemical equilibrium of K^+ ions using the first two laws of thermodynamics. Recall that for a chemical reaction:

$$\Delta G_{rxn} = \Delta G^{\circ}_{rxn} + RT \log Q$$

where $\Delta G^{\circ}_{rxn} = -RT \log K_{eq}$. This is valid when a chemical reaction is the only "work" done. However, there may be other terms in the expression for ΔG that need to be accounted for. Consider the "chemical reaction" where a potassium ion is shuttled in and out of the cell cytoplasm:

$$\mathrm{K}_0^+ \rightleftharpoons \mathrm{K}_i^+$$

Chemical reaction equilibrium alone would state that

$$\mu_i - \mu_0 = RT \log \left(\frac{[\mathrm{K}^+]_i}{[\mathrm{K}^+]_o} \right)$$

Where $[\mathrm{K}^+]_i$ is the potassium ion concentration inside the cell and $[\mathrm{K}^+]_o$ is its concentration found outside (in the extracellular matrix). The difference $\mu_i - \mu_0$ represents gradient (difference) in the chemical potential across the cell membrane. This chemical potential gradient acts as a driving force to shuttle ions in and out of the cell (depending on whether $[\mathrm{K}^+]_i > [\mathrm{K}^+]_o$ or $[\mathrm{K}^+]_i < [\mathrm{K}^+]_o$). See Fig. 3.21.

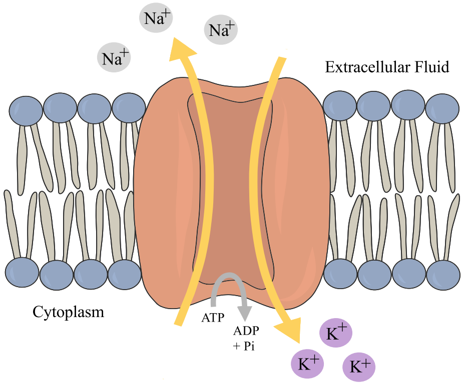

Figure 3.21. Potassium pump.

However, this cannot be the only force because if we shuttle all ions out of the cell (for instance), the electrostatic repulsion among potassium ions in the extracellular matrix will be large enough to drive some of these ions to re-enter the cytoplasm. Thus, we must include electrostatic repulsions.

Electrostatic repulsions can be accounted for by adding electrostatic work. Recall that the electrostatic work is of the form $\delta W_{el.} = \phi \mathrm{d}q$ where $\mathrm{d}q$ is the charge added or removed, and ϕ is the local electrostatic potential. Here we write ϕ_o for the electrostatic potential in the extracellular matrix and ϕ_i for the potential inside the cytoplasm. The total work is obtained by integrating from reactants to products. As far as the integral $\Delta W_{el.} = \int_{reactants}^{products} \phi \mathrm{d}q$ is concerned, going from reactants to products means we *subtract* a charge Q from the extracellular space (work $= -Q\phi_0$) and *add* it to the intracellular space (work $= +Q\phi_i$).

The total integral along this path yields the sum of these two terms: one from the extracellular matrix, and one for the cytoplasm:

$$\Delta W_{el.} = Q(\phi_i - \phi_o),$$

where ϕ_0 acquires a negative sign because we are removing an ion of charge Q from the extracellular matrix (and add it to the cytoplasm). The difference $\phi_i - \phi_o$ is the potential difference across the cell membrane (units: volts). When the electrostatic force balances out the chemical force, $\Delta G = 0$ and these two terms are equal:

$$\boxed{\Delta\phi \equiv \phi_i - \phi_o = \frac{RT}{Q} \log\left(\frac{[K^+]_i}{[K^+]_o}\right).}$$

This potential difference, $\Delta\phi \equiv \phi_i - \phi_o$ (in volts), is called the *Nernst potential.* Inspection of this equation shows that Q must be specified in units of Coulomb per mole; Q in these units is often called the Faraday's constant, $F \equiv 9.65 \times 10^4$ C/mol. (Otherwise, replace RT by k_BT and Q is then specified in units of Coulomb.)

Please note that the above analysis is valid in thermal equilibrium (steady state) and does not describe dynamics, such as those observed in cardiac tissues or neuronal networks.

There are ways to directly measure ion concentrations and voltages. For a discussion of Ca^{2+} and voltage sensing via specially-designed fluorophores, see the paper [**14**].

3.10.27. Affinity of Reaction and Reaction Enthalpy. General chemical reactions are represented by an equation, $\sum_i \nu_i A_i = 0$, where the stoichiometric coefficients ν_i are negative for reactants and positive for products. For example:

$$0 = -\mathrm{N}_2 - 3\mathrm{H}_2 + 2\mathrm{NH}_3.$$

The *extent of reaction* ξ is defined by:

$$\xi = \frac{n_i(\xi) - n_i(0)}{\nu_i},$$

where $n_i(\xi)$ is the amount of substance A_i present when the extent of reaction is ξ. $n_i(0)$ is the amount of A_i present when $\xi = 0$, corresponding to the specified initial conditions. The units of ξ are moles. For example, if 1 mol of N_2 and 3 mol of H_2 are converted completely into 2 mol of NH_3

$$\xi = \frac{n_{NH_3}(\xi) - n_{NH_3}(0)}{\nu_{NH_3}} = \frac{2\text{ mol} - 0\text{ mol}}{2} = 1\text{ mol}$$

$$\xi = \frac{n_{N_2}(\xi) - n_{N_2}(0)}{\nu_{N_2}} = \frac{0 \text{ mol} - 1 \text{ mol}}{-1} = 1 \text{ mol}$$
$$\xi = \frac{n_{H_2}(\xi) - n_{H_2}(0)}{\nu_{H_2}} = \frac{0 \text{ mol} - 3 \text{ mol}}{-3} = 1 \text{ mol}$$

ξ is independent of which chemical is used to compute it. Note also that

$$\boxed{\mathrm{d}\xi = \frac{\mathrm{d}n_i}{\nu_i}.}$$

Using this notation, the fundamental equation

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_i \mu_i \mathrm{d}n_i,$$

becomes:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_i \mu_i \nu_i \mathrm{d}\xi.$$

If we define the *reaction affinity* by:

$$\boxed{\mathcal{A} = -\sum_i \mu_i \nu_i.}$$

Then dG is written:

$$\boxed{\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P - \mathcal{A}\mathrm{d}\xi.}$$

From this, we see that

$$\boxed{\mathcal{A} = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P}.}$$

For the special case of constant T, P, we see that $\mathrm{d}G = -\mathcal{A}\mathrm{d}\xi$. Since G is a state function, integrating from $\xi = 0$ to $\xi = 1$ mol yields:

$$\mathcal{A} = -\Delta G_{rxn} = -\sum_i \nu_i \mu_i \geq 0.$$

(This assumes that $\mathcal{A}$ is independent of ξ.)

In a similar manner, the fundamental equations for the thermodynamic potentials U, S, H, A:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i \quad \rightarrow \quad \mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V - \mathcal{A}\mathrm{d}\xi$$
$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V - \frac{1}{T}\sum_i \mu_i \mathrm{d}n_i \quad \rightarrow \quad \mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V + \frac{\mathcal{A}}{T}\mathrm{d}\xi$$
$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P + \sum_i \mu_i \mathrm{d}n_i \quad \rightarrow \quad \mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P - \mathcal{A}\mathrm{d}\xi$$
$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i \quad \rightarrow \quad \mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V - \mathcal{A}\mathrm{d}\xi$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_i \mu_i \mathrm{d}n_i \qquad \rightarrow \qquad \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P - \mathcal{A}\mathrm{d}\xi$$

3.10.28. Enthalpy is the "Heat Content". Recall the second law, $\mathrm{d}S_{univ} = \mathrm{d}S + \mathrm{d}S_{ext} \geq 0$, where S is the system and S_{ext} is the surroundings. Now consider the system S; the total entropy production for this system can be decomposed into two terms:

$$\mathrm{d}S = \mathrm{d}_e S + \mathrm{d}_i S.$$

The first term, $\mathrm{d}_e S$, is the entropy produced by the interaction of the system with its surroundings, e.g.

$$\mathrm{d}_e S = \frac{\delta Q}{T}. \qquad \text{(if process is reversible)}$$

The second term, $\mathrm{d}_i S$, is the entropy produced by irreversible processes going on inside the system (for example, chemical reactions). **When the only interaction with a system's surroundings is the absorption of heat** δQ, and the only irreversible process going on within the system is a chemical reaction, we can write explicit expressions for $\mathrm{d}_e S$ and $\mathrm{d}_i S$:

The fundamental equation for dS reduces to:

$$\mathrm{d}S = \underbrace{\frac{\delta Q}{T}}_{\mathrm{d}_e S} + \underbrace{\frac{\mathcal{A}}{T}\mathrm{d}\xi}_{\mathrm{d}_i S}.$$

Thus,

$$\boxed{\mathrm{d}_e S = \frac{\delta Q}{T}, \qquad \mathrm{d}_i S = \frac{\mathcal{A}\mathrm{d}\xi}{T}.}$$

These two contributions describe the measurable heat transfer and the irreversible heat (absorbed or released) of the reaction. *We note that the term* $\mathrm{d}_i S$ *can describe a bona fide chemical reaction or the transfer of matter to another subsystem* (essentially, any process that can be described using chemical potentials). When matter is transported, this causes a transfer of heat.

Consider the complete transformation of stoichiometric amounts of reactants at T, P into products at T, P, so that $\Delta\xi = 1$ mol. Because H is a function of the state of the system, the enthalpy change due to the reaction

$$\Delta H_{rxn} = (\Delta Q)_P$$

is equal to the heat absorbed at constant pressure. This quantity was formerly called the *heat of reaction at constant pressure*, but is now called the *reaction enthalpy.* Another historic name for enthalpy is *heat content.* The subscript *rxn* tells us that this is the enthalpy change during the reaction. ΔH_{rxn} is the change in an extensive property, but numerical data always refer to $\Delta\xi = 1$ mol so that the units of ΔH_{rxn} are J/mol, or more commonly kJ/mol.

The idea that enthalpy is the heat transfer at constant pressure is illustrated by the fundamental equation for H:

$$(\mathrm{d}H)_P = T\mathrm{d}S + \cancel{V\mathrm{d}P} - \mathcal{A}\mathrm{d}\xi = T\mathrm{d}S - \mathcal{A}\mathrm{d}\xi$$

which, at constant pressure, features two terms, $T\mathrm{d}S$, the measurable heat transfer and $-\mathcal{A}\mathrm{d}\xi$, the enthalpy associated with mass transport or irreversible chemical reaction. It is because of this property that enthalpy is called *heat content.*

3.10.29. Forces and Fluxes. The fundamental equation in the entropy representation is particularly important because of its special structure:

$$\mathrm{d}S = \left(\frac{1}{T}\right)\mathrm{d}U + \left(\frac{P}{T}\right)\mathrm{d}V - \sum_i \left(\frac{\mu_i}{T}\right)\mathrm{d}n_i.$$

It has the structure of a sum of terms, each of which represent a force times a flux. The forces are:

- $\frac{1}{T}$: tendency for heat flow
- $\frac{P}{T}$: tendency for volume change
- $\frac{\mu}{T}$: tendency for particle exchange

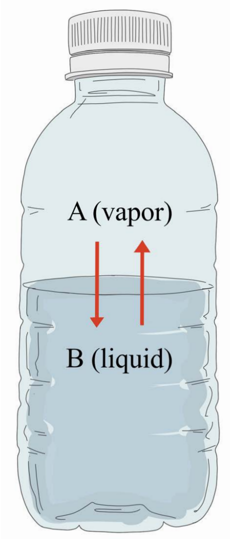

Figure 3.22. A closed, insulated, constant-volume, system contains two phases (A and B). The second law requires that at equilibrium the temperature, pressure and chemical potentials of the two phases will necessarily become equal ($T_A = T_B$, $P_A = P_B$ and $\mu_A = \mu_B$).

Recall our previous analysis of phase equilibrium (Fig. 3.22), which begins by writing down the First Law for each subsystem $\mathrm{d}S = \mathrm{d}S_A + \mathrm{d}S_B$ in the entropy representation ($A + B$

is a closed system, so that $\mathrm{d}U = \mathrm{d}U_A = -\mathrm{d}U_B$, $\mathrm{d}V = \mathrm{d}V_A = -\mathrm{d}V_B$, $\mathrm{d}n = \mathrm{d}n_A = -\mathrm{d}n_B$):

$$\mathrm{d}S = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\mathrm{d}U + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)\mathrm{d}V - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right)\mathrm{d}n.$$

$\mathrm{d}S$ is called the dissipation function because $\mathrm{d}S > 0$ indicates an irreversible process where energy is dissipated (cannot be converted into useful work).

Notice that all the terms in the expression for $\mathrm{d}S$ are of the form of a gradient in intensive property $(1/T, P/T, \mu/T)$ times the differential of an extensive property (U, V, n). The former is called a *force*; the latter is called a *flux*:

$$\boxed{\text{dissipation function} = \text{force} \times \text{flux} \;= X \cdot J}$$

3.10.30. Internal vs External Variables: Heat Transfer Only. A system with only heat transfer can be exemplified as consisting of two pieces of metal at different absolute temperatures, T_1 and T_2, where $T_1 > T_2$. A small quantity of heat, δQ, is allowed to pass from subsystem 1 to subsystem 2 in course of a short time interval, $\mathrm{d}t$ (Fig. 3.23).

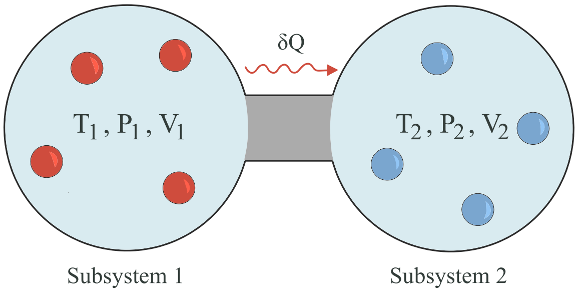

Figure 3.23. Only heat can transfer.

The quantity of heat is so small that changes in the temperatures of the subsystems can be disregarded: Since there is no transfer of matter, each subsystem behaves as a closed system. The transfer of δQ leads to the following changes in the subsystems:

$$\mathrm{d}U_1 = T_1\mathrm{d}S_1 - P_1\mathrm{d}V_1 \qquad \mathrm{d}U_2 = T_2\mathrm{d}S_2 - P_2\mathrm{d}V_2,$$

or with the equations solved with respect to entropy change:

$$\mathrm{d}S_1 = \frac{\mathrm{d}U_1}{T_1} + \left(\frac{P_1}{T_1}\right)\mathrm{d}V_1 \qquad \mathrm{d}S_2 = \frac{\mathrm{d}U_2}{T_2} + \left(\frac{P_2}{T_2}\right)\mathrm{d}V_2.$$

When $P - V$ work is the only work carried out, $\mathrm{d}U_1$ and $\mathrm{d}U_2$ can be expressed by the external variables, which are measurable quantities,

$$\mathrm{d}U_1 = \delta Q_1 - P_1\mathrm{d}V_1 \qquad \mathrm{d}U_2 = \delta Q_2 - P_2\mathrm{d}V_2.$$

The total system is adiabatic,

$$\delta Q = -\delta Q_1 = \delta Q_2,$$

so that

$$dU_1 + dU_2 = -P_1 dV_1 - P_2 dV_2.$$

Total entropy production is:

$$dS = dS_1 + dS_2 = -\frac{\delta Q}{T_1} + \frac{\delta Q}{T_2} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\delta Q = \Delta(1/T)\delta Q,$$

or

$$\frac{dS}{dt} = \Delta(1/T)\frac{\delta Q}{dt}.$$

Multiplying by T_2 gives the dissipated energy

$$T_2\frac{dS}{dt} = T_2\Delta(1/T)\frac{\delta Q}{dt},$$

where $\delta Q/dt$ is the rate of transport of heat. The units of $T_2\frac{dS}{dt}$ and $\delta Q/dt$ are in watts (1 W=1 J/s).

3.10.31. Internal vs External Variables: Heat Transfer + Matter Transport. A system with transfer of heat and matter can be exemplified by two gas containers at different absolute temperatures, T_1 and T_2, where $T_1 > T_2$ (Fig. 3.24).

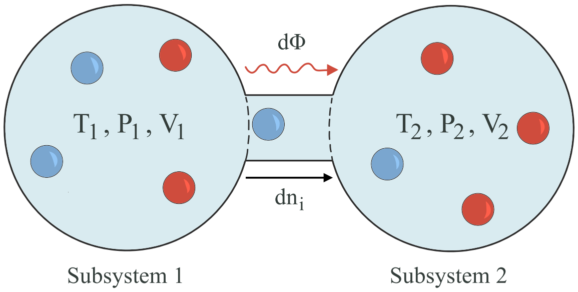

Figure 3.24. Both heat and matter can transfer.

A small quantity of heat, $\delta\Phi$, and small quantities of the different gas components, dn_i, are allowed to pass from subsystem 1 to subsystem 2 in course of the time dt. The total heat transferred, $\delta\Phi$, is composed of a measurable heat and the *enthalpy of the transferred matter*. Since the total system is adiabatic, the total heat removed from subsystem 1 is equal to the total heat received by subsystem 2. The enthalpy of the transferred matter, however, may be different in the two subsystems, and thus the measurable heat change will be different in the two subsystems.

The changes in the subsystems are:

$$\delta\Phi = \delta\Phi_2 = -\delta\Phi_1.$$

In terms of internal variables,

$$dU_1 = T_1 dS_1 - P_1 dV_1 + \sum_i \mu_{i,1} dn_{i,1} \quad dU_2 = T_2 dS_2 - P_2 dV_2 + \sum_i \mu_{i,2} dn_{i,2}.$$

Solving for dS,

$$(3.6)\quad \mathrm{d}S_1 = \frac{\mathrm{d}U_1}{T_1} + \frac{P_1}{T_1}\mathrm{d}V_1 - \frac{1}{T_1}\sum_i \mu_{i,1}\mathrm{d}n_{i,1}, \quad \mathrm{d}S_2 = \frac{\mathrm{d}U_2}{T_2} + \frac{P_2}{T_2}\mathrm{d}V_2 - \frac{1}{T_2}\sum_i \mu_{i,2}\mathrm{d}n_{i,2}.$$

In terms of external variables, when we only have $P - V$ work:

$$(3.7)\qquad \mathrm{d}U_1 = \delta\Phi_1 - P_1\mathrm{d}V_1 \quad \mathrm{d}U_2 = \delta\Phi_2 - P_2\mathrm{d}V_2,$$

$$\mathrm{d}U_1 + \mathrm{d}U_2 = -P_1\mathrm{d}V_1 - P_2\mathrm{d}V_2.$$

Since $\delta\Phi = \delta\Phi_2 = -\delta\Phi_1$. Then, plugging Eq. (3.7) into (3.6),

$$(3.8)\qquad \mathrm{d}S_1 = -\frac{\delta\Phi}{T_1} + \frac{1}{T_1}\sum_i \mu_{i,1}\mathrm{d}n_i, \quad \mathrm{d}S_2 = \frac{\mathrm{d}\Phi}{T_2} - \frac{1}{T_2}\sum_i \mu_{i,2}\mathrm{d}n_i.$$

The production of entropy in the total system is $\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2$ and therefore

$$\mathrm{d}S = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\mathrm{d}\Phi + \sum_i \left(\frac{\mu_{i,2}}{T_2} - \frac{\mu_{i,1}}{T_1}\right)\mathrm{d}n_i,$$

$$(3.9)\qquad \mathrm{d}S = \Delta(1/T)\delta\Phi - \sum_i \Delta(\mu_i/T)\mathrm{d}n_i.$$

Multiplying by T_2 and dividing by time (dt), we have the dissipated energy (J/s)

$$\boxed{T_2\frac{\mathrm{d}S}{\mathrm{d}t} = T_2\Delta(1/T)\frac{\delta\Phi}{\mathrm{d}t} - T_2\sum_i \Delta(\mu_i/T)\frac{\mathrm{d}n_i}{\mathrm{d}t}.}$$

It is possible to develop Eq. (3.9) further and put it in a more useful form (see Section 3.10.32):

$$\mathrm{d}S = \Delta(1/T)\delta Q_1 - \frac{1}{T}\sum_i \Delta\mu_{i,T}\mathrm{d}n_i.$$

3.10.32. Algebraic Details. Starting from Eq. (3.8),

$$\mathrm{d}S_1 = -\frac{\delta\Phi}{T_1} + \frac{1}{T_1}\sum_i \mu_{i,1}\mathrm{d}n_i, \quad dS_2 = \frac{\delta\Phi}{T_2} - \frac{1}{T_2}\sum_i \mu_{i,2}\mathrm{d}n_i,$$

and solving for $\delta\Phi$, we have:

$$\delta\Phi = -T_1\mathrm{d}S_1 + \sum_i \mu_{i,1}\mathrm{d}n_{i,1} = T_2\mathrm{d}S_2 + \sum_i \mu_{i,2}\mathrm{d}n_{i,2}.$$

The entropy of an open system can be expressed as a function of temperature, pressure and amounts of substances, $S = S(T, P, \{n_i\})$. The experiment can be arranged such that the pressure within each subsystem is kept constant. The change in entropy with temperature and amounts of substances for subsystem 1 can be written,

$$\begin{aligned}\mathrm{d}S_1 =&\left(\frac{\partial S_1}{\partial T}\right)_{P,n_i}\mathrm{d}T+\sum_i\left(\frac{\partial S_1}{\partial n_{i,1}}\right)_{P,T,n_{j\neq i}}\mathrm{d}n_{i,1}\\ =&(C_{P,1}/T_1)\mathrm{d}T+\sum_i S_{i,1}\mathrm{d}n_{i,1},\end{aligned}$$

and in a similar way for subsystem 2. The heat capacity of the system multiplied by the change in temperature is equal to the measurable heat absorbed by the system, $C_{P,1}\mathrm{d}T = -\delta Q_1$ where δQ_1 is the heat removed from subsystem 1. Here it is assumed that $\mathrm{d}T$ is so small that changes in $C_{P,1}$ can be neglected. When the amounts of substances transferred from subsystem 1 to subsystem 2 are small, the change in partial molar entropy, $S_{i,1}$ can be neglected. Thus, for subsystem 1,

$$\mathrm{d}S_1 = -\delta Q_1/T_1 - \sum_i S_{i,1}\mathrm{d}n_i.$$

This equation combines with Eq. (3.8) for $\mathrm{d}S_1$ to give

$$\delta\Phi = \delta Q + \sum_i(\mu_{i,1} + T_1S_{i,1})\mathrm{d}n_i,$$

or, since $G = H - TS$, the partial molar quantity at constant T is:

$$G_i \equiv \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_T = \left(\frac{\partial H}{\partial n_i}\right)_T - T\left(\frac{\partial S}{\partial n_i}\right)_T \equiv H_i - TS_i.$$

Or $H_i = \mu_i + TS_i$,

$$\delta\Phi = \delta Q_1 + \sum_i H_{i,1}\mathrm{d}n_i. \tag{3.10}$$

In a similar way, we can express $\mathrm{d}\Phi$ by the heat *absorbed* by subsystem 2, δQ_2, and the enthalpy added to subsystem 2 by the transfer of $\mathrm{d}n_i$ moles of substance:

$$\mathrm{d}\Phi = \delta Q_2 + \sum_i H_{i,2}\mathrm{d}n_i. \tag{3.11}$$

Comparing Eq. (3.10) and (3.11) we see that the difference in δQ values corresponds to a difference in the H values:

$$\delta Q_2 - \delta Q_1 = \sum_i(H_{i,1} - H_{i,2})\mathrm{d}n_i.$$

For gases, $H_{i,1} - H_{i,2} \approx 0$.

The enthalpies, H_i, do not have absolute values, and therefore $\delta\Phi$ does not have an absolute value. We shall choose subsystem 1 as the reference state, and replace $\delta\Phi$ in Eq. (3.9) by the expression given in Eq. (3.10). The second term in Eq. (3.9), $\sum_i \Delta(\mu_i/T)\mathrm{d}n_i$, can also be referred to subsystem 1 as the reference state. The chemical potentials are functions of temperature, pressure and composition, and for small differences in these parameters between the two subsystems, we have by the rules of derivation

$$\Delta(\mu_i/T) = \Delta(1/T)\mu_{i,1} + \frac{1}{T_1}(\partial\mu_{i,1}/\partial T)_{P,n_i}\Delta T + \frac{1}{T_1}\Delta\mu_{i,T},$$

where $\Delta\mu_{i,T}$ gives the variation in μ_i with changes in composition and pressure. Since (from $H_i = \mu_i + TS_i$)

$$(\partial\mu_{i,1}/\partial T)_{P,n_i} = -S_{i,1},$$

and

$$\Delta(1/T) = \left(\frac{1}{T+\Delta T} - \frac{1}{T}\right) \approx -\frac{\Delta T}{T^2},$$

and

$$T_1 \approx T.$$

Therefore,

$$\sum_i \Delta(\mu_i/T)\mathrm{d}n_i = \Delta(1/T)\sum_i(\mu_{i,1} + TS_{i,1})\mathrm{d}n_i + \frac{1}{T}\sum_i \Delta\mu_{i,T}\mathrm{d}n_i. \tag{3.12}$$

Introducing Eq. (3.10) and (3.12) into (3.9) we obtain

$$\mathrm{d}S = \Delta(1/T)\delta Q_1 - \frac{1}{T}\sum_i \Delta\mu_{i,T}\mathrm{d}n_i.$$

This form may be better because it explicitly separates the two contributions to the entropy production originating from heat transfer and particle transport.

3.10.33. Gibbs Free Energy: Ideal Gas Equilibria. We have seen that the progress of a chemical reaction $\sum_i \nu_i A_i = 0$ can be described using the *extent of the reaction*, $\xi = \frac{n_i(\xi)-n_i(0)}{\nu_i}$. From this, $\mathrm{d}\xi = \mathrm{d}n_i/\nu_i$ or $\mathrm{d}\xi/\mathrm{d}t = (1/\nu_i)\mathrm{d}n_i/\mathrm{d}t$. The fundamental equation, $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_i \mu_i \mathrm{d}n_i$, can be rewritten as $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_i \nu_i\mu_i\mathrm{d}\xi$, or $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P - \mathcal{A}\mathrm{d}\xi$, where $\mathcal{A} = -\sum_i \mu_i\nu_i$ or $\mathcal{A} = -\left(\frac{\partial G}{\partial\xi}\right)_{T,P}$. Finally, $\mathcal{A} = -\Delta G_{rxn} = -\sum_i \nu_i\mu_i$.

Consider a gas-phase reaction $A \rightleftharpoons B$. If the pressures are low enough, the gases can be considered ideal gases. Recall that for ideal gases, the chemical potentials are:

$$\mu_A(T,P) = \mu_A^\circ(T) + RT\log(P_A/1\text{ atm})$$
$$\mu_B(T,P) = \mu_B^\circ(T) + RT\log(P_B/1\text{ atm})$$

where P_A and P_B are partial pressures in units of 1 atm.

Inserting these expressions into the expression for $\left(\frac{\partial G}{\partial\xi}\right)$ gives:

$$\left(\frac{\partial G}{\partial\xi}\right) = \mu_B - \mu_A = (\mu_B^\circ + RT\log P_B) - (\mu_A^\circ + RT\log P_A) = \Delta G^\circ_{rxn} + RT\log\frac{P_B}{P_A},$$

where $\Delta G^\circ_{rxn} = \mu_B^\circ - \mu_A^\circ$. Writing $Q = P_B/P_A$, this is

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT\log Q.$$

At equilibrium $\Delta G_{rxn} = 0$, Q is denoted by K, and we have:

$$\Delta G_{rxn} = -RT \log K + RT \log Q = RT \log(Q/K).$$

This expression, together with the second law $\Delta G_{rxn} \leq 0$, allows us to study the direction of a reaction.

For a general chemical reaction of the form $\sum_i \nu_i A_i = 0$,, the quantity $\Delta G_{rxn} \equiv \left(\frac{\partial G}{\partial \xi}\right) = \sum_i \mu_i \nu_i$, is the Gibbs free energy change of the reaction. Then,

$$\begin{aligned}\left(\frac{\partial G}{\partial \xi}\right) =& \Delta G_{rxn} = \sum_i \left[\mu_i^0 + RT \log(P_i/P^\circ)\right] \nu_i \\ =& \Delta G^0_{rxn} + RT \sum_i \nu_i \log(P_i/P^0),\end{aligned}$$

where P° is a reference pressure (usually 1 atm or 1 bar). Then,

$$\boxed{\Delta G_{rxn} = RT \log(Q/K),}$$

where

$$Q = \prod_i (P_i/P^\circ)^{\nu_i},\ K = \prod_i (P_{i,eq}/P^\circ)^{\nu_i},\ \Delta G^0_{rxn} = \sum_i \nu_i \mu_i^0 = -RT \log(K).$$

Recall that although Q has the *form* of an equilibrium constant, the pressures are not necessarily at equilibrium.

The quantity $\Delta G^\circ_{rxn}(T)$ is the change in standard Gibbs energy for the reaction between unmixed reactants in their standard states at temperature T and a pressure of one bar to form unmixed products in their standard states at the same temperature T and a pressure of P_0 (usually, taken to be 1 atm or 1 bar). If all pressures are referenced to 1 bar (or 1 atm), Q is unitless.

From the previous equation,

$$\Delta G_{rxn}(T) = -RT \log(K) + RT \log(Q) = RT \log(Q/K).$$

We see that:

- At equilibrium, $Q = K$.
- If $Q < K$ then Q must increase as the system moves toward equilibrium. Partial pressures of the products must increase and those of reactants must decrease. The reaction proceeds from left to right. In terms of ΔG_{rxn}, if $Q < K$, then $\Delta G_{rxn} < 0$, indicating that the reaction is spontaneous from left to right as written.
- If $Q > K$, then Q must decrease as the reaction proceeds to equilibrium. Pressures of products must decrease and those of reactants must increase. Equivalently, if $Q > K$ then $\Delta G_{rxn} > 0$, indicating that the reaction is spontaneous from right to left as written.

3.10.34. Enthalpy and Entropy Contribute to ΔG°_{rxn}. We know that at constant temperature we have:

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}.$$

Consequently, we may express the equilibrium constant as a product of two contributions, one from enthalpy and one from entropy:

$$K = \exp\left(-\frac{\Delta G^\circ_{rxn}}{RT}\right) = \exp\left(-\frac{\Delta H^\circ_{rxn}}{RT}\right)\exp\left(\frac{\Delta S^\circ_{rxn}}{R}\right). \tag{3.13}$$

3.10.35. Example 1: Three Components Reaction. The above formula states that the change in standard Gibbs energy for a reaction is related to the equilibrium constant. But the latter depends on equilibrium partial pressures. For example,

$$3\mathrm{NO}(g) \rightleftharpoons \mathrm{N_2O}(g) + \mathrm{NO_2}(g)$$

has

$$K = \frac{(P_{\mathrm{N_2O}})_{eq}\cdot(P_{\mathrm{NO_2}})_{eq}}{(P_{\mathrm{NO}})^3_{eq}}$$

so (taking P_0=1 atm and expressing pressures in units of P_0),

$$\boxed{\Delta G^\circ_{rxn} = -RT\log\frac{(P_{\mathrm{N_2O}})_{eq}(P_{\mathrm{NO_2}})_{eq}}{(P_{\mathrm{NO}})^3_{eq}}.}$$

3.10.36. Example 2: Four Components Reaction. For a reaction of the type:

$$\nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_Y Y(g) + \nu_Z Z(g),$$

we have:

$$\begin{aligned}\Delta G_{rxn} =& \nu_Y\mu_Y + \nu_Z\mu_Z - \nu_A\mu_A - \nu_B\mu_B \\ =& \nu_Y\mu^\circ_Y(T) + \nu_Z\mu^\circ_Z(T) - \nu_A\mu^\circ_A(T) - \nu_B\mu^\circ_B(T) \\ &+ RT\left(\nu_Y\log\frac{P_Y}{P_0} + \nu_Z\log\frac{P_Z}{P_0} - \nu_A\log\frac{P_A}{P_0} - \nu_B\log\frac{P_B}{P_0}\right),\end{aligned}$$

which can be written in the form:

$$\Delta G_{rxn}(T) = \Delta G^\circ_{rxn}(T) + RT\log Q,$$

where

$$\Delta G^\circ_{rxn}(T) = \nu_Y\mu^\circ_Y(T) + \nu_Z\mu^\circ_Z(T) - \nu_A\mu^\circ_A(T) - \nu_B\mu^\circ_B(T),$$

and

$$Q = \frac{(P_Y/P_0)^{\nu_Y}(P_Z/P_0)^{\nu_Z}}{(P_A/P_0)^{\nu_A}(P_B/P_0)^{\nu_B}}.$$

3.10.37. Standard Gibbs Energies of Reactions (Using Tabulated Values). Standard entropies (ΔS°_{rxn}) and enthalpies (ΔH°_{rxn}) of reactions can be combined to obtain the standard Gibbs energy of a reaction, $\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$ (valid for constant temperature). The standard Gibbs energy of a reaction is the difference in standard molar Gibbs energies of the products and reactants in their standard states at the temperature specified for the reaction as written.

In Oxtoby [**9**], what we denote here as μ_i^0 is called standard Gibbs energy of formation and denoted ΔG°_f. Appendix D of your book can be used to calculate equilibrium constants; e.g.

$$\nu_A A + \nu_B B \rightarrow \nu_Y Y + \nu_Z Z$$

has

$$\Delta G^\circ_{rxn} = \nu_Y \Delta G^\circ_f[Y] + \nu_Z \Delta G^\circ_f[Z] - \nu_A \Delta G^\circ_f[A] - \nu_B \Delta G^\circ_f[B].$$

where the values for the $\Delta G^\circ_f[Y]$ can be looked up in tables.

The **standard Gibbs energy of formation** of a compound is the change of Gibbs free energy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard states (the most stable form of the element at 1 bar of pressure and the specified temperature, usually 298.15 K or 25°C). Standard Gibbs energies of formation are tabulated. See Appendix D of Oxtoby [**9**] for such a list.

In terms of the **standard Gibbs energies of formation**, ΔG°_f:

$$\Delta G^\circ_{rxn} = \sum_{I \in prod.} \nu_I (\Delta G^\circ_f)_I - \sum_{J \in react.} \nu_J (\Delta G^\circ_f)_J.$$

Example: To calculate the standard Gibbs energy of the reaction

$$\mathrm{CO}(g) + \tfrac{1}{2}\mathrm{O}_2(g) \rightarrow \mathrm{CO}_2(g)$$

at 25°C. Looking up tabulated values for each substance in Appendix D, we write:

$$\begin{aligned}\Delta G^\circ_{rxn} =& \Delta G^\circ_f(\mathrm{CO}_2, g) - \left\{\Delta G^\circ_f(\mathrm{CO}, g) + \tfrac{1}{2}\Delta G^\circ_f(\mathrm{O}_2, g)\right\}\\ =& -394.4 \text{ kJ/mol} - \left\{(-137.2) + \tfrac{1}{2}(0)\right\} \text{ kJ/mol}\\ =& -257.2 \text{ kJ/mol}\end{aligned}$$

3.10.38. Adiabatic Decompression. The process of adiabatic decompression is used for cooling gases. The principle is illustrated in Fig. 3.25. In the equations below, '1' refers to the 'initial' state and '2' refers to the 'final' state. Step 1 uses the law for isothermal compression (see Section 3.3.6):

$$\Delta W = -nRT \log\left(\frac{V_2}{V_1}\right)$$

with $\Delta U = 0$ for an ideal gas (isothermal process), so that $\Delta Q = \Delta W$. The second step uses the law for adiabatic expansion:

$$\boxed{T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}.}$$

Problem: Derive the law for adiabatic expansion.

Problem: Explain how this leads to cooling.

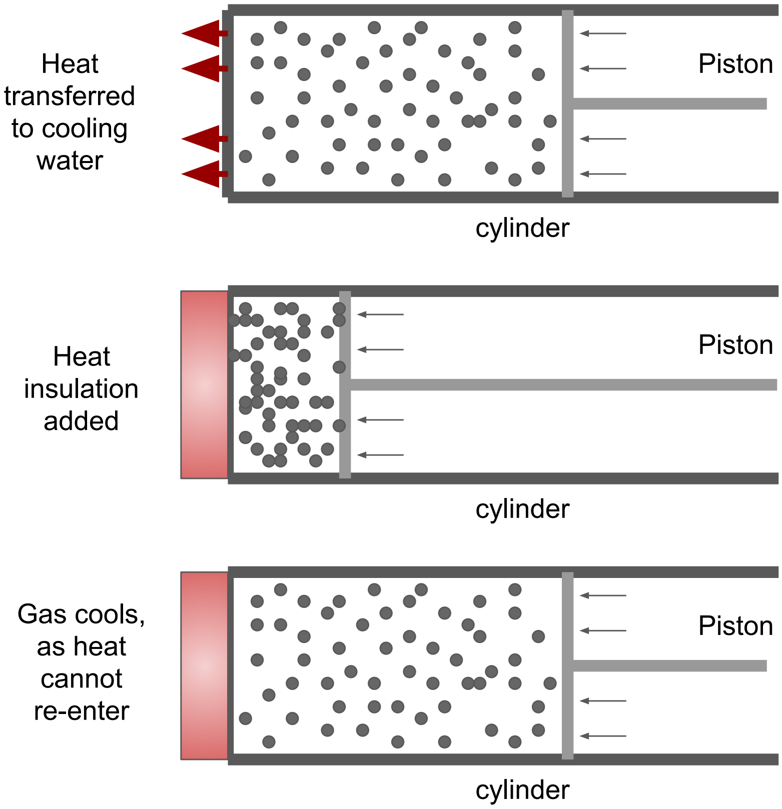

Figure 3.25. Adiabatic decompression leads to cooling of gas.

3.11. Electric and Magnetic Work

Can electric and magnetic fields generate work? In this section we look at the case of electrical charges subjected to the influence of electric and magnetic fields. This material is standard and can be found in most textbooks of electrodynamics, e.g. see Griffith [**15**] or Jackson [**16**]. In electrodynamics, the electric field is denoted **E**. There is an associated quantity called the *electric displacements*, denoted **D**. An applied electric field gives rise to a polarization **P** (molecules develop an induced dipole moment). These three fields are related by:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}.$$

In linear media, $\mathbf{D} = \epsilon \mathbf{E}$, where ϵ is the dielectric constant of the linear medium. The corresponding magnetic quantities are **B** (magnetic induction), **H** (magnetic field) and **M** magnetic polarization or magnetization. Magnetic polarization is magnetic moment ($\vec{m}$) per unit volume: $\vec{m} = vol \cdot \mathbf{M}$. Similarly, $\vec{p} = vol \cdot \mathbf{P}$ for the electric dipole moment. The magnetic moments align when an external magnetic field is applied. These three fields are related by:

$$\mathbf{H} = \frac{1}{\mu_0}\mathbf{B} - \mathbf{M}.$$

In linear media, we have $\mathbf{H} = \frac{1}{\mu}\mathbf{B}$, where μ is the magnetic permeability of the medium. **E** and **B** are the fundamental fields because they determine the force on electric charges according to the Lorentz force law:

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}).$$

H and **D** are called *auxiliary fields.*

3.11.1. Derivation. Upon first reading, you may skip this section, which is provided for completeness and whose details are not essential to the development of thermodynamical relations. We start with the Lorentz force,

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}).$$

Take the dot product[23] with d**l**, an element of length:

$$\mathbf{F} \cdot \mathrm{d}\mathbf{l} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \cdot \mathrm{d}\mathbf{l}.$$

We replace d**l** by $\mathbf{v}\mathrm{d}t$, where **v** is the velocity of electric charges, then divide by $\mathrm{d}t$ to get $\mathrm{d}W/\mathrm{d}t$, the rate of change in the work (why we use the rate of change will be clear later, as the Poynting vector emerges). Also, because electric charge is possibly distributed elsewhere in space, we really should replace q by a charge density, ρ, and integrate over volume to get the total work (and use $\mathbf{J} = \rho\mathbf{v}$):

$$\frac{\mathrm{d}W}{\mathrm{d}t} = -\int_{vol} \rho(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \cdot \mathbf{v}\,\mathrm{d}^3\mathbf{r} = -\int_{vol} \rho\mathbf{E} \cdot \mathbf{v}\,\mathrm{d}^3\mathbf{r} = -\int_{vol} \mathbf{E} \cdot \mathbf{J}\,\mathrm{d}^3\mathbf{r}. \tag{3.14}$$

The negative sign appears because we are calculating the work done *on the charge* against the action of the field (see Jackson [**16**], Chapter 1).

The magnetic force term dropped out because the triple product[24] $(\mathbf{v} \times \mathbf{B}) \cdot \mathbf{v}$ vanishes, as two of its vectors are parallel. However, this does not mean that the magnetic field does not play a role. Let us look at the current density, **J**. We can obtain an expression for $\mathbf{E} \cdot \mathbf{J}$ by invoking Ampère's law:

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}.$$

---

[23] The dot product is defined in Section **??**.

[24] A triple product, $(\mathbf{A} \times \mathbf{B}) \cdot \mathbf{C}$, is a scalar (number) which equals to the volume generated by the three vectors $\mathbf{A}, \mathbf{B}, \mathbf{C}$. When any two vectors are parallel, the volume is zero.

Take the dot product with **E**:

$$\mathbf{E}\cdot\mathbf{J} = \mathbf{E}\cdot(\nabla\times\mathbf{H}) - \mathbf{E}\cdot\frac{\partial\mathbf{D}}{\partial t}. \tag{3.15}$$

Next, we use the identity,[25]

$$\mathbf{H}\cdot(\nabla\times\mathbf{E}) - \mathbf{E}\cdot(\nabla\times\mathbf{H}) = \nabla\cdot(\mathbf{E}\times\mathbf{H}),$$

in which we substitute Faraday's law

$$\nabla\times\mathbf{E} = -\frac{\partial\mathbf{B}}{\partial t},$$

to get

$$-\mathbf{H}\cdot\frac{\partial\mathbf{B}}{\partial t} - \mathbf{E}\cdot(\nabla\times\mathbf{H}) = \nabla\cdot(\mathbf{E}\times\mathbf{H}). \tag{3.16}$$

In Eq. (3.15), we replace $\mathbf{E}\cdot(\nabla\times\mathbf{H})$ by Eq. (3.16), to get:

$$\mathbf{E}\cdot\mathbf{J} = -\mathbf{H}\cdot\frac{\partial\mathbf{B}}{\partial t} - \nabla\cdot(\mathbf{E}\times\mathbf{H}) - \mathbf{E}\cdot\frac{\partial\mathbf{D}}{\partial t}.$$

Substituting this expression into Eq. (3.14), we get:

$$\frac{\mathrm{d}W}{\mathrm{d}t} = -\int_{vol}\left(-\mathbf{H}\cdot\frac{\partial\mathbf{B}}{\partial t} - \nabla\cdot(\mathbf{E}\times\mathbf{H}) - \mathbf{E}\cdot\frac{\partial\mathbf{D}}{\partial t}\right)\mathrm{d}^3\mathbf{r}. \tag{3.17}$$

The middle term can be converted to a surface integral using the Gauss divergence theorem:

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \int_{vol}\left(\mathbf{H}\cdot\frac{\partial\mathbf{B}}{\partial t} + \mathbf{E}\cdot\frac{\partial\mathbf{D}}{\partial t}\right)\mathrm{d}^3\mathbf{r} + \int_{\partial vol}(\mathbf{E}\times\mathbf{H})\cdot\mathrm{d}\mathbf{s}. \tag{3.18}$$

In linear media, $\mathbf{B} = \mu\mathbf{H}$ and $\mathbf{D} = \epsilon\mathbf{E}$, and we can write this as:

$$\boxed{\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\int_{vol}\frac{1}{2}\left(\mathbf{H}\cdot\mathbf{B} + \mathbf{E}\cdot\mathbf{D}\right)\mathrm{d}^3\mathbf{r} + \int_{\partial vol}(\mathbf{E}\times\mathbf{H})\cdot\mathrm{d}\mathbf{s}.} \tag{3.19}$$

The first integral is the total energy stored in the electromagnetic fields. The first term represents the rate of change in the total energy stored. The quantity

$$\boxed{W_{EH} = \frac{1}{2}\left(\mathbf{H}\cdot\mathbf{B} + \mathbf{E}\cdot\mathbf{D}\right)}$$

is the energy density of the electromagnetic field. The second term describes the transport of energy in and out of the volume (vol), through the surface ∂vol. The vector $\mathbf{S} \equiv \mathbf{E}\times\mathbf{H}$ is called the *Poynting vector*. The Poynting vector is relevant in cases where electromagnetic radiation is present.

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[25] This can be verified as follows:

$$\nabla\cdot(\mathbf{E}\times\mathbf{H}) = \partial_i(\epsilon_{inm}E_nH_m) = \epsilon_{inm}(\partial_iE_n)H_m + \epsilon_{inm}E_n(\partial_iH_m) = \mathbf{H}\cdot(\nabla\times\mathbf{E}) - \mathbf{E}\cdot(\nabla\times\mathbf{H}),$$

where in the second term we have used $\epsilon_{inm} = \epsilon_{nmi} = -\epsilon_{nim}$.

The first term in Eq. (3.19) can also be written as (for *linear media*):

$$\mathrm{d}W = \int_{vol} \mathrm{d}\frac{1}{2}\left(B^2/\mu + \epsilon E^2\right) \mathrm{d}^3\mathbf{r} = \int_{vol} \frac{1}{2}\left(\mu^{-1}\mathbf{B}\cdot \mathrm{d}\mathbf{B} + \epsilon \mathbf{E}\cdot \mathrm{d}\mathbf{E}\right) \mathrm{d}^3\mathbf{r}. \tag{3.20}$$

If the fields **E** and **B** are spatially uniform (over the volume *vol*), integration over the volume yields a factor *vol*. Then, the total energy differential is:

$$\mathrm{d}W = vol\left(\mu^{-1}\mathbf{B}\cdot \mathrm{d}\mathbf{B} + \epsilon \mathbf{E}\cdot \mathrm{d}\mathbf{E}\right).$$

This is often written as:

$$\boxed{\mathrm{d}W = vol\left(\mathbf{H}\cdot \mathrm{d}\mathbf{B} + \mathbf{E}\cdot \mathrm{d}\mathbf{D}\right).} \tag{3.21}$$

Note: some authors go directly from Eq. (3.18) to

$$\mathrm{d}W = \int_{vol} \left(\mathbf{H}\cdot \mathrm{d}\mathbf{B} + \mathbf{E}\cdot \mathrm{d}\mathbf{D}\right) \mathrm{d}^3\mathbf{r} + \mathrm{d}t\int_{\partial vol} \left(\mathbf{E}\times\mathbf{H}\right)\cdot \mathrm{d}\mathbf{s}.$$

This implies elimination of the time parametrization

$$\frac{\partial \mathbf{B}}{\partial t}\mathrm{d}t \to \mathrm{d}\mathbf{B}, \quad \frac{\partial \mathbf{D}}{\partial t}\mathrm{d}t \to \mathrm{d}\mathbf{D}. \tag{3.22}$$

Since **B** and **D** are functions of position and time, their total derivatives are:

$$\mathrm{d}\mathbf{B} = \frac{\partial \mathbf{B}}{\partial \mathbf{r}}\cdot \mathrm{d}\mathbf{r} + \frac{\partial \mathbf{B}}{\partial t}\mathrm{d}t, \quad \mathrm{d}\mathbf{D} = \frac{\partial \mathbf{D}}{\partial \mathbf{r}}\cdot \mathrm{d}\mathbf{r} + \frac{\partial \mathbf{D}}{\partial t}\mathrm{d}t.$$

Thus, the substitution (3.22) can only be justified if spatial variations of **B** and **D** are small (i.e. $\frac{\partial \mathbf{B}}{\partial \mathbf{r}} \approx 0$ and $\frac{\partial \mathbf{D}}{\partial \mathbf{r}} \approx 0$) or if *vol* is sufficiently large so that edge effects (spatial non-uniformities) contribute negligibly to the volume integral.

3.11.2. Magnetic and Electric Polarizations. In Eq. (3.21), namely $\mathrm{d}W = vol\left(\mathbf{H}\cdot \mathrm{d}\mathbf{B} + \mathbf{E}\cdot \mathrm{d}\mathbf{D}\right)$, only the fields $\mathbf{E}, \mathbf{D}, \mathbf{B}, \mathbf{H}$ appear. When we derived Eq. (3.21), we could have just as easily written instead (reader should check this):[26]

$$\mathrm{d}W = vol\left(\mathbf{B}\cdot \mathrm{d}\mathbf{H} + \mathbf{D}\cdot \mathrm{d}\mathbf{E}\right).$$

---

[26] Check also that substituting, $\mathbf{B} = \mu_0\mathbf{H} + \mathbf{M}$ and $\mathbf{D} = \epsilon_0\mathbf{E} + \mathbf{P}$ into $\mathrm{d}W = vol\left(\mathbf{H}\cdot \mathrm{d}\mathbf{B} + \mathbf{E}\cdot \mathrm{d}\mathbf{D}\right)$ yields:

$$\begin{aligned}\mathrm{d}W =& vol\left(\mathbf{H}\cdot \mathrm{d}(\mu_0\mathbf{H} + \mathbf{M}) + \mathbf{E}\cdot \mathrm{d}(\epsilon_0\mathbf{E} + \mathbf{P})\right)\\ =& vol\left[(\mu_0\mathbf{H}\cdot \mathrm{d}\mathbf{H} + \epsilon_0\mathbf{E}\cdot \mathrm{d}\mathbf{E}) + \mathbf{H}\cdot \mathrm{d}\mathbf{M} + \mathbf{E}\cdot \mathrm{d}\mathbf{P}\right]\\ =& vol\left[\frac{1}{2}\mathrm{d}\left(\mu_0 H^2 + \epsilon_0 E^2\right) + \mathbf{H}\cdot \mathrm{d}\mathbf{M} + \mathbf{E}\cdot \mathrm{d}\mathbf{P}\right]\end{aligned}$$

It's a matter of convenience which set of independent variables one uses. However, $\vec{m} = vol\cdot\mathbf{M}$ and $\vec{p} = vol\cdot\mathbf{P}$ are extensive variables whereas **H** and **E** are intensive. We recall from Section 3.4.7 that work differentials are of the form $\delta W =$ (intensive quantity) × d(extensive quantity). Thus, the correct form is:

$$\mathrm{d}W = vol\left[\frac{1}{2}\mathrm{d}\left(\mu_0 H^2 + \epsilon_0 E^2\right)\right] + \mathbf{H}\cdot \mathrm{d}\vec{m} + \mathbf{E}\cdot \mathrm{d}\vec{p}.$$

It would be desirable to decompose the contributions of the external and internal fields. Since $\mathbf{B} = \mu_0\mathbf{H} + \mathbf{M}$ and $\mathbf{D} = \epsilon_0\mathbf{E} + \mathbf{P}$, we have:

$$\begin{aligned} \mathrm{d}W =& vol\,((\mu_0\mathbf{H} + \mathbf{M}) \cdot \mathrm{d}\mathbf{H} + (\epsilon_0\mathbf{E} + \mathbf{P}) \cdot \mathrm{d}\mathbf{E}) \\ =& vol\,[(\mu_0\mathbf{H} \cdot \mathrm{d}\mathbf{H} + \epsilon_0\mathbf{E} \cdot \mathrm{d}\mathbf{E}) + \mathbf{M} \cdot \mathrm{d}\mathbf{H} + \mathbf{P} \cdot \mathrm{d}\mathbf{E}] \end{aligned}$$

A useful approximation can be obtained by decomposing the fields $\mathbf{E}, \mathbf{H}$ as the sum of externally applied fields (subscript 0) and any additional fields (subscript dm)[27] arising after introduction of the sample in the external field:

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_{dm}, \qquad \mathbf{E} = \mathbf{E}_0 + \mathbf{E}_{dm}.$$

The dm fields are usually very small compared to the externally applied fields: $\|\mathbf{H}_{dm}\| \ll \|\mathbf{H}_0\|$ and $\|\mathbf{E}_{dm}\| \ll \|\mathbf{E}_0\|$. In this approximation the expression for work reduces to:[28]

$$\mathrm{d}W = vol\left[\frac{1}{2}\mathrm{d}\left(\mu_0 H_0^2 + \epsilon_0 E_0^2\right) + \mathbf{M} \cdot \mathrm{d}\mathbf{H}_0 + \mathbf{P} \cdot \mathrm{d}\mathbf{E}_0\right]. \tag{3.23}$$

The advantages of this expression are two-fold:

(1) The terms are broken down into two parts: the energy required to create[29] the external field (the $\mu_0 H_0^2 + \epsilon_0 E_0^2$ term), and the energy required to realign the external fields (the $\mathbf{M} \cdot \mathrm{d}\mathbf{H}_0 + \mathbf{P} \cdot \mathrm{d}\mathbf{E}_0$ term).

(2) For the $\mathbf{M} \cdot \mathrm{d}\mathbf{H}_0 + \mathbf{P} \cdot \mathrm{d}\mathbf{E}_0$, we see that the external fields ($\mathbf{H}_0$ and $\mathbf{E}_0$) are the control parameters. This is better representative of real experimental conditions, where the experimentalist controls the external fields rather than the polarization fields inside the material.

3.11.3. Linear Media, Curie's Law.

The internal energy differential with electromagnetic work, Eq. (3.23), reads:

$$\mathrm{d}U = \delta Q + vol\left[\frac{1}{2}\mathrm{d}\left(\mu_0 H_0^2 + \epsilon_0 E_0^2\right) + \mathbf{M} \cdot \mathrm{d}\mathbf{H}_0 + \mathbf{P} \cdot \mathrm{d}\mathbf{E}_0\right].$$

In paramagnetic materials, the Curie-Weiss law holds,

$$\mathbf{M} = \chi\mathbf{H}, \quad \chi = \frac{C}{T},$$

where C is a material-dependent constant. In dielectric materials a similar law often holds,

$$\mathbf{P} = \chi_e\epsilon_0\mathbf{E} = \alpha\mathbf{E},$$

---

[27] An example of field perturbation is the *demagnetizing field* associated with magnets.

[28] The factor of $\frac{1}{2}$ arises because we used $H\mathrm{d}H = \frac{1}{2}\mathrm{d}H^2$.

[29] Energy is required to bring the charges and currents required to create the fields.

where α is a material-dependent constant called the polarizability (see Section **??** and Table **??**). Under these circumstances[30], we have:

$$\begin{aligned}\mathrm{d}U =&\delta Q + vol\left[\frac{1}{2}\mathrm{d}\left(\mu_0 H_0^2 + \epsilon_0 E_0^2\right) + \frac{1}{2}\mathrm{d}\left(\frac{C}{T}H_0^2 + \alpha E_0^2\right)\right]\\ =&\delta Q + \frac{vol}{2}\mathrm{d}\left[(\mu_0 + \frac{C}{T})H_0^2 + (\epsilon_0 + \alpha)E_0^2\right]\end{aligned}$$

The term C/T is much larger than μ_0;[31] thus, we neglect the μ_0 term.

3.11.4. Adiabatic Demagnetization. Adiabatic demagnetization (W.F. Giauque) can be used for cooling (Fig. 3.26) in a process that is analogous to adiabatic decompression (Section 3.10.38) but instead involves the spin degrees of freedom of paramagnetic salts.[32] Adiabatic demagnetization[33] of a paramagnetic salt is a two-steps sequence that enables cooling below 1 K. Temperatures around 1 mK have been reached. The steps are: (1) isothermal magnetization followed by (2) adiabatic demagnetization (Fig. 3.26):

(1) **Isothermal magnetization** (thermal contact with cold He gas). At time zero, spins in the paramagnetic salt are randomly oriented (disordered state). The system undergoes isothermal demagnetization in the presence of a strong magnetic field. The entropy of the spin system decreases, as the spins align with the magnetic field (ordered state). While the final temperature is unchanged, heat is lost to the surroundings in order to dissipate the entropy. (Lowering the temperature would also lead to alignment of the spins.)

(2) **Adiabatic demagnetization** (He gas pumped away; no thermal contact with He). Next, heat transfer is stopped (paramagnetic salt is insulated) and the external field is turned off, leading the spins to randomly reorient. However, the temperature has decreased. While heat transfer outside the system is not allowed, heat can be transferred between spin and lattice. However, the lattice entropy is much lower than the spin entropy. The total entropy of the isolated

---

[30] The conditions include: Curie law, linear media, and approximating $\mathbf{H} \approx \mathbf{H}_0$ and $\mathbf{E} \approx \mathbf{E}_0$.

[31] For those interested in a justification of this approximation: The Curie constant is given by $\frac{\mu_0 \mu_B^2}{3k_B} N g^2 J(J+1)$, where J is the total angular momentum quantum number of the paramagnetic atoms, g is the Landé factor, $g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$ (S: spin, L: orbital, J: total angular momenta). For an electron spin, $g \approx 2$. N is the density of magnetic atoms (10-100 $\times 10^{27}$ atoms/m^3 for solids). μ_B is the Bohr magneton (9.274 $\times 10^{-24}$ J/T). Plugging these typical values at room temperature gives $C/T \approx 10^3 \mu_0$, which is much larger than μ_0. In adiabatic demagnetization experiments, the temperature is typically much lower (liquid helium), so the approximation is well justified.

[32] The isothermal compression of a gas (we apply pressure and the entropy decreases) is analogous to the isothermal magnetization of a paramagnet or a soft ferromagnet: we apply an external magnetic field and the magnetic entropy decreases. The subsequent adiabatic expansion of a gas (we lower pressure at constant entropy and temperature decreases) is equivalent to adiabatic demagnetization (we remove the external field, the total entropy remains constant and temperature decreases since the magnetic entropy increases).

[33] Giauque Nobel prize lecture:
`http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1949/giauque-lecture.pdf`

system (paramagnetic salt) has not changed much, since heat was not allowed to transfer ($\mathrm{d}S{=}\delta Q/T \approx 0$).

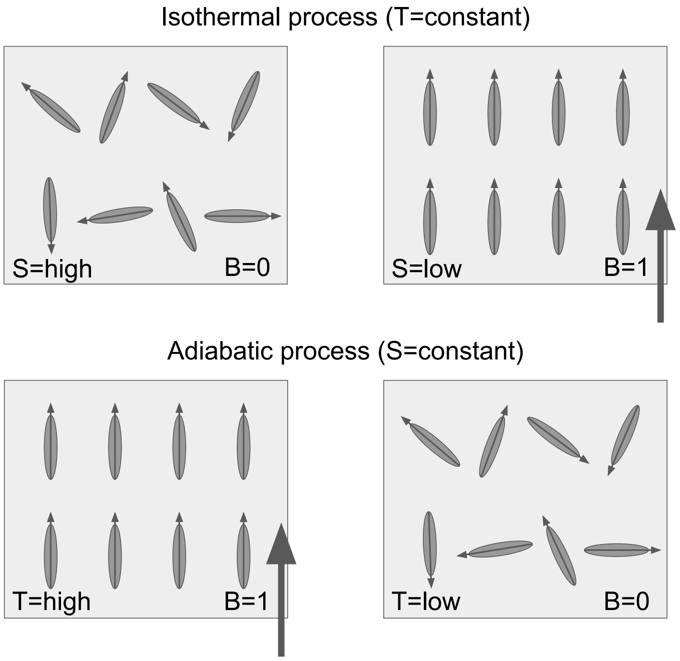


Figure 3.26. Adiabatic demagnetization. The first step involves turning on a magnetic field at constant temperature. The spins align with the magnetic field, reducing the entropy. In the second step, the entropy is held constant while the field is turned off. Since the entropy remains constant, the only possible outcome left to compensate for the loss of magnetic field is for the temperature to decrease.

Let us see how this two-step process could possibly work (Fig. 3.27). Our starting point is Eq. (3.23). Let us take the "system" as the paramagnetic salt plus electromagnetic coils as well as the surrounding helium (liquid helium bath plus helium gas in contact with the salt). This forms an isolated system. For isolated systems, the change in internal energy is zero ($\mathrm{d}U = 0$). During isothermal magnetization, heat is allowed to exchange between the helium and the salt in order to maintain the salt temperature constant:

$$\delta Q_{\mathrm{He}} = -\delta Q_{salt}.$$

If the process is reversible and isothermal,

$$T_{\mathrm{He}}\mathrm{d}S_{\mathrm{He}} = -T_{salt}\mathrm{d}S_{salt},$$

we have $T_{\mathrm{He}} = T_{salt} \equiv T$ and $\mathrm{d}S_{\mathrm{He}} = -\mathrm{d}S_{salt}$. The entropy in the context of heat transfer is the lattice entropy (random atomic motions). The paramagnetic salt also has spin entropy, which does not exchange with the helium in any way because no exchange mechanism exists[34].

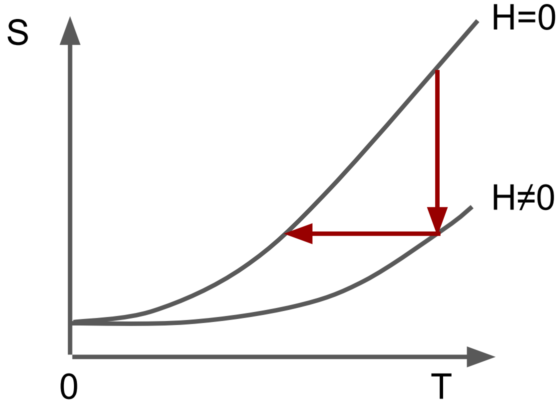


Figure 3.27. Process of adiabatic demagnetization. During isothermal magnetization, the entropy of the spins is lowered. During adiabatic demagnetization, entropy remains constant but temperature decreases.

The total salt entropy should be viewed as the sum of lattice (L) and spin (S) contributions:

$$\mathrm{d}S_{salt} = \mathrm{d}S^{L}_{salt} + \mathrm{d}S^{S}_{salt}.$$

Our previous statement $\delta Q_{\mathrm{He}} = -\delta Q_{salt}$ refers to the lattice contributions because heat can only be transferred via lattice motions. We are left with a non-vanishing $T\mathrm{d}S^{S}_{salt}$ term describing changes in the spin entropy. ($T\mathrm{d}S^{S}_{\mathrm{He}} = 0$ because helium is not magnetic.) The physical origin of $\mathrm{d}S^{S}_{salt}$ is the alignment of the magnetic moments of the paramagnetic salt due to the ramping up of the magnetic field.

The first law then reads (with $E_0 = 0$ and neglecting the μ_0 term):

$$\mathrm{d}U = 0 = T\mathrm{d}S^{S}_{salt} + \frac{vol}{2}\mathrm{d}\left[\frac{C}{T}H_0^2\right].$$

During isothermal magnetization, the field is ramped up from 0 to some value H. The spin entropy decreases by an amount proportional to $(H/T)^2$:

$$\Delta S^{S}_{salt} = \int \mathrm{d}S^{S}_{salt} = S^{S}_{salt}(H) - S^{S}_{salt}(0) = -\frac{vol}{2}C\left(\frac{H}{T}\right)^2.$$

During adiabatic demagnetization, the entropy remains constant since $\delta Q = T\mathrm{d}S = 0$. The field is ramped down from H to H_{int}, where H_{int} is the internal magnetic field due to coupling to neighboring magnetic moments. If the entropy is proportional to $(H/T)^2$, the

---

[34] For spin entropy to exchange, we would need a spin-spin coupling mechanism, which does not exist here.

condition of the initial entropy to equal the final entropy:

$$S^S_{salt}(initial) = const \times \left(\frac{H}{T_i}\right)^2 = S^S_{salt}(final) = const \times \left(\frac{H_{int}}{T_f}\right)^2,$$

leads to:

$$\boxed{T_f = T_i\left(\frac{H_{int}}{H}\right).}$$

The internal field is typically on the order of a few Gauss (10^{-4} T). The external field (H) is on the order of a Tesla. Therefore, cooling by 3-4 orders of magnitude is possible.

3.12. Problems

Problem 93. We have seen that the standard Gibbs free energy of a reaction, ΔG°_{rxn}, is given as a sum of standard Gibbs energy of formation, for each reactant and products (with reactants taken as negative):

$$\Delta G^\circ_{rxn} = \sum_i \nu_i(\Delta G^\circ_f)_i$$

where the sum i runs over all reactants and products. (a) Prove that this formula follows from the fact that dG is an exact differential. (b) Using only the formula from (a) and the relationship between G, H and S, prove also that:

$$\Delta H^\circ_{rxn} = \sum_i \nu_i(\Delta H^\circ_f)_i, \qquad \Delta S^\circ_{rxn} = \sum_i \nu_i S^\circ_i$$

where S°_i and $(\Delta H^\circ_f)_i$ are the entropies (absolute) and enthalpies of formation for species i, respectively. ΔH°_{rxn} and ΔS°_{rxn} are the standard enthalpy and entropy changes for the reaction.

Solution. (a) $\Delta G^\circ_{rxn} = \sum_i \nu_i(\Delta G^\circ_f)_i$ follows from the fact that G is a state function, i.e. $\Delta G = \int_{reactants}^{products} \mathrm{d}G$. Integrate along the following path: Destroy all reactants one by one (order is unimportant) and Form all the products one by one (order is unimportant). Each molecule destroyed and formed contributes a term in the summation (with appropriate sign).

(b) First we have the basic relationship from thermodynamics (constant T), $\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$. Each term in the summation $\Delta G^\circ_{rxn} = \sum_i \nu_i(\Delta G^\circ_f)_i$, we view $(\Delta G^\circ_f)_i$ as a small increment dG_i that contributes to the integral, for which we apply the following decomposition $\mathrm{d}G_i = \mathrm{d}H_i - T\mathrm{d}S_i$. Let's call each term $\mathrm{d}H_i \equiv (\Delta H^\circ_f)_i$ and $\mathrm{d}S_i \equiv S^\circ_i$, respectively. This gives the decomposition

$$\Delta G^\circ_{rxn} = \sum_i \nu_i(\Delta G^\circ_f)_i = \sum_i \nu_i(\Delta H^\circ_f)_i - T\sum_i \nu_i S^\circ_i.$$

And since $\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$, in the limit $T \to 0$, the second term vanishes, we have $\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn}$ and $\Delta G^\circ_{rxn} = \sum_i \nu_i(\Delta H^\circ_f)_i$. Therefore,

$$\Delta H^\circ_{rxn} = \sum_i \nu_i(\Delta H^\circ_f)_i.$$

Taking the limit $T \to \infty$, the first term is negligible compared to the second term, leaving only $\Delta G^\circ_{rxn} = -T\Delta S^\circ_{rxn}$ and $\Delta G^\circ_{rxn} = -T\sum_i \nu_i S^\circ_i$. It follows that:

$$\Delta S^\circ_{rxn} = \sum_i \nu_i S^\circ_i.$$

■

Problem 94. Hess's law states that *the total enthalpy change during the complete course of a reaction is the same whether the reaction is made in one step or in several steps.* Mathematically, the statement of Hess's law, as pertains to the *net or overall reaction*, is:

$$\boxed{\Delta H^\circ_{rxn} = \sum_{I\in products} \nu_I(\Delta H^\circ_f)_I - \sum_{J\in reactants} \nu_J(\Delta H^\circ_f)_J,}$$

where the reaction is the *net reaction.* The summation is over all reactants (products) in the *net equation.* $(\Delta H^\circ_f)_I$ is called *enthalpy of formation* (of species I) and ν_I is the stoichiometric coefficient of species I. (Here, ν_I and ν_J are all positive.) When the conditions are standard, the enthalpy of formation is denoted as $(\Delta H^\circ_f)_I$ (standard enthalpy of formation).

(a) Prove that Hess's law is a consequence of the fact that H is a state function (dH is an exact differential), i.e. it does not depend on the path taken to get from the reactants to the products. Prove that the above statement for the *net reaction* is entirely equivalent to summing up reaction enthalpies from individual reactions:

$$\boxed{\Delta H^\circ_{rxn} = \sum_{i\in reactions} \Delta H^\circ_{rxn}(i),}$$

where $\Delta H^\circ_{rxn}(i)$ denotes the net (overall) reaction enthalpy of the i-th reaction. The sum runs over all reactions that make up the net reaction. Suppose that we have two concurrent reactions taking place:

$$\begin{aligned} &\mathrm{C}(s, gr) + \mathrm{O_2}(g) \to \mathrm{CO_2}(g), && \Delta H^\circ_{rxn}(1) = -393.5 \text{ kJ} \\ &\mathrm{CO_2}(g) \to \mathrm{CO}(g) + \tfrac{1}{2}\mathrm{O_2}(g) && \Delta H^\circ_{rxn}(2) = +283.0 \text{ kJ}. \end{aligned}$$

(b) Apply Hess's law to obtain ΔH°_{rxn} for the net reaction.

Solution. (a) Hess's law follows from $\Delta H^\circ_{rxn} = \int_{reactants}^{products} \mathrm{d}H^\circ_{rxn}$ and choosing a path in the net reaction that destroys all reactant molecules regardless of order (destruction implies a negative sign) and creates all product molecules (without regards to order). This is equivalent to summing over all reactions: because H is a state function, the value of

ΔH°_{rxn} is the same, regardless of the choice of path. Here, we choose a different path, which takes us through all reactions one by one. This is entirely equivalent, because the chemical reaction is treated as an equation; multiple reactions are added to give the net reaction. The integral is a linear operator, hence, it is applied to each term in the summation (and the summation is identical whether we look at the net reaction or the sum of individual reactions).

(b) The net reaction (and net enthalpy change) is the sum:

$$C(s, gr) + \tfrac{1}{2}O_2(g) \to CO(g) \qquad \Delta H^\circ_{rxn} = \Delta H^\circ_{rxn}(1) + \Delta H^\circ_{rxn}(2) = -110.5 \text{ kJ}.$$

■

Problem 95. METHOD OF BOND ENTHALPIES. In chemical reactions, bonds are broken and new ones are formed. Think about reactants: one way to consume reactants is to destroy all the chemical bonds of all reactants, until atoms are separate. On the products side: to form the product molecules, we assemble the atoms together and create a number of chemical bonds. There is an energy associated with breaking and forming these bonds. It is possible to use this information to estimate the enthalpy change ΔH°_{rxn} of a reaction, which can be calculated from:

$$\Delta H^\circ_{rxn} = \sum_{\substack{I \in bonds \\ broken}} \Delta H^\circ_I - \sum_{\substack{J \in bonds \\ formed}} \Delta H^\circ_J,$$

where ΔH°_I is the energy absorbed when a particular bond is broken and ΔH°_J is the energy released when a bond is formed. (a) Prove that this restatement of Hess's law is entirely equivalent to the one in Problems 1 and 2. (b) Prove also that this new statement follows from the fact that H is a state function (and dH is an exact differential). (c) Consider the following example on cracking of propane (thermal decomposition, $\Delta H^\circ_{rxn} > 0$ endothermic) to make ethene (Fig. 3.28).

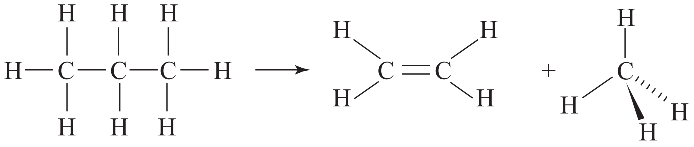


Figure 3.28. Method of bond enthalpy illustrated.

Here is some data on average bond enthalpy (units are kJ/mol)

C – H bond: +415
C – C bond: +345
C = C bond: +611

Add up all the energies of the broken bonds; add up all the energies of the bonds that are reformed and subtract one from the other. Show that $\Delta H^\circ_{rxn} = 4,010 - 3,931 = 79$ kJ/mol. (Hint: 10 bonds must be broken on the reactants side to consume the reactants, whereas 9 bonds must be formed on the products side to synthesize the needed products.)

Solution. (a) This reformulation of Hess's law is justified by the choice of path, which here involves destroying molecules or forming them, one chemical bond at a time. (This is longer, and involves more steps, but the end result is the same, i.e. the value of ΔH°_{rxn} is identical.)

(b) This follows from the fact that dH is an exact differential because the original Hess's law is also based on this fact. And since the two are equivalent, the proof follows.

(c) We have, for the left hand side (bonds broken):

$$\begin{aligned} 2\ \mathrm{C-C} &\qquad 2 \times 345 = 690 \\ 8\ \mathrm{C-H} &\qquad 8 \times 415 = 3,320 \end{aligned}$$

These energies add up to a total of 4,010 kJ/mol.

For the right hand side (bonds formed),

$$\begin{aligned} 1\ \mathrm{C=C} &\qquad 1 \times 611 = 611 \\ 8\ \mathrm{C-H} &\qquad 8 \times 415 = 3,320 \end{aligned}$$

for a total of 3,931 kJ/mol. The net difference between reactant bonds destroyed and product bonds formed is:

$$\Delta H^\circ_{rxn} = 4,010 - 3,931 = 79 \text{ kJ/mol.}$$

■

Problem 96. (e) Is it really necessary to completely break down all bonds and reform them or can you find a short-cut to computing ΔH of the reaction without having to completely take apart all molecules and reform them (including reforming the same bonds that were broken!)? Reformulate the statement for the method of bond enthalpies with this short-cut in mind.

Solution. No, it is not necessary to break ALL the bonds and reform them. When we break a bond and reform it, there is no net change in this particular bond, so why bother breaking and reforming it? Such pairs of events can be discounted because they cancel each other out. In other words, for a given reaction (reactants + products), the initial conditions (reactants) and final conditions (products) are fixed regardless of the path (from reactants to products) we choose. Instead of the 'long path" (that involves breaking ALL bonds), we can instead choose a shorter path that does not involve destroying ALL bonds. Instead we may limit the breaking and forming of bonds to the bare minimum necessary. In real reactions, not all bonds in all reactants are broken; only a small number of bonds are broken. ■

Problem 97. Prove the following formula

$$\mathrm{d}(\Delta G) = (\Delta V)\mathrm{d}P - (\Delta S)\mathrm{d}T,$$

which allows us to calculate how ΔG varies with temperature and pressure. $\Delta G = \int \mathrm{d}G$ denotes a change in G, for example, $\Delta G = G(\mathit{products}) - G(\mathit{reactants})$ being one possible application. (Note: we have not derived this formula in class; the fundamental equation of thermodynamics (1st law) was given in terms of G, not ΔG.)

Solution. Apply the fundamental equation, $\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$, twice, once to all the reaction products collectively, $G(\mathit{products})$, and once to all the reactants collectively, $G(\mathit{reactants})$:

$$\mathrm{d}G_{prod} = V_{prod}\mathrm{d}P - S_{prod}\mathrm{d}T, \qquad \mathrm{d}G_{react} = V_{react}\mathrm{d}P - S_{react}\mathrm{d}T$$

$$\begin{aligned}\mathrm{d}G_{prod} - \mathrm{d}G_{react} =& \mathrm{d}(G_{prod} - G_{react}) = \mathrm{d}(\Delta G)\\ =& (V_{prod} - V_{react})\mathrm{d}P - (S_{prod} - S_{react})\mathrm{d}T = (\Delta V)\mathrm{d}P - (\Delta S)\mathrm{d}T.\end{aligned}$$

■

Problem 98. Consider the reaction $\mathrm{CuBr_2}(s) \rightleftharpoons \mathrm{CuBr}(s) + \frac{1}{2}\ \mathrm{Br_2}(g, 1\ \mathrm{atm})$. (a) In what direction does this reaction proceed at 300 K and 1 atm pressure? At 300 K, 1 atm, the following data is available from tables:

	ΔH_f° kcal/mol	$S^\circ_{300\ K}$ cal/mol/K
$CuBr_2$(s)	-33.2	30.1
CuBr(s)	-25.1	21.9
Br_2(g, 1 atm)	+7.34	58.64

Solution. The favored direction of reaction will be indicated by the sign of ΔG°_{300}, to calculate which we need only determine ΔH°_{300} and ΔS°_{300} for the reaction.

$$\begin{aligned}\Delta H^\circ_{300} =& (\Delta H_f^\circ)_{\mathrm{CuBr}} + \tfrac{1}{2}(\Delta H_f^\circ)_{\mathrm{Br_2}} - (\Delta H_f^\circ)_{\mathrm{CuBr_2}}\\ =& -25.1 + 3.67 - (-33.2) = +11.8\ \mathrm{kcal/mol}.\end{aligned}$$

$$\begin{aligned}\Delta S^\circ_{300} =& (S^\circ_{300})_{\mathrm{CuBr}} + \tfrac{1}{2}(S^\circ_{300})_{\mathrm{Br_2}} - (S^\circ_{300})_{\mathrm{CuBr_2}}\\ =& +21.9 + 29.32 - 30.1 = +21.1\ \mathrm{kcal/mol}.\end{aligned}$$

$$\Delta G^\circ_{300} = \Delta H^\circ_{300} - T\Delta S^\circ_{300} = 11,800 - (298)(21.1) = 5500\ \mathrm{cal/mol} = 5.5\ \mathrm{kcal/mol}$$

Not rightward, but rather, leftward progress of the reaction is thus strongly favored at 300 K, and will reduce the Br_2 pressure far below 1 atm. ■

Problem 99. (b) For the previous reaction, at what temperature will the three substances coexist at equilibrium under a pressure of 1 atm?

Solution. At whatever temperature (T) the three substances coexist at 1 atm pressure, we will have $\Delta H_T^\circ - T\Delta S_T^\circ = \Delta G_T^\circ = 0$. Noting that ΔH° and ΔS° are the same in sign, we essay the approximation in which the two terms are treated as substantially constant over the temperature range concerned. In that case,

$$\Delta H_T^\circ \approx \Delta H_{300}^\circ = 11.8 \text{ kcal/mol}$$
$$\Delta S_T^\circ \approx \Delta S_{300}^\circ = 21.1 \text{ kcal/mol.K}$$

and then

$$11,800 - T(21.1) = \Delta G_T^\circ = 0, \qquad T = 11,800/21.1 = 560^\circ \text{ K}.$$

■

Problem 100. (a) Which is the more stable form of carbon at 300 K and 1 atm pressure, diamond or graphite? (b) At 300 K, what pressure would be required to form diamond (density, 3.5 g/ml) from graphite (density, 2.25 g/ml)? (c) How can you be confident of the soundness of this entire mode of analysis? Some relevant data are as follows:

Heat capacity data yield for diamond (300 K), $\overline{S}_{300}^\circ = 0.58$ cal/mol.K, where $\overline{S} = -(\mathrm{d}\overline{G}/\mathrm{d}T)_P$ and $\overline{G}$ is the *molar* Gibbs free energy.

Heat capacity data yield for graphite (300 K), $\overline{S}_{300}^\circ = 1.37$ cal/mol.K

For C(graphite) → C(diamond), $\Delta\overline{S}_{300}^\circ$ = -0.79 cal/mol.K

On combustion: C(graphite) + $O_2 \rightleftharpoons CO_2$, $\Delta\overline{H}_{300}^\circ$ = -94.03 kcal.

On combustion: C(diamond) + $O_2 \rightleftharpoons CO_2$, $\Delta\overline{H}_{300}^\circ$ = -94.48 kcal.

For C(graphite) → C(diamond): $\Delta\overline{H}_{300}^\circ$ = +450 cal/mol.

And the given densities imply:

For diamond: gram-atomic volume = 12/3.5 = 3.4 ml/gr-atom. (Note: Gram atomic mass is another term for the mass, in grams, of one mole of atoms of that element. "Gram atom" is a former term for a mole of substance (expressed in grams). Example: gram atomic mass of Hydrogen is mass of 1 mole atoms =1.008 grams.)

For graphite: gram-atomic volume = 12/2.25 = 5.3 ml/gr-atom.

For C(graphite) → C(diamond): $\Delta\overline{V}_{300}$ = -1.9 ml/gr-atom, where $\overline{V} = (\mathrm{d}\overline{G}/\mathrm{d}t)_T$.

Solution. (a) For the reaction C(graphite) → C(diamond),

$$\Delta\overline{G}_{300}^\circ = \Delta\overline{H}_{300}^\circ - T\Delta\overline{S}_{300}^\circ = 450 - 300(-0.79) = +685 \text{ cal/mol}$$

At room temperature and atmospheric pressure, the favored direction of reaction is thus the inverse change of diamond into graphite. Under ordinary conditions diamond is therefore a thermodynamically unstable species, which exists only because of the extreme slowness of its conversion into the more stable graphite.

(b) At atmospheric pressure the reaction C(graphite) → C(diamond) is characterized by $\Delta\overline{G}^{\circ}_{300} > 0$. But with $\Delta\overline{V} < 0$ in this reaction, a sufficient rise of pressure should change the sign of $\Delta\overline{G}$ and, hence, the favored direction of reaction at 300 K. For consider that the effect of a change of pressure at constant temperature will be given by the following reduced form

$$\mathrm{d}(\Delta\overline{G}) = \Delta\overline{V}\mathrm{d}P.$$

If we approximate by treating $\Delta\overline{V}$ as constant (=-0.0019 lit) over the entire pressure range involved, the last equation can easily be integrated. For the upper limit we choose that pressure (P^*) at which $\Delta\overline{G}^{\circ}_{300} = 0$, i.e. the pressure under which diamond and graphite stand in equilibrium with each other at 300 K. For the lower limit we use the standard pressure of 1 atm, at which we have just found $\Delta\overline{G}^{\circ}_{300} = +685$ cal/mol. However, with $\Delta\overline{V}$ in liters and pressure in atmospheres, the appropriate unit for $\Delta\overline{G}$ is not calories but lit-atm (1 lit-atm = 101.325 J). Multiplication by the factor 0.0413 converts a-figure in calories to one in lit-atm, so that $\Delta\overline{G}^{\circ}_{300} = 0.0413(685) = 28.3$ lit atm. We have then,

$$\int_{28.3}^{0} \mathrm{d}(\Delta\overline{G}) = -0.0019 \int_{1}^{P^*} \mathrm{d}P,$$

$$0 - 28.3 = -0.0019(P^* - 1),$$

$$P^* \approx 15,000 \text{ atm}.$$

At 25°C diamond and graphite would stand in equilibrium under a pressure of 15,000 atm. At still higher pressures graphite becomes thermodynamically unstable, and its conversion into diamond is then possible in principle, though so slow in practice as to be wholly undetectable.

(c) Since at room temperature no equilibrium of graphite with diamond ever is attained in practice, there remains room for skepticism that we have correctly calculated what would be the equilibrium condition. But, given expressions for $\Delta\overline{H}$ and $\Delta\overline{V}$ as functions of temperature and pressure, by integration of equation $\mathrm{d}(\Delta\overline{G}) = \Delta\overline{V}\mathrm{d}P$, we can calculate that the equilibrium pressure is of the order of 75,000 atm at 1500°K. And here the soundness of our calculation is attested by an unmistakable production of diamond from graphite at pressures that exceed the equilibrium pressure. ■

Problem 101. Iron has a heat capacity of 25.1 J K^{-1} mol^{-1}, approximately independent of temperature between 0°C and 100°C.

(a) Calculate the enthalpy and entropy change of 1.00 mol iron as it is cooled at atmospheric pressure from 100°C to 0°C.

(b) A piece of iron weighing 55.85 g and at 100°C is placed in a large reservoir of water held at 0°C. It cools irreversibly until its temperature equals that of the water. Assuming the water reservoir is large enough that its temperature remains close to 0°C, calculate the entropy changes for the iron and the water and the total entropy change in this process.

Solution. a)

$$\begin{aligned}\Delta H_{\mathrm{Fe}} =& nc_{\mathrm{P}}\Delta T = (1.00\ \mathrm{mol})(25.1\ \mathrm{J\ K^{-1}\ mol^{-1}})(273.15 - 373.15\ \mathrm{K}) \\ =& -2510\ \mathrm{J} = -2.51 \times 10^{3}\ \mathrm{J}\end{aligned}$$

$$\Delta S_{\mathrm{Fe}} = nc_{\mathrm{P}} \log \frac{T_{\mathrm{f}}}{T_{\mathrm{i}}} = (1.00\ \mathrm{mol})(25.1\ \mathrm{J\ K^{-1}\ mol^{-1}}) \log \frac{273.15}{373.15} = -7.83\ \mathrm{J\ K^{-1}}$$

b) The entropy S is a function of state, and the initial and final states of the piece of iron are the same as in part a). Therefore, ΔS_{Fe} = -7.83 J $\mathrm{K^{-1}}$. The reservoir of water gains the 2510 J of heat from the piece of iron at a constant temperature of 273.15 K. Therefore $\Delta S_{\mathrm{water}} = 2510\ \mathrm{J}/273.15\ \mathrm{K} = +9.19\ \ \mathrm{J\ K^{-1}}$.

$$\Delta S_{\mathrm{total}} = \Delta S_{\mathrm{Fe}} + \Delta S_{\mathrm{water}} = 1.36\ \mathrm{J\ K^{-1}}$$

■

Problem 102. (a) Use data from Appendix D from Oxtoby [**9**] to calculate ΔH° and ΔS° at 25 °C for the reaction

$$2\mathrm{CuCl_2}(g) \rightleftharpoons 2\mathrm{CuCl}(s) + \mathrm{Cl_2}(g)$$

(b) Calculate ΔG° at 590 K, assuming ΔH° and ΔS° are independent of temperature.
(c) Careful high-temperature measurements show that when this reaction is performed at 590 K, ΔH°_{590} is 158.36 kJ and ΔS°_{590} is 177.74 J $\mathrm{K^{-1}}$. Use these facts to compute an improved value of ΔG°_{590} for this reaction. Determine the percentage error in ΔH°_{590} that comes from using the 298-K values in place of the 590-K values in this case.

Solution. a) The reaction of interest is

$$2\mathrm{CuCl_2}(s) \rightarrow 2\mathrm{CuCl}(s) + \mathrm{Cl_2}(g)$$

Text Appendix D supplies $\Delta H^\circ_{\mathrm{f}}$ and S° values at 298 K for the computation of ΔH°_{298} and ΔS°_{298}

$$\Delta H^\circ_{298} = 2(-137.2) + 1(0) - 2(-220.1) = 165.8\ \mathrm{kJ}$$
$$\Delta S^\circ_{298} = 2(86.2) + 1(222.96) - 2(108.07) = 179.2\ \mathrm{J\ K^{-1}}$$

b)

$$\Delta G_{590} \approx \Delta H^\circ_{590} - T\Delta S^\circ_{590} = 165.8\ \mathrm{kJ} - (590\ \mathrm{K})(0.1792\ \mathrm{kJ\ K^{-1}}) = 60.1\ \mathrm{kJ}$$

c) Use the experimental values at 590 K instead of the values at 298.15 K

$$\Delta G_{590} = \Delta H^\circ_{590} - T\Delta S^\circ_{590} = 158.36\ \mathrm{kJ} - (590\ \mathrm{K})(0.17774\ \mathrm{kJ\ K^{-1}}) = 53.5\ \mathrm{kJ}$$

The answer using ΔH°_{298} and ΔS°_{298} is about 12 % larger than the actual ΔG_{590}. Tip. The temperature dependence of ΔH° and ΔS° should not always be neglected. Taking it into consideration becomes important when the temperature differs a lot from 298.15 K. ■

Problem 103. Find the Gibbs free energy and the entropy associated with mixing 10 g of liquid water, 5 g of liquid ethanol, and 1 g of liquid methanol at 298 K?

Solution.

$$G_i = n_{\mathrm{H_2O}}\mu^*_{\mathrm{H_2O}} + n_{\mathrm{EtOH}}\mu^*_{\mathrm{EtOH}} + n_{\mathrm{MeOH}}\mu^*_{\mathrm{MeOH}}$$

$$G_f = n_{\mathrm{H_2O}}(\mu^*_{\mathrm{H_2O}} + RT\log(X_{\mathrm{H_2O}})) + n_{\mathrm{EtOH}}(\mu^*_{\mathrm{EtOH}} + RT\log(X_{\mathrm{EtOH}})) + n_{\mathrm{MeOH}}(\mu^*_{\mathrm{MeOH}} + RT\log(X_{\mathrm{MeOH}}))$$

$$G_{mix} = G_f - G_i = nRT(X_{\mathrm{H_2O}}\log(X_{\mathrm{H_2O}}) + X_{\mathrm{EtOH}}\log(X_{\mathrm{EtOH}}) + X_{\mathrm{MeOH}}\log(X_{\mathrm{MeOH}}))$$

$$S_{mix} = -nR(X_{\mathrm{H_2O}}\log(X_{\mathrm{H_2O}}) + X_{\mathrm{EtOH}}\log(X_{\mathrm{EtOH}}) + X_{\mathrm{MeOH}}\log(X_{\mathrm{MeOH}}))$$

$$n_{\mathrm{H_2O}} = 0.555 \text{ mol}, n_{\mathrm{EtOH}} = 0.108 \text{ mol}, n_{\mathrm{MeOH}} = 0.0312 \text{ mol}, n = 0.694 \text{ mol}$$

$$X_{\mathrm{H_2O}} = 0.800, X_{\mathrm{EtOH}} = 0.156, X_{\mathrm{MeOH}} = 0.0450$$

$$G_{mix} = -454 \text{ J}$$

$$S_{mix} = 1.52 \text{ J/K}$$

■

Problem 104. Find the reaction affinity at constant pressure and temperature for the following reaction going to completion:

$$\mathrm{CH_3COOH}(g) + 2\mathrm{O_2}(g) \rightarrow 2\mathrm{CO_2}(g) + 2\mathrm{H_2O}(g)$$

Data: $G^\circ_f(\mathrm{CO_2}(g)) = -394.36$ kJ/mol, $G^\circ_f(\mathrm{H_2O}(g)) = -228.59$ kJ/mol, $G^\circ_f(\mathrm{CH_3COOH}(g)) = -374.1$ kJ/mol

Solution. $\Delta G_{rxn} = G_f(products) - G_f(reactants) = 2 \times G^\circ_f(\mathrm{CO_2}(g)) + 2 \times G^\circ_f(\mathrm{H_2O}(g)) - G^\circ_f(\mathrm{CH_3COOH}(g)) = -871.8$ kJ/mol
$Affinity = -(\frac{\partial G}{\partial \xi})_{T,P}$
$Affinity = -\Delta G_{rxn} = -871.8$ kJ/mol ■

Problem 105. For the reaction $2\,\mathrm{Ca(s)} + \mathrm{O_2(g)} \rightarrow 2\,\mathrm{CaO(s)}$ find the equilibrium constant at 300 K given that μ°_{CaO} = -604.17 kJ mol^{-1} at that temperature. What can you conclude about the reaction based on the magnitude of the equilibrium constant?

Solution. $\Delta\mu^\circ = \mu^\circ_{\mathrm{CaO}}(2) - \mu^\circ_{\mathrm{O_2}}(1) - \mu^\circ_{\mathrm{Ca}}(2) = -1208.34$ kJ mol^{-1}
$\Delta\mu^\circ = -RT \log K$
$K = \exp[\frac{-\Delta\mu^\circ}{RT}]$
$K = 2.5 \times 10^{210}$ ■

Problem 106. Assume the reaction $\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} \rightarrow 2\,\mathrm{NH_3(g)}$ has taken place in a 2 L container and has reached equilibrium. There are 0.1 mole of $\mathrm{H_2}$(g), 0.15 mole of $\mathrm{N_2}$(g), and 1.5 moles of $\mathrm{NH_3(g)}$ present at a temperature of 500 K. Find the change in chemical potential for the reaction if the equilibrium constant is 0.1744 under the stated conditions.

Solution. $\mu_i = \mu_i^\circ + \mathrm{RT}\ \log(\mathrm{P_i})$
$\Delta\mu = \mu^\circ_{\mathrm{NH_3}}(2)$ - $\mu^\circ_{\mathrm{H_2}}(3)$ - $\mu^\circ_{\mathrm{N_2}}(1) + \mathrm{RT}\ \log\ (\frac{\mathrm{P^2_{NH3}}}{P^3_{\mathrm{H2}}P_{\mathrm{N2}}})$
Let $\Delta\mu^\circ = \mu^\circ_{\mathrm{NH_3}}(2)$ - $\mu^\circ_{\mathrm{H_2}}(3)$ - $\mu^\circ_{\mathrm{N_2}}$
$\Delta\mu^\circ$ = -RT log (K) = 7260 J $\mathrm{mol^{-1}}$
If we treat the gases as ideal then we have:
$\mathrm{P_{H2}}$ = nRT/V = (0.1 mol)(0.08312 L bar $\mathrm{mol^{-1}\ K^{-1}}$)(500 K)/(2 L) = 2.0786 bar
$\mathrm{P_{N2}}$ = 3.1179 bar
$\mathrm{P_{NH3}}$ = 31.179 bar
RT log $(\frac{\mathrm{P^2_{NH3}}}{\mathrm{P^2_{H2}P_{N2}}})$ = (4157.24 J $\mathrm{mol^{1-}}$)(3.55)= 14758 J $\mathrm{mol^{-1}}$
$\Delta\mu$ = 22018 J $\mathrm{mol^{-1}}$ ■

Problem 107. Suppose we have an ideal gas. We double the gas volume by an isothermal expansion that proceeds (1) reversibly and (2) irreversibly into a vacuum. What is the change in entropy during this process (1 and 2)?

Solution. (1) For the reversible expansion

$$\Delta S = nR\log(V_2/V_1) = (2.30)(1)(1.99)\log 2 = +1.38 \text{ cal/mol.K.}$$

(2) For the irreversible expansion to the same final state, the entropy change in the gas must again by +1.38 cal/mol.K. ■

Problem 108. What is the change in entropy of the surroundings when the volume of an ideal gas is doubled by an isothermal expansion that proceeds (1) reversibly or (2) irreversibly?

Problem 109. When the volume of an ideal gas is reduced two-fold by a reversible isothermal compression, what is the change of entropy of (1) the gas and (2) the surroundings?

Problem 110. Under 1 atm pressure at 279 K, the reversible crystallization of benzene from its melt is accompanied by an entropy change of -8.53 cal/mol.K. What is the molar heat of fusion of benzene at its melting point?

Problem 111. The heat capacity at constant pressure (c_P) for carbon monoxide is 7.0 cal/mol.K (ignore temperature dependences). What is the entropy change when a mole of CO is (1) heated from 100 K to 200 K, or (2) cooled from 1500 K to 750 K?

Problem 112. At 1000 K, 4.49×10^{-2} as many molecules in a sample of carbon monoxide (CO) are in the first excited vibrational-energy state as in the ground state. How far above the ground state is the first excited state, in kJ/mol?

Solution. Given $T = 1000\ K$, molecule=CO (carbon monoxide) and $N_1/N_0 = 4.49\times10^{-2}$ (vibrational energy). Let x=number of molecules in the ground state (vibrational) and

$4.49{\times}10^{-2}x$ = number of molecules in the 1st excited vibrational state. Using the equation

$$\frac{N_i}{N_j}e^{-(\epsilon_i-\epsilon_j)/k_BT} = e^{-\Delta\epsilon/k_BT}$$

$$\frac{N_1}{N_0} = \frac{4.49\times10^{-2}x}{x} = e^{-\Delta\epsilon/(1.38\times10^{-23}\ \mathrm{J/K})(1000\ \mathrm{K})}$$

$$\log(4.49\times10^{-2}) = \frac{-\Delta\epsilon}{1.38\times10^{-20}\ \mathrm{J}}$$

$$(-3.10)(1.38\times10^{-20}\ \mathrm{J}) = -\Delta\epsilon$$

$$\Delta\epsilon = 4.28\times10^{-20}\ \mathrm{J}$$

Now, to convert to the final units of kJ/mol.

$$(4.28\times10^{-20}\ \mathrm{J})\left(\frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}\right)\left(\frac{6.022\times10^{23}}{1\ \mathrm{mol}}\right) = 25.8\ \mathrm{kJ/mol}$$

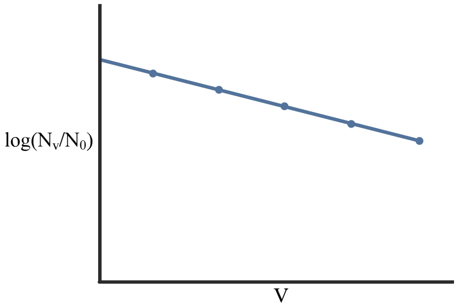
■

Problem 113. Molecular nitrogen has a vibrational energy $h\nu = 2230\ \mathrm{cm}^{-1}$. A sample of nitrogen is heated in an electric arc. Spectroscopic methods are used to determine the relative populations of excited vibrational levels. The results are presented in the table below

Vibrational level (v)	0	1	2	3	4	...
N_v/N_0	1.000	0.200	0.040	0.008	0.002	...

Use these results in combination with the information about the spacing of vibrational energy levels to determine whether the nitrogen is in thermodynamic equilibrium with respect to vibrational energy. In other words, does the vibrational population obey the Maxwell-Boltzmann distribution law? If so, what is the vibrational temperature of the gas? Is this value necessarily the same as the translational temperature of the gas? Why or why not? Hint: try to rearrange the Maxwell-Boltzmann equation appropriate for this problem so that there is a linear relationship between v and some function of N_V/N_0. Then plot the data and calculate the slope.

Solution. Given: molecule is $N_2(g)$ and $h\nu = 2230\ cm^{-1}$. Relative populations of the first four excited state to the ground state. One way to approach this problem is to rearrange the Maxwell-Boltzmann distribution (equation) to look like a linear function, graph the function and calculate T from the slope. We are looking at vibrational energy, so we use: $\epsilon_v = (v + 1/2)h\nu$ and $N_v/N_0 = e^{-(\epsilon_v-\epsilon_0)/k_BT} = e^{-((v+1/2)h\nu-(1/2)h\nu)/k_BT}$, where the second term in the exponent is from $\epsilon_0 = (0 + 1/2)h\nu$. Therefore, $N_V/N_0 = e^{-vh\nu/k_BT}$ Linearize this equation by taking the log of both sides: $\log(N_v/N_0) = -nk\nu/k_BT$ or $\log(N_V/N_0) = -v(h\nu/k_BT)$ which is of the form $y = mx$.



The slope of this line is $m = -1.5649 = -k\nu/k_BT$. Note: depending on your program and graphing the data, the slope value may differ from mine. Solving for T, we get: $T = 2050K$, which becomes $T = 2000\ K$ (1 sig. fig.). The T_v is usually the same as $T_{translational}$ but doesn't have to be under certain conditions. ■

Problem 114. A tank is filled with 1000 g of nitrogen at 0.00°C and 16.0 atm pressure. The tank is then heated to 50.00°C and the valve is opened. What is the total mass (in grams) of the nitrogen that escapes if the external pressure is 1.00 atm. and the temperature is maintained at 50.00°C?

Solution. Using $PV = nRT$ we can calculate the volume of the tank from the initial data. $PV = nRT$, $V = nRT/P$, $n =?$.

$$n = (1000.\text{ g N}_2(g))\left(\frac{1\text{ mol N}_2(g)}{28.00\text{ g N}_2(g)}\right) = 35.714\text{ mol N}_2(g)$$

$$V = \frac{(35.714\text{ mol})(0.08206\text{ L.atm/mol/K})(273.15\text{ K})}{16.0\text{ atm}} = 50.03\text{ L} \rightarrow 50.0\text{ L}$$

This gas will continue to escape until the internal pressure equals the external pressure of 1.00 atm. The amount of gas remaining in the tank:

$$n = \frac{PV}{RT} = \frac{(1.00\text{ atm})(50.03\text{ L})}{(0.08206\text{ L.atm/mol/K})(323.15\text{ K})} = 1.8867\text{ mol N}_2(g)$$

$$(1.8867\text{ mol N}_2(g))\left(\frac{28.00\text{ g N}_2(g)}{1\text{ mol N}_2(g)}\right) = 52.827\text{ g N}_2(g)$$

The amount of gas that escaped = 1000. g-52.827 g=947.172 g → 927 g $N_2(g)$. ■

Problem 115. The Lennard-Jones potential is as follows: $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where ϵ and σ are constants. The ϵ corresponds to the potential well depth at the equilibrium intermolecular (interatomic) distance. (i.e. where the potential energy is a minimum). Calculate the intermolecular (interatomic) distance in Å that corresponds to ϵ for a He..He interaction. Derive an expression in terms of σ for this distance for any atomic/molecular interaction.

Solution. You might start out by sketching a potential energy curve. From such a graph we see that the distance we need to calculate occurs at the minimum of the function, so one technique to calculate this r is to take the derivative of the function and set it equal to zero and solve for an r value that makes the derivative equal to zero.

You may also want to find the constants for He.

$$\epsilon = 1.41 \times 10^{-22}\ J, \qquad \sigma = 2.56 \times 10^{-10} m = 2.56\ \mathring{A}.$$

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

$$V(r) = 4\epsilon\sigma^{12}r^{-12} - 4\epsilon\sigma^{6}r^{-6}.$$

$$\frac{\mathrm{d}V(r)}{\mathrm{d}r} = (-12)(4\epsilon)\sigma^{12}r^{-11} - (-6)(4\epsilon)(\sigma^{6})(r^{-5})$$

$$= (-6)(4\epsilon)(\sigma)\left[2\left(\frac{\sigma}{r}\right)^{11} - \left(\frac{\sigma}{r}\right)^{5}\right] = 0$$

When the square bracket equals zero, $\mathrm{d}V/\mathrm{d}r = 0$. Thus, $2(\sigma^{11}/r^{11}) - (\sigma^{5}/r^{5}) = 0$ and $2(\sigma^{11}/r^{11}) = (\sigma^{5}/r^{5})$ which gives $2(\sigma)^{6} = (r)^{6}$ and $r = (2\sigma^{6})^{1/6} = \sigma(2)^{1/6} = \sigma(1.122)$. This is the general expression in terms of σ for the distance r. Now, plug in σ for He to obtain the specific answer

$$e = (2.56\ \mathring{A})(1.122) = 2.87\ \mathring{A}$$

for the He...He interaction. ■

Problem 116. The vapor pressures of each component in a mixture of propanone (acetone, A) and trichloromethane (chloroform, C), were measured at 35° C with the following results:

χ_c	0	0.2	0.4	0.6	0.8	1.0
P_C/torr	0	35	82	142	219	293
P_A/torr	347	270	185	102	37	0

Confirm that the mixture "conforms" to Raoult's law for the component in large excess and to Henry's law for the component that is minor. Estimate the Henry's law constants, K_A and K_C.

Solution. You should graph this data and realize that it shows a general conformity to Raoult's law by both components. Both components exhibit a negative deviation to Raoult's law. So, at large mole fractions the component obeys Raoult's law (experimental data will approach the line) and at small mole fractions the component obeys Henry's law. ■

Problem 117. Ethanol (CH_3CH_2OH) has a normal boiling point, T_b of 78.4°C. When 46.58 g of Na_2SO_4 (sodium sulfate) is dissolved in the ethanol (mass = 1000 g) the boiling point becomes 79.6°C. Calculate the K_B for ethanol (including appropriate units). Assume the salt completely dissolves in the ethanol and behaves as a strong electrolyte.

Solution. We will use: $\Delta T_b = K_b \cdot m$. The solute, Na_2SO_4 has a molar mass of 142.04 g/-mol. There is 1000 g of solvent (1.000 kg solvent). Therefore, the molality can be calculated. Strong electrolyte:

$$\underbrace{\mathrm{Na_2SO_4}}_{1\text{ mol}} \to \underbrace{\underbrace{2\mathrm{Na}^+}_{2\text{ mol}} + \underbrace{\mathrm{SO_4^{2-}}}_{1\text{ mol}}}_{3\text{ mol}}$$

$$(46.58\text{ g Na}_2\text{SO}_4)\left(\frac{1\text{ mol Na}_2\text{SO}_4}{142.04\text{ g Na}_2\text{SO}_4}\right) = 0.3279\text{ mol Na}_2\text{SO}_4 \times 3$$

$$= 0.9837\text{ mol particles}$$

$$m = \frac{\text{moles of solute particles}}{\text{kg of solvent}} = \frac{0.9837}{1.000\text{ kg}} = 0.9837\text{ m}$$

So, $\Delta T = T_{new} - T_b = K_b \cdot m = 79.6°\mathrm{C} - 78.4°\mathrm{C} = 1.2°\mathrm{C}$. So, $1.2°\mathrm{C} = (K_b)(0.9837\text{ mol/kg})$ and $K_b = \frac{1.2°\mathrm{C}}{0.9837\text{ mol/kg}} = 1.22°\mathrm{C}$ kg/mol which gives 1.2°C kg/mol. ■

Problem 118. In thermodynamics, the partial derivatives of physical quantities are related to one another by application of the commutativity property of partial derivatives, $\partial_x \partial_y f(x,y) = \partial_y \partial_x f(x,y)$, which follows from the equality of mixed partial derivatives for sufficiently smooth functions. For example, if the internal energy is expressed as

$$\mathrm{d}U = T\mathrm{d}S + \mu \mathrm{d}N$$

it follows that

$$T = \left.\frac{\partial U}{\partial S}\right|_N \qquad \text{and} \qquad \mu = \left.\frac{\partial U}{\partial N}\right|_S$$

The joint second derivative of U is then given by

$$\frac{\partial^2 U}{\partial S \partial N} = \frac{\partial^2 U}{\partial N \partial S} = \left.\frac{\partial T}{\partial N}\right|_S = \left.\frac{\partial \mu}{\partial S}\right|_N$$

Since $(\partial y/\partial x) = (\partial x/\partial y)^{-1}$, the above equation can be inverted to give

$$\left.\frac{\partial S}{\partial \mu}\right|_N = \left.\frac{\partial N}{\partial T}\right|_S .$$

Similar identities can be obtained from the variations of other state functions. Show that:

$$+\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V}$$
$$+\left(\frac{\partial T}{\partial P}\right)_S = +\left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial S \partial P}$$
$$+\left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial^2 A}{\partial T \partial V}$$
$$-\left(\frac{\partial S}{\partial P}\right)_T = +\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial T \partial P}$$

Recall that $U = U(S,V)$, $H = H(S,P)$, $A = A(T,V)$ and $G = G(T,P)$.

Solution. These "Maxwell relations" are all derived the same way. Take the third one, for example, $A(T,V) = U - TS$ and $\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V$ lead to

$$S = -\left.\frac{\partial A}{\partial T}\right|_V \qquad \text{and} \qquad P = -\left.\frac{\partial A}{\partial V}\right|_T$$

Equating the second partial derivatives ($\partial^2 A/\partial T \partial V$) we get

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V$$

similarly for all other relations. ■

Problem 119. The reaction

$$\tfrac{1}{2}\mathrm{O}_2(g) + \mathrm{H}_2(g) \rightarrow \mathrm{H}_2\mathrm{O}(l)$$

is used to produce an electrical current. The details of the production of electrical current are not important for solving this problem; we only need to assume that the free energy can be converted into current (electrical work) through some process.

From tables of thermodynamic data, we find the following information in J/mol/K for the standard entropies of formation (ΔS_f°): $O_2(g)$: 205.0, $H_2(g)$: 130.6, $H_2O(l)$: 70.0. Standard enthalpy of formation for water, ΔH_f°=-285.9 kJ/mol; those for H_2 and O_2 are zero.

Use this information to find:
a) The amount of heat released if the reaction were to take place by direct combustion (of oxygen and hydrogen)
b) The amount of electrical work the same reaction can perform when carried out in a fuel cell at 298K under reversible conditions
c) The amount of heat released under the same conditions (when electrical current is produced)

Solution. First, we need to find ΔH°_{rxn} and ΔS°_{rxn} for the process. Recalling that the standard enthalpy of formation of the elements is zero, $\Delta H^\circ_{rxn} = H^\circ_f(products) - H^\circ_f(reactants) = -285.9\,\text{kJ mol}^{-1} - 0 = -285.9\,\text{kJ mol}^{-1}$. Similarly, $\Delta S^\circ_{rxn} = S^\circ_f(products) - S^\circ_f(reactants) = (70.0) - (\frac{1}{2} \times 205.0 + 130.6) = -163$ JK^{-1}mol^{-1}.
a) When the hydrogen and oxygen are combined directly, the heat released will be ΔH°_{rxn} = -285.9 kJ mol^{-1}.
b) The maximum electrical work the fuel cell can perform is given by $\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$ = -285.9 kJ mol^{-1} - (298 K)(-163 JK^{-1} mol^{-1}) = -237.2 kJ mol^{-1}.
c) The heat released in the reaction is the difference between the enthalpy change (the total energy available) and the reversible work that was expended: $\Delta H^\circ_{rxn} - \Delta G^\circ_{rxn} = T\Delta S^\circ_{rxn}$ = (298 K)(-163 J.K^{-1}mol^{-1}) = -48800 J mol^{-1} = -48.8 kJ mol^{-1}. ■

Problem 120. Two ideal gases at constant temperature and pressure are separated by a partition. There are 0.07 mol of gas A and 0.12 mol of gas B. Find the entropy change of the system after the partition is released and the two gases are allowed to mix. It is useful to know that entropy is a state function and that the entropy of a system is given by $S = k_B \log \Omega$ where Ω is the number of accessible microstates to the system and log is the natural logarithm. For an ideal gas, $\Omega \propto V^N$ where V is the volume of the gas and N is the number of gas particles. Since S depends on N through Ω, S is an extensive property. To find the entropy change, you will want to consider the system as two subsystems, one consisting of gas A and the other consisting of gas B, and then calculate the entropy of the system before and after the gases mix. The change is equal to the difference between pre- and post-mixing.

Solution. Since entropy is a state function, the entropy change is equal to the entropy of the mixture subtracted by the entropy of the two gases prior to mixing.

$$\Delta S = S_{mixture} - S_A - S_B$$

$$S_{mixture} = k_B \log(C(V_A + V_B)^{N_A + N_B})$$

where C is some constant of proportionality.

$$\begin{aligned} S_{mixture} - S_A - S_B =& k_B(N_A + N_B)\log(C(V_A + V_B)) - k_B N_A \log(CV_A) \\ & - k_B N_B \log(CV_B) \\ =& k_B N_A \log\left(\frac{V_A + V_B}{V_A}\right) + k_B N_B \log\left(\frac{V_A + V_B}{V_B}\right) \end{aligned}$$

Since we are dealing with ideal gases, we can relate the volumes to moles.

$$\frac{V_A + V_B}{V_A} = \frac{n_A + n_B}{n_B}$$

Next we insert $k_B = R/N_{Avogadro}$ and $X_A = \frac{n_A + n_B}{n_A}$.

$$\Delta S = R(n_A \log X_A + n_B \log X_B)$$

$$= 8.314 \text{ J K}^{-1}\left[0.07\log\left(\frac{0.19}{0.07}\right) + 0.12\log\left(\frac{0.19}{0.12}\right)\right] = 1.04 \text{ J K}^{-1}$$

■

Problem 121. A non-uniform chemical potential ($\mathrm{d}\mu/\mathrm{d}x \neq 0$) leads to a mass flux from regions of high concentration to regions of low concentration. Let's see how we can relate this gradient (slope, $\mathrm{d}\mu/\mathrm{d}x$) to the diffusion of particles. We know that the chemical potential for an ideal gas is of the form

$$\mu = \mu_0 + k_B T \log(c/c_0)$$

where μ_0 is a reference chemical potential (only depends on T, but otherwise a constant), $c(x,t)$ is the concentration ($[M]$) of a chemical species of interest at position x and time t, and c_0 is a reference concentration (say, 1 M).

Let's first establish the principle of "conservation of mass". Let us consider a 1D flow of particles along the x direction and a "volume element" of length $\mathrm{d}x$ centered at $\frac{x+\mathrm{d}x}{2}$. Since we are working in 1D we may take the concentration $c(x,t)$ to have units of particles per unit length. The flow of particles can be described in terms of the particle flux, $J = c(x,t)v$, where v is the velocity of particles. J has units of particles per unit time. Of course, J represents a *net flux*, meaning that $J = 0$ describes equal number of particles moving to the left as to the right. Thus, when $J = 0$, there is no change in the number of particles in the volume element $\mathrm{d}x$. Therefore, its rate of change is zero: $\partial c/\partial t = 0$. Moreover, even when $J = constant$, we still have $\partial c/\partial t = 0$ because even though there may be a net flux of particles, the number of particles that enter dx equals the number that leaves $\mathrm{d}x$ during some time interval $\mathrm{d}t$. The only way that $\partial c/\partial t$ can be nonzero is if J is not spatially uniform. If there is a slope in J, there will be a change in c over time.

In a time interval $\mathrm{d}t$, the increase in concentration with time, $\partial c/\partial t$, will equal the excess of molecules diffusing into the region at position x over those diffusing out at position $x + \mathrm{d}x$, divided by the volume ($\mathrm{d}x$):

$$\frac{\partial c}{\partial t} = \frac{1}{\mathrm{d}x}\left[J(x) - J(x + \mathrm{d}x)\right]$$

(a) Show that $\partial c/\partial t = -\partial J/\partial x$. This is a statement of the conservation of mass. Explain why/how this equation amounts to mass conservation.[35]

Next we must deal with the particle flux $J = c(x,t)v$. What should v be? It turns out that according to *linear response theory*, systems near equilibrium have currents proportional to the first derivative (gradient) of their properties. The examples given in class are Fourier's law, $J = k(\partial T/\partial x)$ (heat flow proportional to temperature gradient), and Fick's law, $J =$

---

[35] Hint: Taylor expand $J(x + \mathrm{d}x)$. Recall from calculus that the Taylor expansion of $f(x)$ at x is the series $\sum_{i=0}^{\infty} \frac{f^{(n)}(a)}{n!}(x-a)^n$, where $f^{(n)}$ denotes the n-th derivative of f evaluated at the point a. In practice (i.e. in the physical sciences), only the lowest order terms are needed when x is close to a. In that case, we only need Taylor's theorem, $f(x) = f(a) + f'(a)(x-a) + O((x-a)^2)$, where $O((x-a)^2)$ is a term that tends to zero as $(x-a)$ goes to zero.

$-D(\partial\mu/\partial x)$ (particle flux proportional to the chemical potential gradient). Other examples include Ohm's law (electrical current proportional to the gradient of the electromagnetic potential) and in viscous fluids, where the shear rate is proportional to the shear stress.

Thus, we set $v = -\gamma(\partial\mu/\partial x)$, where γ is a coefficient of mobility. This gives $J \propto \partial\mu/\partial x$. Namely, $J = -\gamma c(x,t)\partial\mu/\partial x$.

b) Insert the ideal gas expression for μ into $J = -\gamma c(x,t)\partial\mu/\partial x$ to find $J = -\gamma k_B T \partial c/\partial x$. Then use the expression found in part (a) to arrive at a diffusion equation where $D = \gamma k_B T$. Confirm that this diffusion equation is identical to the one derived in class using Einstein's method.

(c) Consider two solutes, A and B, dissolved in solution. Write an expression to describe the diffusion of the sum of A and B and call $c_{AB}(x,t) = c_A(x,t) + c_B(x,t)$. (Hint: no work is needed here, just borrow the result you derived in the previous question.)

Solution. a) Taylor expansion of $J(x + \mathrm{d}x)$ gives

$$J(x+\mathrm{d}x) = J(x) + \mathrm{d}x\left(\frac{\partial J}{\partial x}\right) + \mathcal{O}(\mathrm{d}x^2)$$

where $\mathcal{O}(\mathrm{d}x^2)$ are terms of order equal to or higher than $\mathrm{d}x^2$. Hence, in the limit $\mathrm{d}x \to 0$:

$$\frac{\partial c}{\partial t} = \frac{1}{\mathrm{d}x}\left[\cancel{J(x)} - \cancel{J(x)} - \mathrm{d}x\left(\frac{\partial J}{\partial x}\right) + \mathcal{O}(\mathrm{d}x^2)\right] = -\frac{\partial J}{\partial x}$$

b) Inserting the expression for μ for the ideal gas, we find:

$$\begin{aligned} J = -\gamma c(x,t)\frac{\partial\mu}{\partial x} &= -\gamma c(x,t)\frac{\partial(k_B T\log(c(x,t)/c_0))}{\partial x} \\ &= -\gamma c(x,t)\frac{k_B T}{c}\frac{\partial c}{\partial x} = -\gamma k_B T\frac{\partial c}{\partial x} \end{aligned}$$

and thus the rate of change of $c(x,t)$ is given by the diffusion equation

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} = \gamma k_B T\frac{\partial^2 c}{\partial x^2}$$

where $D = \gamma k_B T$.

c) The above treatment is for ideal solutions by choice of $\mu = \mu_0 + k_B T\log(c/c_0)$. Thus, solutes A and B are non-interacting and the diffusion of the sum, $c_{AB}(x,t)$, is the sum of the parts, $c_A(x,t)$ and $c_B(x,t)$.

$$c_{AB}(x,t) = c_A(x,t) + c_B(x,t)$$

$$\frac{\partial c_{AB}}{\partial t} = \frac{\partial c_A}{\partial t} + \frac{\partial c_B}{\partial t} = \gamma_A k_B T\frac{\partial^2 c_A}{\partial x^2} + \gamma_B k_B T\frac{\partial^2 c_B}{\partial x^2}$$

■

Problem 122. For the given equation of states (a) and (b) below, find the 2$^{\text{nd}}$ virial coefficient, $B_2(T)$, by both methods (1) and (2) which are explained below. Recall that

the virial expansion is a polynomial expansion of $\frac{P}{k_BT}$ with respect to the number density $\rho = N/V$. To find $B_2(T)$, you will want to re-write the given equation of state in the proper form on the left hand side, and then do a polynomial expansion with respect to ρ on the remaining terms on the right hand side. Recall that a Taylor expansion of $f(\rho)$ at $\rho = 0$ will yield a polynomial expansion. Note: You may want to rationalize why it is a sound idea to Taylor expand $\frac{P}{k_BT}$ at $\rho = 0$. Once you have the virial expansion, you can find $B_2(T)$ by two methods.
(1) You can group terms by powers of ρ and then "select" the coefficient that goes with ρ^2.
(2) You can divide your virial expansion by ρ, subtract by one, divide by ρ again, then take the limit as $\rho \to 0$ for the remaining terms. You may recognize the term $Z = \frac{PV}{Nk_BT}$.
(a) $P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m+b)}$
(b) $P = \frac{RT}{V_m - b} + \frac{RT}{V_m}(1 - \exp(b/V_m))$

Solution. The general strategy is to write the given equation of state in the form of the virial expansion $\frac{P}{k_BT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$ and then compare orders of ρ to determine the second virial coefficient, $B_2(T)$. Alternatively, we can manipulate the expression then take the limit as $\rho \to 0$. Both methods are demonstrated below.
(a) First we rewrite the expression to isolate constants and then do Taylor expansions with respect to ρ to write the equation of state in powers of ρ.

$$\begin{aligned} P &= \frac{Nk_BT}{V}\frac{1}{1-\frac{Nb}{V}} - \frac{aN^2}{\sqrt{T}V^2N_A^2}\frac{1}{1-\frac{Nb}{VN_A}} \\ &= \rho k_BT\frac{1}{1-b\rho} - \frac{a\rho^2}{\sqrt{T}N_A^2}\frac{1}{1-\frac{b\rho}{N_A}} \end{aligned}$$

By Taylor expansion,

$$\begin{aligned} \frac{1}{1-b\rho} &= 1 + b\rho + (b\rho)^2 + \dots \\ \frac{1}{1-\frac{b\rho}{N_A}} &= 1 + \frac{b\rho}{N_A} + \Big(\frac{b\rho}{N_A}\Big)^2 + \dots \end{aligned}$$

Now utilizing the Taylor expansions and fitting to the form of the virial expansion,

$$\frac{P}{k_BT} = \rho + \rho^2\Big(b - \frac{a}{\sqrt{T}N_A^2}\Big) + \mathcal{O}(\rho^3)$$

where $\mathcal{O}(\rho^3)$ means terms of order equal to or higher than ρ^3. By method (1), clearly $B_2(T) = \Big(b - \frac{a}{\sqrt{T}N_A^2}\Big)$. Alternatively by method (2), we can manipulate the expression then take limit as $\rho \to 0$. Let $Z = \frac{P}{k_BT\rho}$.

$$Z = 1 + \rho\Big(b - \frac{a}{\sqrt{T}N_A^2}\Big) + \mathcal{O}(\rho^2)$$

$$\lim_{\rho\to 0}\frac{Z-1}{\rho}=\lim_{\rho\to 0}\Big(b-\frac{a}{\sqrt{T}N_A^2}+\mathcal{O}(\rho)\Big)=b-\frac{a}{\sqrt{T}N_A^2}=B_2(T)$$

Since $\mathcal{O}(\rho)$ depends on ρ or higher orders of ρ, it will vanish as $\rho\to 0$.

(b) We use the same strategy as in part (a)

$$P=k_BT\rho\Big(\frac{1}{1-b\rho}\Big)-k_BT\rho\big(1-\exp(b\rho/N_A)\big)$$

By Taylor expansion,

$$\frac{1}{1-b\rho}=1+b\rho+(b\rho)^2+\ldots$$

$$1-\exp(b\rho/N_A)=\frac{b\rho}{N_A}+\frac{1}{2!}\Big(\frac{b\rho}{N_A}\Big)^2+\ldots$$

Now plugging in those Taylor expansions and fitting to the form of virial expansion,

$$\frac{P}{k_BT}=\rho+\rho^2\Big(b+\frac{b}{N_A}\Big)+\mathcal{O}(\rho^3)$$

Since we have grouped terms by order of ρ it is clear that

$$B_2(T)=b+\frac{b}{N_A}$$

Alternatively,

$$Z=1+\rho\Big(b+\frac{b}{N_A}\Big)+\mathcal{O}(\rho^2)$$

$$\lim_{\rho\to 0}\frac{Z-1}{\rho}=\lim_{\rho\to 0}\Big(b+\frac{b}{N_A}+\mathcal{O}(\rho)\Big)=b+\frac{b}{N_A}=B_2(T)$$

■

Problem 123. Thermodynamic relationships can be used to accurately describe the slopes of phase diagram coexistence curves. Specifically, the Clapeyron equation can be used to characterize the discontinuous phase transition of a single material.

a) Show that at constant temperature T and pressure P, the infinitesimal change in Gibbs free energy can be written as

$$\mathrm{d}G=(\mu^{\mathrm{g}}-\mu^{\mathrm{l}})\mathrm{d}n^{\mathrm{g}}$$

Note that for a liquid-gas phase change, $\mathrm{d}n^{\mathrm{l}}=-\mathrm{d}n^{\mathrm{g}}$, the Gibbs free energy of a liquid-gas mixture is given by $G=G^l+G^g$, and the chemical potential μ can be defined as

$$\mu=\left(\frac{\partial G}{\partial n}\right)_{P,T}$$

b) Derive the Clapeyron equation (subscript t=phase transition),

$$\frac{\mathrm{d}P}{\mathrm{d}T}=\frac{\Delta_t\overline{H}}{T\Delta_t\overline{V}}$$

by taking the total derivative* of both sides of the following expression

$$\mu^\alpha(T,P) = \mu^\beta(T,P)$$

where α and β represent two states of a phase transition at equilibrium. You may find the following relationships useful, where the overline indicates the intensive molar quantity

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \left(\frac{\partial \overline{G}}{\partial P}\right)_T = \overline{V} \quad \text{and} \quad \left(\frac{\partial \mu}{\partial T}\right)_P = \left(\frac{\partial \overline{G}}{\partial T}\right)_P = -\overline{S}$$

$$\Delta_t \overline{S} = \frac{\Delta_t \overline{H}}{T}$$

*The total derivative $\mathrm{d}f$ is best explained by an example: consider a function $f(x,y)$. Its total derivative is

$$\mathrm{d}f = \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y + \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x.$$

c) How much does the melting point of benzene increase per atmosphere of pressure (within the vicinity of 1 atm)? Take $\Delta_{\text{fus}}\overline{H}$ (at 278.7 K) to be 9.95 kJ mol^{-1} and $\Delta_{\text{fus}}\overline{V}$ (at 278.7 K) to be 10.3 cm^3 mol^{-1}.

Solution. a) Take the derivative of $G = G^l + G^g$ with respect to n at constant T and P.

$$\mathrm{d}G = \left(\frac{\partial G^{\mathrm{g}}}{\partial n^{\mathrm{g}}}\right)_{P,T} \mathrm{d}n^{\mathrm{g}} + \left(\frac{\partial G^{\mathrm{l}}}{\partial n^{\mathrm{l}}}\right)_{P,T} \mathrm{d}n^{\mathrm{l}}$$

Since $\mathrm{d}n^{\mathrm{l}} = -\mathrm{d}n^{\mathrm{g}}$,

$$\mathrm{d}G = \left[\left(\frac{\partial G^{\mathrm{g}}}{\partial n^{\mathrm{g}}}\right)_{P,T} - \left(\frac{\partial G^{\mathrm{l}}}{\partial n^{\mathrm{l}}}\right)_{P,T}\right] \mathrm{d}n^{\mathrm{g}}$$

$$\mathrm{d}G = (\mu^{\mathrm{g}} - \mu^{\mathrm{l}})\mathrm{d}n^{\mathrm{g}} \qquad \text{(constant } T \text{ and } P)$$

b) Take the total derivative

$$\left(\frac{\partial \mu^\alpha}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial \mu^\alpha}{\partial T}\right)_P \mathrm{d}T = \left(\frac{\partial \mu^\beta}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial \mu^\beta}{\partial T}\right)_P \mathrm{d}T$$

Evoking the relationships

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \left(\frac{\partial \overline{G}}{\partial P}\right)_T = \overline{V} \qquad \text{and} \qquad \left(\frac{\partial \mu}{\partial T}\right)_P = \left(\frac{\partial \overline{G}}{\partial T}\right)_P = -\overline{S}$$

results in

$$\overline{V}^\alpha \mathrm{d}P - \overline{S}^\alpha \mathrm{d}T = \overline{V}^\beta \mathrm{d}P - \overline{S}^\beta \mathrm{d}T$$

Since this expression is in equilibrium, it is appropriate to evoke

$$\Delta_t \overline{S} = \frac{\Delta_t \overline{H}}{T}$$

where it follows that

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_t \overline{H}}{T\Delta_t \overline{V}}$$

c) $\dfrac{\mathrm{d}P}{\mathrm{d}T}$ evaluates to:

$$\frac{9950 \text{ J mol}^{-1}}{(278.68 \text{ K})(10.3 \text{ cm}^3 \text{ mol}^{-1})}\left(\frac{10 \text{ cm}}{1 \text{ dm}}\right)^3\left(\frac{0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}\right)$$
$$= 34.2 \text{ atm K}^{-1}$$

Taking the reciprocal

$$\frac{\mathrm{d}T}{\mathrm{d}P} = 0.0292 \text{ K atm}^{-1}$$

■

Problem 124. A chemical reaction is at equilibrium, according to its equilibrium constant, K. It is possible to estimate the equilibrium constant at temperatures other than standard conditions by using the enthalpy of reaction $\Delta H^\circ_{\text{rxn}}$ and the van't Hoff equation.

a) First, show that the expression

$$\Delta G_{\text{rxn}} = \Delta G^\circ_{\text{rxn}} + RT\log(Q)$$

follows from the definition

$$\mathrm{d}G = \sum_{\mathrm{J}} \mu_{\mathrm{J}} \mathrm{d}n_{\mathrm{J}}$$

Recall that $\mu_{\mathrm{J}} = \mu^\circ_{\mathrm{J}} + RT\log(a_{\mathrm{J}})$ where μ_{J} and a_{J} are the chemical potential and activity of species J, respectively. Furthermore, the extent of reaction ξ can be defined by the expression $\mathrm{d}n_{\mathrm{J}} = v_{\mathrm{J}}\mathrm{d}\xi$ where v_{J} is the stoichiometric number of species J.

b) Derive the van't Hoff equation

$$\frac{\mathrm{d}(\log K)}{\mathrm{d}(1/T)} = -\frac{\Delta H^\circ_{rxn}}{R}$$

by taking the derivative with respect to temperature of $\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT\log Q$ *at equilibrium standard conditions.* Use the Gibbs-Helmholtz equation

$$\frac{\mathrm{d}(\Delta G^\circ_{rxn}/T)}{\mathrm{d}T} = -\frac{\Delta H^\circ_{rxn}}{T^2}$$

in your derivation.

c) Consider the synthesis of ammonia at 298 K

$$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g) \qquad K = 6.1 \times 10^5$$

and using the van't Hoff equation, estimate the equilibrium constant at 500 K. Take $\Delta H^\circ_{rxn} = -92.2$ kJ mol^{-1} and assume it is constant over this temperature range.

Solution. a) Express the infinitesimal change in Gibbs free energy in terms of extent of reaction ξ

$$\mathrm{d}G = \sum_{\mathrm{J}} \mu_{\mathrm{J}} \mathrm{d}n_{\mathrm{J}} = \left(\sum_{\mathrm{J}} v_{\mathrm{J}} \mu_{\mathrm{J}} \right) \mathrm{d}\xi$$

It follows that

$$\Delta G_{\mathrm{rxn}} = \left(\frac{\partial G}{\partial \xi} \right)_{P,T} = \sum_{\mathrm{J}} v_{\mathrm{J}} \mu_{\mathrm{J}}$$

Substituting the chemical potential of species J

$$\Delta G_{\mathrm{rxn}} = \sum_{\mathrm{J}} v_{\mathrm{J}} \mu^\circ_{\mathrm{J}} + RT \sum_{\mathrm{J}} v_{\mathrm{J}} \log(a_{\mathrm{J}}) = \Delta G^\circ_{\mathrm{rxn}} + RT \sum_{\mathrm{J}} \log(a_{\mathrm{J}}^{v_{\mathrm{J}}})$$

where the identity $a \log x = \log x^a$ has been used. Finally, evoking the identity $\log x + \log y + ... = \log(xy \dots)$ results in

$$\Delta G_{\mathrm{rxn}} = \Delta G^\circ_{\mathrm{rxn}} + RT \prod_{\mathrm{J}} a_{\mathrm{J}}^{v_{\mathrm{J}}} = \Delta G^\circ_{\mathrm{rxn}} + RT \log(Q)$$

where

$$Q = \prod_{\mathrm{J}} a_{\mathrm{J}}^{v_{\mathrm{J}}}$$

b) Taking the derivative with respect to T of the following

$$\log K = -\frac{\Delta G^\circ_{rxn}}{RT}$$

which results in

$$\frac{\mathrm{d} \log K}{\mathrm{d}T} = -\frac{1}{R} \frac{\mathrm{d}(\Delta G^\circ_{rxn}/T)}{\mathrm{d}T}$$

Substitute the Gibbs-Helmholtz equation

$$\frac{\mathrm{d} \log K}{\mathrm{d}T} = \frac{\Delta H^\circ_{rxn}}{RT^2}$$

The required form of the van't Hoff equation can be obtained by substituting the following identity

$$\frac{\mathrm{d}(1/T)}{\mathrm{d}T} = -\frac{1}{T^2} \quad \text{so} \quad \mathrm{d}T = -T^2 \mathrm{d}(1/T)$$

c) Integrate the result of part (b) assuming constant standard enthalpy of reaction

$$\log K_2 - \log K_1 = -\frac{1}{R} \int_{1/T_1}^{1/T_2} \Delta H^\circ_{rxn} \mathrm{d}(1/T) = -\frac{\Delta H^\circ_{rxn}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log K_2 = \log(6.1 \times 10^5) - \frac{(-92.2 \times 10^3 \text{ J mol}^{-1})}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{500 \text{ K}} - \frac{1}{298 \text{ K}} \right) = -1.71$$

Thus

$$K_2 = 0.18$$

■

Problem 125. Consider the chemical equilibrium reaction under standard conditions

$$\mathrm{H_2}(g) \rightleftharpoons \mathrm{H}(g) + \mathrm{H}(g)$$

By what factor is the rate of the reverse reaction greater than that of the forward? Take the chemical potential of monatomic hydrogen gas μ_{H}° to be 203.26 kJ/mol.

Solution.

$$\Delta G_{rxn}(T,P) = \sum_{\mathrm{J}} v_{\mathrm{J}}\mu_{\mathrm{J}}$$

$$2(203.26\ \mathrm{kJ/mol}) - 1(0) = 406.52\ \mathrm{kJ/mol}$$

$$\Delta G_{rxn}^{\circ}(T,P) = -RT\log K_{\mathrm{eq}} = 406.52 \times 10^{3}\ \mathrm{kJ/mol}$$

$$K_{\mathrm{eq}} = \frac{K_+}{K_-} = 5.5 \times 10^{-72}$$

The reverse reaction occurs at a rate on the order of 10^{72} times faster (under standard conditions). ■

Problem 126. Consider the following situation: (a) Let $K = \exp\left(\frac{-\Delta G_{rxn}^{\circ}}{k_B T}\right)$. If $K_w = 10^{-14}$ at RT, will K_w be greater or less than 10^{-14} at $T = 0°\mathrm{C}$? (b) At a different temperature $K_w = 6.3 \times 10^{-13}$. Find pH of neutral water at this temperature. (c) Relate pH and pOH using the value of K_w given in the previous step.

Solution. (a) $K \propto \frac{1}{e^x}$, so it will be lower since the argument of the exponential will be larger.
(b) $K_w = [\mathrm{H^+}][\mathrm{OH^-}] = [\mathrm{H^+}]^2$
pH =-log$[\sqrt{6.3 \times 10^{-13}}] = 6.10$
(c) pH + pOH = 12.2 ■

Entropy Production, Chemical Kinetics and Irreversibility

In the context of chemical reactions we have stated that the reaction rate, $\dot{\xi}$, can be written down by inspection of the reaction mechanism (elementary reactions) as a sum of terms describing various molecular collision events times a reaction rate. We also previously stated, in the context of the Second Law, that differences in the chemical potential, $\Delta(\mu/T)$ give rise to a driving force for chemical transformations (or mass transport, if the properties are spatially inhomogeneous). The method of molecular collisions for determining $\dot{\xi}$ agrees with experiments and molecular dynamics simulations. On the other hand, $\dot{\xi}$ should also depend on $\Delta(\mu/T)$. But exactly how? An arbitrary function of $\Delta(\mu/T)$ could be expressed as a power series in $\Delta(\mu/T)$. For small deviations from equilibrium, the affinity is very low and only the first power matters. Thus, $\dot{\xi}$ should depend linearly on $\Delta(\mu/T)$ in this near-equilibrium regime.

This chapter is a very short introduction to a vast subject. To learn more about non-equilibrium phenomena in the context of thermodynamics, see [**5, 17, 18**]. Our presentation follows Chapter 14 of McQuarrie [**5**]. We use both upper and lower case letters for the state variables, with the latter referring to "per unit volume" quantities, i.e. $u \equiv U/V$ is the internal energy per unit volume.

About notation: we consider the case of two variables (time, t, and space, x) and write $\mathrm{d}/\mathrm{d}x$ for the spatial derivative, where it is understood that when differentiating we keep t constant (i.e. it means partial differentiation, $\partial/\partial x$). In several spatial dimensions, $\partial/\partial x$ is replaced by the gradient operator, ∇. (And of course, an equation that involves $\mathrm{d}/\mathrm{d}x$ and $\mathrm{d}/\mathrm{d}t$ implies that both are partial derivatives: $\partial/\partial x$ and $\partial/\partial t$, respectively.)

4.1. Entropy Production

The change in the entropy of a system, $\mathrm{d}S$, can be decomposed into two terms,

$$\mathrm{d}S = \mathrm{d}_e S + \mathrm{d}_i S,$$

where $\mathrm{d}_e S$ is the entropy *supplied to the system by its surroundings* (e, external), and $\mathrm{d}_i S$ is the entropy produced inside the system (i, internal). The second law states that $\mathrm{d}_i S = 0$ for a reversible process and positive for irreversible transformations of the system, i.e.

$$\mathrm{d}_i S \geq 0.$$

This statement is true regardless of the nature of the system (provided that the e and i contributions are correctly identified).

The term $\mathrm{d}_i S$ is called the *entropy production*, and describes the various irreversible phenomena which may occur inside the system. It will be convenient to divide S by V to get the specific entropy s, i.e. the entropy per unit volume. Division of $\mathrm{d}s$ by $\mathrm{d}t$ will be called the rate of entropy production:

$$\dot{s} = \frac{\mathrm{d}_i s}{\mathrm{d}t} = \frac{\mathrm{d}_i}{\mathrm{d}t}\frac{S}{V}.$$

Furthermore, we shall assume that the fundamental equation of thermodynamics (also known as the Gibbs equation) holds at every point in space, and even away from equilibrium:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i.$$

This equation was previously assumed to hold for a reversible process. Here, *we assume that it holds for an irreversible process as well.* This assumption may be justified in a volume element that is sufficiently small. We will write it in terms of specific quantities, $u = U/V$, $s = s/V$, $[X_i] = n_i/V$. For constant volume ($\mathrm{d}V = 0$),

$$\mathrm{d}u = T\mathrm{d}s + \sum_i \mu_i \mathrm{d}[X_i].$$

Dividing by $\mathrm{d}t$, and solving for $\mathrm{d}s/\mathrm{d}t$, we get the rate of change in the entropy:

$$\boxed{\dot{s} \equiv \frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}u}{\mathrm{d}t} - \sum_i \frac{\mu_i}{T}\frac{\mathrm{d}[X_i]}{\mathrm{d}t}.} \tag{4.1}$$

The first term is the heat transfer (can be positive or negative). The second term, which always non-negative[1] (≥ 0), is entropy production, an irreversible process. Entropy production describes the thermodynamic lost work. It quantifies irreversibility, and is therefore a measure of inefficiency. $\frac{\mathrm{d}[X_i]}{\mathrm{d}t}$ is discussed in the next section.

4.2. Chemical Reaction Away From Equilibrium

Suppose that we have a reversible first-order elementary chemical reaction

$$X \underset{k_{YX}}{\overset{k_{XY}}{\rightleftharpoons}} Y.$$

The reaction rate is:

$$\dot{\xi} = -\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{Y}]}{\mathrm{d}t} = k_{XY}[\mathrm{X}] - k_{YX}[\mathrm{Y}]. \tag{4.2}$$

Close to equilibrium, $\dot{\xi}$ should be a linear function of $\mathcal{A}$ (lowest order term in a power series in $\mathcal{A}$). Indeed, according to Eq. (4.2), $\dot{\xi}$ should be a function of $\mathcal{A}$ because it depends on the differences in concentrations of X and Y. Close to equilibrium, where $\mathcal{A}$ is small, we expect $\dot{\xi}$ to depend linearly on $\mathcal{A}$:

$$\dot{\xi} = L\left(\frac{\mathcal{A}}{T}\right) = L\left(\frac{\mu_X - \mu_Y}{T}\right), \tag{4.3}$$

where L is a coefficient to be determined.

At equilibrium, $\dot{\xi} = 0$, and we have $k_{XY}[\mathrm{X}]_{\mathrm{eq}} = k_{YX}[\mathrm{Y}]_{\mathrm{eq}}$, or $k_{XY} = k_{YX}[\mathrm{Y}]_{\mathrm{eq}}/[\mathrm{X}]_{\mathrm{eq}}$. In the first term, let's substitute this relationship for k_{XY}; in the second term, let's multiply it by $1 = [\mathrm{Y}]_{\mathrm{eq}}/[\mathrm{Y}]_{\mathrm{eq}}$:

$$\dot{\xi} = \underbrace{k_{YX} \cdot \frac{[\mathrm{Y}]_{\mathrm{eq}}}{[\mathrm{X}]_{\mathrm{eq}}}}_{k_{XY}} \cdot [\mathrm{X}] - k_{YX} \cdot [\mathrm{Y}] \cdot \underbrace{\frac{[\mathrm{Y}]_{\mathrm{eq}}}{[\mathrm{Y}]_{\mathrm{eq}}}}_{1} = k_{YX} \cdot [\mathrm{Y}]_{\mathrm{eq}} \left(\frac{[\mathrm{X}]}{[\mathrm{X}]_{\mathrm{eq}}} - \frac{[\mathrm{Y}]}{[\mathrm{Y}]_{\mathrm{eq}}}\right).$$

On the other hand, consider the affinity, $\mu_X - \mu_Y$, in the case where we have ideal solutions. Choosing the reference conditions to be the chemical equilibrium concentrations:

$$\mu_X = \mu_X^\circ + RT \log \frac{[\mathrm{X}]}{[\mathrm{X}]_{\mathrm{eq}}}, \qquad \mu_Y = \mu_Y^\circ + RT \log \frac{[\mathrm{Y}]}{[\mathrm{Y}]_{\mathrm{eq}}}.$$

Then,

$$\frac{\mu_X - \mu_Y}{T} = R\left(\log \frac{[\mathrm{X}]}{[\mathrm{X}]_{\mathrm{eq}}} - \log \frac{[\mathrm{Y}]}{[\mathrm{Y}]_{\mathrm{eq}}}\right),$$

---

[1] This term is also equal to $\dot{\xi}(-\Delta G_{rxn}/T)$. If a reaction proceeds from left to right, $\Delta G_{rxn} < 0$, and $\dot{\xi} > 0$. (And conversely, if the reaction proceeds from right to left, $\Delta G_{rxn} > 0$, $\dot{\xi} < 0$.) At equilibrium, of course, $\Delta G_{rxn} = 0$. Thus, the term can never be negative.

Adding and subtracting the same quantity is like adding zero; a given term does not change. Thus, we rewrite

$$\frac{[\mathrm{X}]}{[\mathrm{X}]_{\mathrm{eq}}} = \frac{([\mathrm{X}]-[\mathrm{X}]_{\mathrm{eq}})+[\mathrm{X}]_{\mathrm{eq}}}{[\mathrm{X}]_{\mathrm{eq}}} = \frac{[\mathrm{X}]-[\mathrm{X}]_{\mathrm{eq}}}{[\mathrm{X}]_{\mathrm{eq}}}+1,$$

and similarly for Y. The term $\frac{[\mathrm{X}]-[\mathrm{X}]_{\mathrm{eq}}}{[\mathrm{X}]_{\mathrm{eq}}}$ now is a small parameter if we are close to equilibrium. Thus, the logs are now of the form $\log(1+x)$, where x is small. Taylor expansion for small x gives $\log(1+x) \approx x$ and

$$\frac{\mu_X-\mu_Y}{T} \approx R\left(\frac{[\mathrm{X}]}{[\mathrm{X}]_{\mathrm{eq}}}-\frac{[\mathrm{Y}]}{[\mathrm{Y}]_{\mathrm{eq}}}\right).$$

Thus,

$$\dot{\xi} = k_{YX}\cdot[\mathrm{Y}]_{\mathrm{eq}}\left(\frac{[\mathrm{X}]}{[\mathrm{X}]_{\mathrm{eq}}}-\frac{[\mathrm{Y}]}{[\mathrm{Y}]_{\mathrm{eq}}}\right) = \underbrace{\frac{k_{YX}\cdot[\mathrm{Y}]_{\mathrm{eq}}}{R}}_{L}\cdot\underbrace{\left(\frac{\mu_X-\mu_Y}{T}\right)}_{\mathcal{A}/T} = L\left(\frac{\mathcal{A}}{T}\right).$$

This is an example of a flux-force term. L is the flux and $\mathcal{A}/T$ is the force. Therefore, we have established the following equivalence close to equilbrium:

$$\boxed{\dot{\xi} = -\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{Y}]}{\mathrm{d}t} = k_{XY}[\mathrm{X}]-k_{YX}[\mathrm{Y}] \approx \underbrace{\frac{k_{YX}\cdot[\mathrm{Y}]_{\mathrm{eq}}}{R}}_{L}\cdot\underbrace{\left(\frac{\mu_X-\mu_Y}{T}\right)}_{\mathcal{A}/T}.}$$

4.2.1. Entropy Production. For the previous reaction (consider the system to be isolated), at constant u the Gibbs equation is

$$\dot{s} = -\sum_i \frac{\mu_i}{T}\frac{\mathrm{d}[X_i]}{\mathrm{d}t} = -\frac{\mu_X}{T}\frac{\mathrm{d}[X]}{\mathrm{d}t}-\frac{\mu_Y}{T}\frac{\mathrm{d}[Y]}{\mathrm{d}t} = -\frac{\mathrm{d}[X]}{\mathrm{d}t}\left(\frac{\mu_X}{T}-\frac{\mu_Y}{T}\right) = \dot{\xi}\left(\frac{\mathcal{A}}{T}\right),$$

where $\mathcal{A}$ is called the *affinity*. Recall that $\mathcal{A} = -\Delta G_{rxn}$, where $\Delta G_{rxn} \equiv \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_i \nu_i\mu_i$, with the convention that ν_i is negative for reactants and positive for products. Thus, differences in chemical potential drive entropy production. Since entropy production describes the evolution of the reaction toward equilibrium, affinity is a driving force of the chemical reaction.

4.2.2. Example with Three Components. Consider the reaction:

$$X+Y \rightleftharpoons Z.$$

Let's check that the affinity is:

$$\frac{\mathcal{A}}{T} = \frac{\mu_X+\mu_Y-\mu_Z}{T}.$$

The flow of reaction from left to right is:

$$\dot{\xi} = -\frac{\mathrm{d}[X]}{\mathrm{d}t} = -\frac{\mathrm{d}[Y]}{\mathrm{d}t} = +\frac{\mathrm{d}[Z]}{\mathrm{d}t}$$

so the equation for $\dot{s}$ is

$$\dot{s} = -\frac{\mu_X}{T}\frac{\mathrm{d}[X]}{\mathrm{d}t} - \frac{\mu_Y}{T}\frac{\mathrm{d}[Y]}{\mathrm{d}t} - \frac{\mu_Z}{T}\frac{\mathrm{d}[Z]}{\mathrm{d}t} = -\frac{\mathrm{d}[X]}{\mathrm{d}t}\left(\frac{\mu_X}{T} + \frac{\mu_Y}{T} - \frac{\mu_Z}{T}\right) = \dot{\xi}\left(\frac{\mathcal{A}}{T}\right),$$

where $\mathcal{A}/T = \left(\frac{\mu_X}{T} + \frac{\mu_Y}{T} - \frac{\mu_Z}{T}\right)$.

4.3. External vs Internal Variables

As mentioned previously, the change in the entropy of a system, $\mathrm{d}S$, can be decomposed into two terms,

$$\mathrm{d}S = \mathrm{d}_e S + \mathrm{d}_i S,$$

where $\mathrm{d}_e S$ is the entropy *supplied to the system by its surroundings* (e=external), and $\mathrm{d}_i S$ is the entropy produced inside the system (i=internal). The second law states that $\mathrm{d}_i S = 0$ for a reversible process and positive for irreversible transformations of the system, i.e.

$$\mathrm{d}_i S \geq 0.$$

The entropy supplied, $\mathrm{d}_e S$, however, may be positive, zero or negative, depending on the interaction of the system with its surroundings. Thus, for an adiabatically insulated system (i.e. a system which can exchange neither heat nor matter with its surroundings), $\mathrm{d}_e S$ is equal to zero, and it follows that

$$\boxed{\mathrm{d}S \geq 0.} \quad \text{(for an adiabatically insulated system)}$$

For a so-called **closed system**, which may only exchange heat with its surroundings, we have

$$\mathrm{d}_e S = \frac{\delta Q}{T}, \qquad \text{(Carnot's theorem)}$$

where δQ is the heat supplied to the system by its surroundings and T is the absolute temperature at which heat is received by the system. It then follows that

$$\mathrm{d}S = \mathrm{d}_e S + \mathrm{d}_i S = \frac{\delta Q}{T} + \underbrace{\mathrm{d}_i S}_{\mathrm{d}_i S \geq 0} \quad \rightarrow \quad \boxed{\mathrm{d}S \geq \frac{\delta Q}{T}} \text{ (for a closed system)}$$

For open systems (heat+matter exchange allowed w/surroundings), $\mathrm{d}_e S$ contains also a term connected with the transfer of matter. The theorem of Carnot-Clausius, $\mathrm{d}_e S = \delta Q/T$, does not apply to such systems (we will see later how to correct it). However, $\mathrm{d}S = \mathrm{d}_e S + \mathrm{d}_i S$ and $\mathrm{d}_i S \geq 0$ remain valid.

4.3.1. General Form of Entropy Production. Previously, we used the first law (fundamental equation for dS) to write down an equation for the time-derivative of the entropy:

$$\dot{s} \equiv \frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}u}{\mathrm{d}t} - \sum_i \frac{\mu_i}{T}\frac{\mathrm{d}[X_i]}{\mathrm{d}t}.$$

The first term, $\frac{1}{T}\frac{\mathrm{d}u}{\mathrm{d}t}$, is associated with heat transfer (can be positive or negative). The last term can be rewritten as $\dot{\xi}(\mathcal{A}/T)$ or $\dot{\xi}(-\Delta G_{rxn}/T)$, using $\dot{\xi} = \frac{1}{\nu_i}\frac{\mathrm{d}[X_i]}{\mathrm{d}t}$, since $\mathcal{A} = -\sum_i \mu_i\nu_i$ and $\mathcal{A} = -\Delta G_{rxn}$. This term is also equal to $\dot{\xi}(-\Delta G_{rxn}/T)$. If a reaction proceeds from left to right, $\Delta G_{rxn} < 0$, and $\dot{\xi} > 0$. And conversely, if the reaction proceeds from right to left, $\Delta G_{rxn} > 0$, $\dot{\xi} < 0$. At equilibrium, $\Delta G_{rxn} = 0$. Thus, the term can never be negative. This nonnegative (≥ 0) term, is called entropy production, and describes an irreversible process. We obtain a restatement of the Clausius theorem,

$$\dot{s} \geq \frac{1}{T}\frac{\mathrm{d}u}{\mathrm{d}t}.$$

We have seen in the specific case of a reaction $X \rightleftharpoons Y$ that the reaction term is equal to[2]

$$\dot{\xi}(\mathcal{A}/T) = -\frac{\mathrm{d}[X]}{\mathrm{d}t}\left(\frac{\mu_X - \mu_Y}{T}\right).$$

We have also found that for that particular reaction ($X \rightleftharpoons Y$),

$$\dot{\xi} = \frac{k_{YX}[Y]_{\mathrm{eq}}}{R}\left(\frac{\mu_X - \mu_Y}{T}\right) = L\left(\frac{\mathcal{A}}{T}\right)$$

where $L = k_{YX}[Y]_{\mathrm{eq}}/R = k_{XY}[X]_{\mathrm{eq}}/R$. Thus, $\dot{s}$ has the form

$$\dot{s} = L\left(\frac{\mathcal{A}}{T}\right)\left(\frac{\mathcal{A}}{T}\right) = LXX,$$

where $X = \left(\frac{\mathcal{A}}{T}\right)$ is a *force*. LX is a *flux*. The flux, often denoted $J = LX$, is proportional to the force (no forces, no fluxes).

This turns out to be a general principle. In the general case there may be several forces (and fluxes) acting on the system. Then, $\dot{s}$ will be of the form:

$$\boxed{\dot{s} = \sum_{i=1}^{N}\sum_{j=1}^{N} L_{ij}X_iX_j,}$$

where the L_{ij} are called *Onsager coefficients* and the X_i's are the thermodynamic forces. The quantities

$$J_j = L_{1j}X_1 + L_{2j}X_2 + L_{3j}X_3 + \cdots + L_{Nj}X_N$$

---

[2] The form $\dot{\xi}(\mathcal{A}/T)$ of the chemical term is generally true for any reaction. $\mathcal{A}/T$ is a *driving force* for the chemical reaction (i.e. differences in chemical potential lead to transformation, whereas equilibrium is reached when the chemical potentials are equal). $\dot{\xi}$ is a *flux*.

are called *fluxes*. We can think of the fluxes as the leading terms of a Taylor expansion of J_j as a power series in $X_1, X_2, \ldots, X_N$. Close to equilibrium, only the first order term is needed. Also, there are no constant terms because the fluxes all vanish if all the forces vanish. The Onsager coefficients are reciprocal, $L_{ij} = L_{ji}$.

Some examples of commonly encountered fluxes and forces can be found in Table 4.1.

Table 4.1. Fluxes and forces.

	Flux, J	Force, X
Heat	J_u	$\frac{\mathrm{d}(1/T)}{\mathrm{d}x} = -\frac{1}{T^2}\frac{\mathrm{d}T}{\mathrm{d}x}$
Matter	J_i	$-T\frac{\mathrm{d}(\mu_i/T)}{\mathrm{d}x}$
Electric current density	$J_I = I/A$	$-\frac{1}{T}\frac{\mathrm{d}\phi}{\mathrm{d}x}$ (voltage/T)
Chemical reaction	$\dot{\xi}$	$\mathcal{A} = -\sum_i \nu_i\mu_i$

4.4. Particle Flux and Heat Flux

So far we have looked at chemical reactions localized in the same volume element. These chemical reactions are driven by differences in the chemical potential. Now let's look at spatially dependent processes. For simplicity, we consider at processes that vary along a single dimension (x). The system is subdivided into slices of thickness $\Delta x = x_2 - x_1$, as shown in Fig. 4.1.

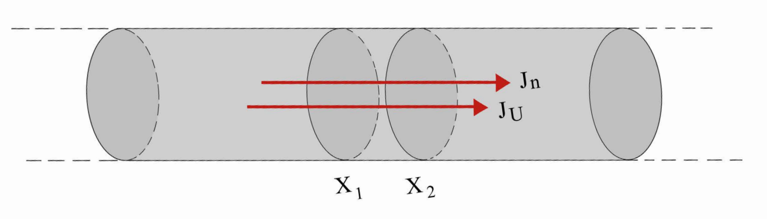


Figure 4.1. Flux of heat (J_U) and particles (J_n).

Δx is small enough so that T, P, μ are constant over the volume element and so that local thermodynamic equilibrium can be assumed.

Recall (see section 3.10.19) that in the case of two volume elements A and B adjacent to each other (setting $\mathrm{d}V = 0$), we found that

$$\mathrm{d}S = (T_A^{-1} - T_B^{-1})\mathrm{d}U_A - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right)\mathrm{d}n_A,$$

where $\mu_{A/B}$ are in molar units. (This equation was obtained by applying the fundamental equation of thermodynamics in the entropy representation.)

Now take A and B to be thin slices centered around x_1 and x_2 in the above diagram. Dividing by $\mathrm{d}t$ gives the equation for entropy production:

$$\dot{S} = \frac{\mathrm{d}U_1}{\mathrm{d}t}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{\mathrm{d}n_1}{\mathrm{d}t}\left(\frac{\mu_2}{T_2} - \frac{\mu_1}{T_1}\right) \geq 0.$$

which can be written in the form,

$$\dot{S} = J_U X_U + J_n X_n,$$

where

$$J_U = \frac{\mathrm{d}U_1}{\mathrm{d}t} = -\frac{\mathrm{d}U_2}{\mathrm{d}t},\ J_n = \frac{\mathrm{d}n_1}{\mathrm{d}t} = -\frac{\mathrm{d}n_2}{\mathrm{d}t},\ X_U = \frac{1}{T_1} - \frac{1}{T_2},\ X_n = \frac{\mu_2}{T_2} - \frac{\mu_1}{T_1}.$$

X_U is the thermal force and X_n is the chemical force.

Writing $\Delta(1/T) = 1/T_2 - 1/T_1$, $\Delta(\mu/T) = \mu_2/T_2 - \mu_1/T_1$, and dividing by the volume $V = A\Delta x$ gives:

$$\dot{s} = -\frac{1}{A}\frac{\mathrm{d}U_1}{\mathrm{d}t}\frac{\Delta(1/T)}{\Delta x} + \frac{1}{A}\frac{\mathrm{d}n_1}{\mathrm{d}t}\frac{\Delta(\mu/T)}{\Delta x}.$$

Taking the limit of small Δx gives:

$$\dot{s} = -\frac{1}{A}\frac{\mathrm{d}U_1}{\mathrm{d}t}\frac{\mathrm{d}(1/T)}{\mathrm{d}x} - \frac{1}{A}\frac{\mathrm{d}n_1}{\mathrm{d}t}\frac{\mathrm{d}(-\mu/T)}{\mathrm{d}x},$$

which can be written as

$$\dot{s} = J_U\frac{\mathrm{d}(1/T)}{\mathrm{d}x} + J_n\frac{\mathrm{d}(-\mu/T)}{\mathrm{d}x}, \tag{4.4}$$

where the derivatives are called gradients of $1/T$ and $-\mu/T$, respectively, and

$$J_U = -\frac{1}{A}\frac{\mathrm{d}U_1}{\mathrm{d}t}, \quad J_n = -\frac{1}{A}\frac{\mathrm{d}n_1}{\mathrm{d}t}$$

are fluxes.

4.5. Conservation of Mass

In the case of diffusion and reaction taking place simultaneously, the flow of the reaction from reactant to product is:

$$\boxed{\underbrace{\frac{\mathrm{d}_{tot}[X_j]}{\mathrm{d}t}}_{\text{total rate}} \quad = \quad \underbrace{-\frac{\mathrm{d}J_j}{\mathrm{d}x}}_{\text{mass transport}} \quad + \quad \underbrace{\nu_j\dot{\xi},}_{\dot{\xi}=\frac{1}{\nu_j}\frac{\mathrm{d}[X_j]}{\mathrm{d}t}} \qquad j = 1,\ldots,n}$$

where $[X_j] = n_j/V$, J_j are the component fluxes (n: number of components), all directed along the x axis, i.e. ν_j are the stoichiometric constants in a chemical reaction, and $\dot{\xi}$ is its rate in the volume element. This is merely the addition of two terms: the component flux term $-\mathrm{d}J_j/\mathrm{d}x$ due to mass transport, plus the chemical reaction term which we know from chemical kinetics, by writing down the rate law, $\dot{\xi} = (1/\nu_j)\mathrm{d}[X_j]/\mathrm{d}t$, for the reaction.

Our convention was to take ν_j as negative for the reactants and positive for the products. Since ν_j are dimensionless, $\dot{\xi}$ has units of mol/m^3/s.

This is the total rate of change, which is the sum of two terms. The second term ($\dot{\xi}$) we have seen already. But where does the first term come from?

Consider a volume $V = A{\cdot}\mathrm{d}x$ of length $\mathrm{d}x$ and transport along the x direction. The volume has cross-sectional area A and length beginning at x and ending at x+$\mathrm{d}x$. The change in the number of moles of a component, n_j, in a small volume V, is due to the difference between the flux of the components in and out of the volume. We have

$$\frac{\mathrm{d}n_j}{\mathrm{d}t} = -A\left[J_j(x+\mathrm{d}x) - J_j(x)\right]$$

where A is the cross sectional area of the volume orthogonal to the flux direction. Positive fluxes J_j indicate particles flowing toward positive x. The flux $-J_j(x+\mathrm{d}x)$ denotes a *decrease* in n_j, as particles leave the volume $\mathrm{d}x$ at x+$\mathrm{d}x$. $+J_j(x)$ denotes particles entering $\mathrm{d}x$ at x.

The fluxes have units of moles per area per unit time. The area is equal to the volume divided by $\mathrm{d}x$. In the limit of small $\mathrm{d}x$, we therefore have

$$\frac{\mathrm{d}n_j}{\mathrm{d}t} = -V\frac{\left[J_j(x+\mathrm{d}x) - J_j(x)\right]}{\mathrm{d}x} = -V\frac{\mathrm{d}J_j(x)}{\mathrm{d}x}.$$

By dividing this equation left and right by the (constant) volume, one obtains the desired result for $\dot{\xi} = 0$

$$\boxed{\frac{\mathrm{d}[X_j]}{\mathrm{d}t} = -\frac{\mathrm{d}J_j(x)}{\mathrm{d}x}}$$

where $[X_j] = n_j/V$. This equation describes the conservation of moles (mass) within the volume.

The total rate of change, $\mathrm{d}_{tot}[X_j]/\mathrm{d}t$, is then formed by adding this mass transport term, $-\frac{\mathrm{d}J_j}{\mathrm{d}x}$, to the chemical reaction term, $\nu_j\dot{\xi}$.

The mass transport term, $-\frac{\mathrm{d}J_j}{\mathrm{d}x}$, is called a *surface term* because it describes particle flux entering and leaving the volume element (by crossing its surface). The chemical reaction term, $\nu_j\dot{\xi}$ is called a *volume term* because the chemical reaction takes place everywhere inside the volume (with zero influence from the surroundings).

4.6. Conservation of Energy

Similarly, we have a conservation law

$$\boxed{\frac{\mathrm{d}u}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}x}J_u.}$$

Here $u = U/V$ is the internal energy density, J_u is the energy flux (e.g. heat flow). Here, there is no "volume term" because energy is not created within the volume unless a "heat source” is added. This equation expresses the fact that energy can only be transferred, never created.

On the other hand, if there is a “heat source” is placed within the volume, then a volumetric term is added:

$$\frac{\mathrm{d}u}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}x}J_u + \dot{q}_V,$$

where $\dot{q}_V$ is a volumetric heat source (units: W/m^3).

4.7. Entropy Balance

The entropy balance equation is

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -A\left[J_s(x+\mathrm{d}x) - J_s(x)\right] + V\sigma$$

where σ is the entropy production per unit volume. Since $A = V/\mathrm{d}x$, we have, in the limit of small $\mathrm{d}x$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -V\frac{[J_s(x+\mathrm{d}x) - J_s(x)]}{\mathrm{d}x} + V\sigma = -V\frac{\mathrm{d}J_s(x)}{\mathrm{d}x} + V\sigma.$$

Dividing by volume V:

$$\boxed{\frac{\mathrm{d}s}{\mathrm{d}t} = -\frac{\mathrm{d}J_s(x)}{\mathrm{d}x} + \sigma.} \tag{4.5}$$

Substituting $\frac{\mathrm{d}[X_j]}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}x}J_j + \nu_j\dot{\xi}$ and $\frac{\mathrm{d}u}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}x}J_u$ into

$$\dot{s} \equiv \frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}u}{\mathrm{d}t} - \sum_i \frac{\mu_i}{T}\frac{\mathrm{d}[X_i]}{\mathrm{d}t},$$

and comparison with Eq. (4.5) enables us to identify J_s and σ:

$$\begin{aligned}\frac{\mathrm{d}s}{\mathrm{d}t} =& \frac{1}{T}\frac{\mathrm{d}u}{\mathrm{d}t} - \frac{1}{T}\sum_j \mu_j\frac{\mathrm{d}[X_j]}{\mathrm{d}t} = \frac{1}{T}\left(-\frac{\mathrm{d}J_u}{\mathrm{d}x}\right) - \frac{1}{T}\sum_j \mu_j\left(-\frac{\mathrm{d}}{\mathrm{d}x}J_j + \nu_j\dot{\xi}\right)\\ =& -\frac{\mathrm{d}}{\mathrm{d}x}\underbrace{\left[\frac{1}{T}\left(J_u - \sum_{j=1}^{n}\mu_j J_j\right)\right]}_{\text{entropy flux, } J_s} + \underbrace{J_u\frac{\mathrm{d}}{\mathrm{d}x}(\frac{1}{T}) + \sum_{j=1}^{n} J_j\frac{\mathrm{d}}{\mathrm{d}x}(-\frac{\mu_j}{T}) + \dot{\xi}\left(-\frac{\Delta G_{rxn}}{T}\right)}_{\text{entropy production rate, } \sigma}\end{aligned}$$

where $\Delta G_{rxn} = \sum_i \nu_i\mu_i$, with the convention that ν_i is negative for reactants and positive for products. In the second line we have twice used the product rule for differentiation: $\mathrm{d}(fg)/\mathrm{d}x = f\cdot\mathrm{d}g/\mathrm{d}x + g\cdot\mathrm{d}f/\mathrm{d}x$.

The surface term, -$\mathrm{d}J_s/\mathrm{d}x$, is given in terms of the entropy flux,

$$J_s = \left[\frac{1}{T}\left(J_u - \sum_{j=1}^{n}\mu_j J_j\right)\right].$$

It describes two phenomena: the measurable heat flux ("reduced" heat flow J_u/T) and the enthalpy of matter transfer (heating due to flows of matter). The enthalpy flux is carried by the component fluxes, J_j. The entropy flux term is a "surface term" which describes changes in entropy of the system due to inputs from the surroundings.

The volume term, which is also called "entropy production",

$$\sigma = \underbrace{J_u \frac{\mathrm{d}}{\mathrm{d}x}(\frac{1}{T})}_{\text{heat conduction}} \underbrace{+\sum_{j=1}^{n} J_j \frac{\mathrm{d}}{\mathrm{d}x}(-\frac{\mu_j}{T})}_{\text{mass diffusion}} + \underbrace{\dot{\xi}\left(-\frac{\Delta G_{rxn}}{T}\right)}_{\text{chemical reaction}}$$

has 3 contributions. The first term arises from heat conduction (temperature gradients), since $\mathrm{d}(1/T)/\mathrm{d}x$=(-$1/T^2$)$\mathrm{d}T/\mathrm{d}x$. The second term is connected to diffusion, which is driven by gradients in the chemical potential; here, $(\mathrm{d}/\mathrm{d}x)(\mu_j/T)$. The third term is due to chemical reactions.

The entropy flux term describes external contributions from the surroundings. It can be positive, negative or zero. This is the d_eS term. The entropy production term is non-negative, $\sigma \geq 0$. Entropy production is the d_iS term.

4.8. Entropy Production vs External Entropy Flow

We recall that $\mathrm{d}S \geq 0$ for an isolated system S. If the system is not isolated, we have the decomposition $\mathrm{d}S = \mathrm{d}_eS + \mathrm{d}_iS$. Some books write $\mathrm{d}S_{exch}$ in lieu of d_eS and $\mathrm{d}S_{prod} = \mathrm{d}_iS$. Thus, $\mathrm{d}S$ consists of two parts. One part is the entropy created in the system by any spontaneous processes occurring within it, and the other part is the change in entropy resulting from the exchange of energy as heat between the system and its surroundings. We *always* have $\mathrm{d}_iS \geq 0$. d_eS can be positive, zero or negative. This quantity is given by $\mathrm{d}_eS = \delta Q/T$, where T is the *temperature of the surroundings.* If the exchange is carried out reversibly, $\delta Q = \delta Q^{rev}$; if it is irreversible, $\delta Q = \delta Q^{irr}$. For any process (reversible or irreversible),

$$\mathrm{d}S = \mathrm{d}_iS + \mathrm{d}_eS = \mathrm{d}_iS + \frac{\delta Q}{T}.$$

For a reversible process, d_iS=0 and $\delta Q = \delta Q^{rev}$, so that we have $\mathrm{d}S = (\delta Q^{rev}/T)$. For an irreversible process, $\mathrm{d}_i > 0$ and $\delta Q = \delta Q^{irr}$, so that $\mathrm{d}S > (\delta Q^{irr}/T)$. Combining these two relations together we obtain the Clausius statement of the second law, $\mathrm{d}S \geq (\delta Q/T)$.

4.8.1. Fluxes Depend Linearly on Forces. Consider two systems, 1 and 2 in contact with teach other. Particles and heat can be exchanged between them. The two combined systems are isolated from their surroundings, thus explaining the term d_eS=0. We are left with the entropy production, d_iS, as the only contribution to the entropy:[3]

$$\frac{\mathrm{d}_iS}{\mathrm{d}t}=\frac{\mathrm{d}U_1}{\mathrm{d}t}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)+\frac{\mathrm{d}n_1}{\mathrm{d}t}\left(\frac{\mu_2}{T_2}-\frac{\mu_1}{T_1}\right)=J_UX_U+J_nX_n\geq 0.$$

where $X_U=1/T_1-1/T_2$, $X_n=\mu_2/T_2-\mu_1/T_1$, $J_U=\mathrm{d}U_1/\mathrm{d}t=-\mathrm{d}U_2/\mathrm{d}t$ and $J_n=\mathrm{d}n_1/\mathrm{d}t=-\mathrm{d}n_2/\mathrm{d}t$. The fluxes and forces are related to each other. Experimentally, the relation is often linear. For example, Fourier's law of heat conduction says that the flux of energy as heat is directly proportional to the temperature difference,

$$J_U\propto T_2-T_1.$$

But $T_2-T_1\propto(T_2-T_1)/T_1T_2=1/T_1-1/T_2=X_U$, so we write $J_U\propto 1/T_1-1/T_2=X_U$. Similarly, Fick's law of (isothermal) diffusion says that the flux of matter is directly proportional to the concentration difference,

$$J_n\propto c_2-c_1$$

which can be expressed[4] in the form $J_n\propto\mu_2-\mu_1$ (constant T). Finally, we have Ohm's law, $V=RI$, which states that the electrical current, I, is proportional to the potential difference, $V=\phi_2-\phi_2$. Thus, in all cases, $J\propto X_i$ (fluxes linearly depend on the forces).

4.8.2. From Discrete to Continuous Case. In the continuum case, it is gradients of thermodynamic quantities that determine the forces (not differences). We have seen that $\frac{\mathrm{d}_iS}{\mathrm{d}t}=\frac{\mathrm{d}U_1}{\mathrm{d}t}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)+\frac{\mathrm{d}n_1}{\mathrm{d}t}\left(\frac{\mu_2}{T_2}-\frac{\mu_1}{T_1}\right)\geq 0$. We take the continuum limit by dividing by $V=A\cdot\Delta x$ and taking the limit $\Delta x\to 0$:

$$\sigma\equiv\frac{1}{V}\frac{\mathrm{d}_iS}{\mathrm{d}t}=\left(-\frac{1}{A}\frac{\mathrm{d}U_1}{\mathrm{d}t}\right)\frac{\Delta(1/T)}{\Delta x}+\frac{1}{A}\left(\frac{\mathrm{d}n_1}{\mathrm{d}t}\right)\frac{\Delta(\mu/T)}{\Delta x},$$

where $\Delta(1/T)=1/T_2-1/T_1$, $\Delta(\mu/T)=\mu_2/T_2-\mu_1/T_1$. Thus,

$$\boxed{\sigma=J_U\frac{\mathrm{d}(1/T)}{\mathrm{d}x}+J_n\frac{\mathrm{d}(-\mu/T)}{\mathrm{d}x}\geq 0,}$$

where $J_U=-\frac{1}{A}\frac{\mathrm{d}U_1}{\mathrm{d}t}$ and $J_n=-\frac{1}{A}\frac{\mathrm{d}n_1}{\mathrm{d}t}$.

4.8.3. Application to Isothermal Diffusion. As an example of the application to continuous systems, we will consider diffusion in an isothermal system (isothermal diffusion). Let T be constant, so it can be factored out of each term. The entropy production is:

$$\sigma=\frac{1}{T}\sum_{i=1}^{n}J_i\left(-\frac{\mathrm{d}\mu_i}{\mathrm{d}x}\right)_{P,T},$$

---

[3] The right hand side was explained previously. It is obtained from the fundamental equation in the entropy representation.

[4] The proof is similar to our previous discussion. c_1 and c_2 are different concentrations of the *same substance*. Write $\mu_1=\mu^\circ+RT\log(c_1/c^\circ)$ and $\mu_2=\mu^\circ+RT\log(c_2/c^\circ)$, so that $\mu_2-\mu_1=RT\,(\log c_2/c^\circ-\log c_1/c^\circ)$. Write $c_2/c^\circ=[(c_2-c^\circ)+c^\circ]/c^\circ=(c_2-c^\circ)/c^\circ+1$ and similarly for c_1, and Taylor expand in the small parameter $(c_2-c^\circ)/c^\circ$. Then, $\mu_2-\mu_1\approx\frac{RT}{c^\circ}(c_2-c_1)$.

where n is the number of components in the system. The chemical potentials are not all independent of each other because of the Gibbs-Duhem equation ($\sum_i n_i \mathrm{d}\mu_i + S\mathrm{d}T - V\mathrm{d}P = 0$), which for constant T, P reads, $\sum_{i=1}^n n_i \mathrm{d}\mu_i = 0$. Dividing by V and $\mathrm{d}x$ gives, $\sum_{i=1}^n c_i \left(-\frac{\mathrm{d}\mu_i}{\mathrm{d}x}\right) = 0$. Solving for $\mathrm{d}\mu_1/\mathrm{d}x$,

$$\frac{\mathrm{d}\mu_1}{\mathrm{d}x} = -\frac{1}{c_1}\sum_{i=2}^n c_i \left(\frac{\mathrm{d}\mu_i}{\mathrm{d}x}\right)_{P,T}.$$

Then,

$$\begin{aligned} T\sigma =& J_1\left(-\frac{\mathrm{d}\mu_1}{\mathrm{d}x}\right) + \sum_{i=2}^n J_i\left(-\frac{\mathrm{d}\mu_i}{\mathrm{d}x}\right) = \frac{J_1}{c_1}\sum_{i=2}^n c_i\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}x}\right) + \sum_{i=2}^n J_i\left(-\frac{\mathrm{d}\mu_i}{\mathrm{d}x}\right) \\ =& \sum_{i=2}^n \underbrace{\left(J_i - \frac{c_i}{c_1}J_1\right)}_{J_i^d}\left(-\frac{\mathrm{d}\mu_i}{\mathrm{d}x}\right), \end{aligned}$$

where $J_i^d = \left(J_i - \frac{c_i}{c_1}J_1\right) = c_i\left(\frac{J_i}{c_i} - \frac{J_1}{c_1}\right) = c(v_i - v_1)$, since particle flux equals concentration times velocity ($J_i = c_i v_i$). (If $v_i = v_1$, then entropy production is zero.) Thus, J_i^d is the flux of solute i relative to solvent (1).

4.8.4. Example of Binary Solution. Let's consider a binary solution, such as sucrose in water or sodium chloride in water. In such cases, there is only 1 independent flow:

$$T\sigma = J_2^d\left(-\frac{\mathrm{d}\mu_2}{\mathrm{d}x}\right)_{T,P}.$$

The force is $X = \frac{\mathrm{d}\mu_2}{\mathrm{d}x}$. There is just one flux force equation $J = LX$:

$$J_2^d = L_{22}\left(-\frac{\mathrm{d}\mu_2}{\mathrm{d}x}\right)_{T,P} = -L_{22}\left(-\frac{\mathrm{d}\mu_2}{\mathrm{d}x}\right).$$

Using $\mu_2 = \mu_2^\circ(T,P) + RT\log c_2$ (c_2 in units of mol/L). Then,

$$\frac{\mathrm{d}\mu_2}{\mathrm{d}x} = \frac{\mathrm{d}\mu_2}{\mathrm{d}c_2}\cdot\frac{\mathrm{d}c_2}{\mathrm{d}x} = \frac{RT}{c_2}\left(\frac{\mathrm{d}c_2}{\mathrm{d}x}\right). \qquad \text{(chain rule)}$$

So that

$$\boxed{J_2^d = -L_{22}\frac{RT}{c_2}\frac{\mathrm{d}c_2}{\mathrm{d}x}.}$$

We get Fick's law of diffusion, which gives the concentration flux as $J_c = -D\frac{\mathrm{d}c}{\mathrm{d}x}$, where $D = L_{22}RT/c$.

From the conservation of mass,

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -\tfrac{\mathrm{d}}{\mathrm{d}x}J_c,$$

where J_c is the concentration flux (particle flux, J_n, divided by V), substitution of $J_c = -D\frac{\mathrm{d}c}{\mathrm{d}x}$ gives the diffusion equation

$$\boxed{\frac{\mathrm{d}c}{\mathrm{d}t} = D\frac{\mathrm{d}^2 c}{\mathrm{d}x^2},}$$

which we derived in Section **??** using Einstein's method.

4.9. Diffusion Leads to Entropy Production

Diffusion is an irreversible process. This is obvious from experiments: releasing a gas in the corner of the room leads to its spreading across the room until the concentration is uniform. The gas will never return to its original position. This can be seen also from the diffusion equation, which is not time-reversal invariant: the transformation $t \to -t$ leads to a sign change. That diffusion leads to entropy production can be seen by computing the flow of entropy.

Recall from Section **??** that the solution to the diffusion equation for initial conditions, $c(x, 0) = n\delta(x)$, is:

$$c(x,t) = \frac{n}{\sqrt{4\pi D t}} e^{-x/4Dt}.$$

4.9.1. Entropy Production and the Gibbs-Shannon Entropy. It can be shown that Boltzmann entropy, $S = k_B \log \Omega$ is a special case of the more general Gibbs-Shannon entropy: for a discrete probability distribution p on the countable set $\{x_1, x_2, \dots\}$, with $p_i = p(x_i)$, the Gibbs-Shannon entropy is defined as

$$S = -k_B \sum_{i \geq 1} p_i \log p_i.$$

Indeed, taking $p_i = 1/\Omega$ (the uniform distribution, $\sum_{i=1}^{\Omega} \frac{1}{\Omega} = 1$), we get:

$$S = k_B \sum_{i=1}^{\Omega} \frac{1}{\Omega} \log \Omega = k_B \log \Omega.$$

For a continuous probability density function $p(x)$, the Shannon entropy is

$$S = -k_B \int_{\mathbb{R}} p(x) \log p(x) \mathrm{d}x.$$

The entropy of the Gaussian density is seen to be:

$$S = -k_B \int_{\mathbb{R}} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2} \left(-\log(\sqrt{2\pi\sigma^2}) - \frac{x^2}{2\sigma^2} \right) \mathrm{d}x = \frac{k_B}{2}(1 + \log(2\pi\sigma^2))$$

where $\sigma^2 = 2Dt$ for the solution to the diffusion equation. Differentiation of S with respect to t gives:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\frac{k_B}{2}(1 + \log(4\pi D t)) = \frac{k_B}{2}\frac{1}{4\pi D t} \cdot 4\pi D = \frac{k_B}{2t} > 0,$$

which is positive for all times $t > 0$, meaning that diffusion leads to entropy production. Note that $\mathrm{d}S/\mathrm{d}t$ decreases with time as the steady state is approached, eventually reaching 0 asymptotically.

Now, a slightly more general proof. We can still show that $\mathrm{d}S/\mathrm{d}t > 0$ without assuming a Gaussian distribution, but instead only invoking the form of the diffusion equation (and not its solution). Take the time derivative of S, then substitute the right hand side of the diffusion equation, $\frac{\mathrm{d}\rho}{\mathrm{d}t} = D\frac{\mathrm{d}^2\rho}{\mathrm{d}x^2}$, for each instance of $\mathrm{d}\rho/\mathrm{d}t$:

$$\begin{aligned}\frac{\mathrm{d}S}{\mathrm{d}t} =& - k_B \int \left[\frac{\mathrm{d}\rho}{\mathrm{d}t}\log\rho(x) + \rho(x)\frac{1}{\rho(x)}\frac{\mathrm{d}\rho}{\mathrm{d}t}\right]\mathrm{d}x \\ =& - k_B D \int \left[\frac{\mathrm{d}^2\rho}{\mathrm{d}x^2}\log\rho(x) + \frac{\mathrm{d}^2\rho}{\mathrm{d}x^2}\right]\mathrm{d}x.\end{aligned}$$

Integration by parts eliminates the second term. Integration by parts of the first term leads to:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -k_B D \int \frac{\mathrm{d}\rho}{\mathrm{d}x}(-1)\frac{1}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}x}\mathrm{d}x,$$

which is a non-negative quantity:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = k_B D \int \left(\frac{\mathrm{d}\rho}{\mathrm{d}x}\right)^2 \frac{1}{\rho}\mathrm{d}x \geq 0,$$

because the integrand is the product of two positive quantities: $(\mathrm{d}\rho/\mathrm{d}x)^2 \geq 0$ and $\rho^{-1} > 0$.

4.10. Heat Conduction Leads to Entropy Production

We have seen that the heat conduction term

$$\sigma = J_u \frac{\mathrm{d}}{\mathrm{d}x}(\frac{1}{T}) = -J_u \cdot \frac{1}{T^2}\frac{\mathrm{d}T}{\mathrm{d}x}$$

leads to entropy production. From this equation, we see that the force $X = \frac{\mathrm{d}T}{\mathrm{d}x}$. There is a flux-force relation, $J = LX$, of the form:

$$J_u = -L_{qq}\frac{\mathrm{d}T}{\mathrm{d}x}.$$

where L_{qq} is a "constant" (Onsager coefficient; the subscript $_{qq}$ refers to heat), which we will call α in a moment. Starting from the equation for energy conservation (with no heat source term),

$$\frac{\mathrm{d}u}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}x}J_u.$$

Inserting the flux-force relation, invoking $\mathrm{d}u = \mathrm{d}(U/V) = \delta Q/V$ ($\mathrm{d}V = 0$, so no work, change in internal energy is due to heat transfer) and $(\delta Q/V) = \rho c_V\,\mathrm{d}T$ (ρ: density, c_V: specific heat capacity, $C/\rho V$), we obtain the famous Fourier's heat conduction equation

$$\boxed{\frac{\mathrm{d}T}{\mathrm{d}t} = \alpha\frac{\mathrm{d}^2T}{\mathrm{d}x^2},} \tag{4.6}$$

where $\alpha = k/\rho c_V$ is the thermal diffusivity of the medium where heat flows and k is the thermal conductivity (units: W/m.K). It is identical to the diffusion equation. Therefore, heat conduction also leads to entropy production (as the diffusion equation does).

4.11. Summary: Onsager's Formulation of the Second Law

The Second Law can be formulated in terms of the entropy production σ, namely, $\sigma \geq 0$. In Onsager's formulation, the entropy production is given by the product sum of so-called conjugate fluxes, J_i, and forces X_i, in the system. The second law becomes

$$\sigma = \sum_i J_i X_i \geq 0 \tag{4.7}$$

where σ is larger than or equal to zero. Each flux is taken to be a linear combination of all forces,

$$J_i = \sum_j L_{ij} X_j \tag{4.8}$$

and the reciprocal relations

$$L_{ij} = L_{ji}$$

apply. They are called Onsager's reciprocal relations. In order to use the theory, one first has to identify a complete set of extensive independent variables, α_i. The resulting conjugate fluxes and forces are

$$J_i = \frac{\mathrm{d}\alpha_i}{\mathrm{d}t}, \qquad \text{and} \qquad X_i = \left(\frac{\partial S}{\partial \alpha_i}\right)_{\alpha_{j \neq i}},$$

respectively. Here t is the time and S is the entropy of the system. The three equations above contain then all the information on the behavior of the system. Accurate expressions for the fluxes are required to model real systems. The simplest descriptions of heat, mass, charge, and volume transport are the equations of Fourier, Fick, Ohm, Darcy and Newton. Fourier's law expresses the measurable heat flux in terms of the temperature gradient by:

$$J'_q = -\lambda \frac{\mathrm{d}T}{\mathrm{d}x}$$

where λ is the thermal conductivity, T is the absolute temperature, and x is the direction of transport. Fick's law gives the mass flux of one of the components in terms of the gradient of its molar concentration c:

$$J = -D \frac{\mathrm{d}c}{\mathrm{d}x}$$

where D is the diffusion coefficient. Ohm's law gives the electric current in terms of the gradient of the electric potential:

$$J_I = -\kappa \frac{\mathrm{d}\phi}{\mathrm{d}x}$$

where κ is the electrical conductivity, and ϕ is the electric potential. Darcy's law says that the volume flow J_v in a tube is proportional to the pressure gradient $\mathrm{d}P/\mathrm{d}x$ via the coefficient L_p:

$$J_v = -L_p \frac{\mathrm{d}P}{\mathrm{d}x}.$$

The fluxes are all caused by a gradient, or driving force. Fick's law, for instance, says that there is no mass flux if there is no concentration gradient. We know from experiments that a temperature gradient and an electric potential gradient also can give rise to a mass flux. To neglect such effects can have severe consequences. In general situations, we must take all driving forces into account. Equations (4.7) and (4.8) form the second law of thermodynamics

$$\sigma \equiv \frac{\mathrm{d}S}{\mathrm{d}t} = \sum_i J_i X_i = \sum_i \sum_j L_{ij} X_j X_i \geq 0. \tag{4.9}$$

In a stationary state there is no accumulation of internal energy, mass or charge. This means that the heat, molar and electric fluxes are independent of position. The derivative of the above equations with respect to x are then zero. For the first equation, we have:

$$-\frac{\mathrm{d}}{\mathrm{d}x} J'_a = \frac{\mathrm{d}}{\mathrm{d}x} \lambda \frac{\mathrm{d}T}{\mathrm{d}x} = 0.$$

Equations like these can be used to calculate the temperature, concentration, electric potential and pressure as a function of the position, when their values on the boundaries of the system and λ, D, κ, L_p and η are known.

4.12. Problems

Problem 127. Suppose that we have a metal rod whose two end points are held at different temperatures. This is a non-equilibrium situation because thermodynamic equilibrium would imply that the entire rod is at the same temperature. Instead, the temperature is a function of position along the length of the rod. It is a steady state situation because the temperature does not vary with time (i.e. each point along the rod is at a fixed temperature). Use the concepts of non-equilibrium thermodynamics (namely, the heat conduction equation) to calculate the temperature as a function of position between the two end points of the rod. The rod is 10 cm long. The walls are kept at constant temperature, 4 and 25° C, respectively. Assume that the thermal conductivity is constant.

Solution. The heat conduction equation is Eq. 4.6. In the steady state, we have $\mathrm{d}^2T/\mathrm{d}x^2 = 0$. Thus, T is of the form, $T(x) = a + bx$. The constants a and b follow from the boundary conditions. We have $T(0)$=278 K and $T(10)$=298 K. It follows that $T(x) = (278 + 2x/\mathrm{cm})$ K. ■

Problem 128. Indoor ice rinks employ a cooling system placed underneath a concrete slab (similar to radiant floor cooling systems, but lower temperatures). On top of the concrete slab is the ice. Suppose that we place a temperature sensor $d = 8$ cm under the concrete slab. Calculate the entropy production per surface area due to the heat transport through the concrete slab. The temperature sensor reads 243 K. This is the temperature of the radiant cooling system. The concrete is in contact with ice (273 K). The thermal conductivity of the pavement is 0.7 W/K.m (λ parameter in the Fourier's law). Note: this is a 1D problem with depth as the relevant spatial variable.

Solution. Fourier's law for heat conduction is $J_u = -\lambda(\mathrm{d}T/\mathrm{d}x)$, where x is the depth coordinate. The entropy production per surface area is (let $\Delta T = T_{top} - T_{below}$):

$$\left|\int_0^d \sigma \mathrm{d}x\right| = \left|\int_0^d J_u \frac{\mathrm{d}}{\mathrm{d}x}(\frac{1}{T})\mathrm{d}x\right| = \left|\lambda\frac{\Delta T}{d}\left(\frac{1}{T_{top}} - \frac{1}{T_{below}}\right)\right|$$

$$= \left|0.7\frac{(30)}{0.08}\left(\frac{1}{273} - \frac{1}{243}\right)\right| = 0.12\frac{\mathrm{W}}{\mathrm{K.m}^2}.$$

■

Problem 129. For the previous problem, calculate the lost work per surface area near the top of the concrete slab (at the interface of ice and concrete). Lost work is the work lost due to entropy production (a type of $T\Delta S$ term, where ΔS is due to entropy production).

Solution. The lost work (A: area)

$$\Delta W_{lost} = T_{top} \cdot A \int_0^d \sigma \mathrm{d}x$$

per surface area A is $\Delta W_{lost}/A$=273 K $\cdot$ 0.12 W/K.m^2=33 W/m^2. It is typical for heat conduction around room temperature that the entropy production is large. ■

Problem 130. Suppose that a closed 1D system (ideal gas in a pipe) does not undergo any irreversible changes ($\sigma = 0$) and its temperature is spatially uniform $[\mathrm{d}(1/T)/\mathrm{d}x = 0]$ and equal to 300 K everywhere, but that there is an enthalpy flux driven by particle flow. Moreover, the entropy of the system does not change $\mathrm{d}s/\mathrm{d}t = 0$ (isentropic process). There is flow in the pipe which we measure to have an average local velocity of 10 m/s at $x = 0$ and 12 m/s at $x = 1$ m. (Such an acceleration is possible if the pipe diameter narrows slightly; you can assume that the velocity increases uniformly from 10 to 12 m/s over this distance.) The concentration of the substance in the pipe is 1 mol/m^3 and uniform everywhere. Then, because of the nature of this enthalpy flux, we expect the heat flux to be spatially non-uniform. Calculate the gradient in the measurable heat flux, $\mathrm{d}J_u/\mathrm{d}x$.

Solution. Since the particle flux $J = cv$, at $x = 0$ we have

$$J(0) = (1\ \mathrm{mol/m^3})(10\ \mathrm{m/s})$$

and

$$J(1) = (1\ \mathrm{mol/m^3})(12\ \mathrm{m/s}).$$

This gives a gradient $\mathrm{d}J/\mathrm{d}x$ of (1 mol/m^3)(2 m/s)/(1 m)=2 mol/m^3/s. For ideal gas, the chemical potential is $\mu = \frac{\partial U}{\partial n}$, where $U = \frac{3}{2}nRT$. Thus, $\mu = \frac{3}{2}RT$, where $T = 300$ K. Then invoke:

$$\frac{\mathrm{d}s}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{1}{T}\left(J_u - \mu J_j\right)\right] = 0$$

Thus, $\frac{\mathrm{d}}{\mathrm{d}x}J_u = \mu\frac{\mathrm{d}}{\mathrm{d}x}J_j$, where $\mu = \frac{3}{2}RT$. Plug in the numbers. ■

Problem 131. If two systems A and B are in thermal contact, the assembly $(A+B)$ being isolated, exchange a heat quantity 1 kJ every second (i.e., 1 kW), calculate the entropy production if $T_A = 200$ K and $T_B = 300$ K. Is the entropy production positive or negative (explain)?

Solution. Heat flows from B to A (from hot body to the cold body), so $\delta Q = \delta Q_B = -\delta Q_A = -1$ kJ.

$$\sigma = \frac{\delta Q}{\mathrm{d}t}\left(\frac{1}{T_B} - \frac{1}{T_A}\right) > 0 = -(1\text{ kW})\left(\frac{1}{300\text{ K}} - \frac{1}{200\text{ K}}\right) = \frac{5}{3}\,\frac{\text{kW}}{\text{K}}.$$

Entropy production is always positive. ■

Problem 132. Explain what is the driving *force*, X, of a chemical reaction. What is the corresponding *flux*, J? What are the units of the flux and force?

Problem 133. Does a chemical reaction produce entropy? Why (or why not)?

Solution. Yes, spontaneous irreversible reactions produce entropy, the entropy production is $\dot{\xi}(-\Delta G_{rxn}/T)$. ■

Chapter 5

Partition Functions

The concept of the partition function is fundamental to the field of statistical mechanics, providing a crucial link between microscopic states and macroscopic properties. It serves as a mathematical tool that encompasses all possible states of a system and assigns a statistical weight to each, thereby allowing for the derivation of thermodynamic quantities.

5.1. Definition and Significance of the Partition Function

A partition function, denoted typically by Z, is defined for a canonical ensemble as the sum over all states i of the exponential of the negative of the energy E_i of each state divided by the product of the Boltzmann constant k_B and the temperature T:

$$Z = \sum_i e^{-E_i/(k_B T)}.$$

We can also express Z as a sum over energy levels E:

$$Z = \sum_E W(E) e^{-E/(k_B T)}.$$

where $W(E)$ is the degeneracy of the energy level E. The two concepts are entirely equivalent. Notice the difference in notation used. I recommend you work out problems and examples from Kittel's book, especially the chapter on Fermi-Dirac and Bose-Einstein statistics. Kittel carefully explains the difference between sum over states and sum over energy levels. The function Z is not merely a computational tool; it embodies the very essence of equilibrium statistical mechanics. It allows us to calculate average values of physical quantities, which correspond to what is actually measured in an experiment.

5.1.1. Examples of Partition Functions. The generality of the partition function makes it applicable to various systems, from simple ideal gases to complex molecular structures.

5.1.1.1. *Ideal Gas.* For an ideal gas, the partition function can be expressed as a product of the molecular partition functions q, raised to the power of the number of molecules N, and divided by $N!$ to account for indistinguishability:

$$Z_{\text{ideal}} = \frac{z^N}{N!}.$$

The molecular partition function z is further broken down into translational, rotational, vibrational, and electronic components, each of which reflects the contributions of the respective degrees of freedom to the total energy.

5.1.1.2. *Quantum Harmonic Oscillator.* A quantum harmonic oscillator is another instructive example, with a partition function derived from its quantized energy levels:

$$Z_{\text{ho}} = \sum_{n=0}^{\infty} e^{-\hbar\omega(n+\frac{1}{2})/(k_B T)},$$

where $\hbar$ is the reduced Planck constant, ω is the angular frequency of the oscillator, and n is the quantum number.

5.1.1.3. *Spin Systems.* In magnetic systems, such as a lattice of spins, the partition function takes into account the interaction of spins with each other and an external magnetic field B, leading to the form:

$$Z_{\text{spin}} = \sum_{\{\sigma\}} e^{-\beta(-J\sum_{\langle i,j\rangle}\sigma_i\sigma_j - B\sum_i \sigma_i)},$$

where J is the interaction strength, β is the inverse temperature $(k_B T)^{-1}$, and σ_i represents the spin at site i.

5.1.2. The Role of Partition Functions in Thermodynamics. The partition function is the key to unlocking the thermodynamic properties of a system. From it, one can derive the Helmholtz free energy F by:

$$F = -k_B T \log Z,$$

which in turn allows for the calculation of other thermodynamic potentials and quantities such as entropy, internal energy, and pressure. These quantities are essential for understanding the behavior of materials and the outcome of chemical reactions.

5.1.3. Importance. Partition functions unite the diverse phenomena of thermodynamics and statistical mechanics. It is reflects the power of statistical methods in bridging the microscopic world of atoms and molecules with the macroscopic realm that we observe. In this chapter we explore a variety of systems that can be analyzed through the partition function, each example bringing us closer to a complete understanding of the statistical nature of the physical world.

5.2. Equipartition Theorem

Some of the results below allude to the equipartition theorem. We start by discussing the equipartition theorem. The equipartition theorem is a principle from classical statistical mechanics which states that, at thermal equilibrium, the total energy of a system is equally divided among its degrees of freedom. Mathematically, each degree of freedom that appears as a quadratic term in the system's Hamiltonian contributes an amount of $\frac{1}{2}k_BT$ to the average energy, where k_B is the Boltzmann constant and T is the temperature in kelvin.

Theorem 5.1 (Equipartition)**.** *We consider a system of N particles within the framework of classical physics. Let the microstate be given by $\mathbf{x} = (\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{q}_1, \ldots, \mathbf{q}_N)$. If the Hamiltonian function $\mathcal{H}(\mathbf{x})$ satisfies $\mathcal{H}(\mathbf{x}) \to \infty$ for a component $|x_i| \to \infty$ then the following relation holds for an arbitrary polynomial function $f(\mathbf{x})$:*

$$\left\langle f(x)\frac{\partial \mathcal{H}}{\partial x_i}\right\rangle = k_BT\left\langle \frac{\partial f(x)}{\partial x_i}\right\rangle.$$

Proof. This relation is an immediate consequence of the identity

$$0 = \frac{1}{n!h^{3N}Z}\int d^{3N}\mathbf{p}\, d^{3N}\mathbf{q}\, \frac{\partial}{\partial x_i}\left(f(\mathbf{x})e^{-\beta\mathcal{H}(\mathbf{x})}\right) = \left\langle \frac{\partial f(\mathbf{x})}{\partial x_i}\right\rangle - \beta\left\langle f(\mathbf{x})\frac{\partial \mathcal{H}}{\partial x_i}\right\rangle.$$

(The $0 =$ part follows by integration by parts and the requirement that $|\mathcal{H}(\mathbf{x}) \to \infty$ as $|x_i| \to \infty$.) In particular for $f(\mathbf{x}) = x_j$ we obtain

$$\left\langle x_j\frac{\partial \mathcal{H}}{\partial x_i}\right\rangle = \delta_{ij}k_BT. \tag{5.1}$$

□

5.2.1. Application. The equipartition theorem allows us to predict the average energy per molecule in a gas, the contribution of each type of motion to the specific heat, and to understand the behavior of heat capacity at different temperature regimes. For example, a diatomic molecule has three translational degrees of freedom, two rotational degrees of freedom, and one vibrational degree of freedom (counting as two quadratic degrees: one for potential energy and one for kinetic energy). According to the equipartition theorem, at high enough temperatures where all modes are excited, each molecule would have an average energy of $\frac{7}{2}k_BT$.

Let us work out the details. First, we consider $\mathcal{H}(\mathbf{p},\mathbf{q}) = \mathcal{H}_{kin}(\mathbf{p}) + V(\mathbf{q})$ with

$$\mathcal{H}_{kin}(\mathbf{p}) = \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m} = \sum_{\alpha=1}^{3N}\frac{p_\alpha^2}{2m},$$

where we have denoted by p_α, $\alpha = 1, \dots, 3N$ the $3N$ coordinates of the N momenta $(\mathbf{p}_1, \dots, \mathbf{p}_N)$.

Hence, we have for each α:

$$p_\alpha \frac{\partial \mathcal{H}}{\partial p_\alpha} = \frac{p_\alpha^2}{m}$$

from which it follows that

$$\sum_{\alpha=1}^{3N} \left\langle p_\alpha \frac{\partial \mathcal{H}}{\partial \alpha} \right\rangle \equiv 2\langle \mathcal{H}_{kin} \rangle = 2Nk_BT$$

or

$$\langle \mathcal{H}_{kin} \rangle = \frac{3}{2}Nk_BT.$$

Second, when $V(\mathbf{q})$ is of the form

$$V(\mathbf{q}) = \sum_{i=1}^{N} a_i \mathbf{q}_i^2 = \sum_{\alpha=1}^{3N} \tilde{a}_\alpha q_\alpha^2,$$

one obtains

$$\sum_{\alpha=1}^{3N} \left\langle q_\alpha \frac{\partial \mathcal{H}}{\partial q_\alpha} \right\rangle = 2\sum_{\alpha=1}^{3N} \langle \tilde{a}_\alpha q_\alpha^2 \rangle \equiv 2\langle V \rangle,$$

and thus from (5.1),

$$\langle V \rangle = \frac{3}{2}Nk_NT.$$

We note that every canonical variable which appears quadratically in the Hamiltonian function contributes an amount of $\frac{1}{2}k_BT$ to the average energy. Therefore we obtain, e.g., $\langle \mathcal{H} \rangle = \frac{3}{2}Nk_BT$ for the classical ideal gas and we will get $\langle \mathcal{H} \rangle = 3Nk_BT$ from the contribution of the harmonic lattice vibrations to the internal energy of a solid.

To each variable entering quadratically in the Hamiltonian function, one attributes a thermodynamic degree of freedom. The number of degrees of freedom is therefore $f = 3N$ for the ideal gas, and $f = 6N$ for the harmonic oscillator.

Hence, for a system with f degrees of freedom one obtains the so-called equipartition theorem

$$\boxed{\langle \mathcal{H} \rangle = f\frac{1}{2}k_BT.}$$

For an ideal diatomic gas, taking into account the rotations, we find $f = (3 + 2)N = 5N$, and when the vibrations are also taken into account $f = (3 + 2 + 2)N = 7N$ (see below). The diatomic gas in the classical regime therefore has $C_V = \frac{7}{2}Nk_B$. However, a quantum-mechanical treatment of the ideal diatomic gas reveals that in most cases the vibrational excitations do not contribute to the specific heat at room temperature and therefore $C_V = \frac{5}{2}Nk_B$.

Nonlinearities in the potential and quantum corrections will, of course, lead to deviations from this equipartition theorem.

5.2.1.1. *Hamiltonian of a Rigid Rotor Diatomic Molecule.* The total classical Hamiltonian $\mathcal{H}$ for a rigid rotor diatomic molecule, considering translational, vibrational, and rotational motions, is composed of seven terms reflecting the seven degrees of freedom:

$$\mathcal{H} = T_{\text{cm},x} + T_{\text{cm},y} + T_{\text{cm},z} + T_{\text{rel}} + T_{\text{rot},\theta} + T_{\text{rot},\phi} + V_{\text{vib}} + V_{\text{int}},$$

whereas V_{int} represents additional degrees of freedom that may play a role when the molecule is more complex. Here, the kinetic energy of the center of mass in each spatial direction is given by:

$$T_{\text{cm},x} = \frac{P_x^2}{2M},$$
$$T_{\text{cm},y} = \frac{P_y^2}{2M},$$
$$T_{\text{cm},z} = \frac{P_z^2}{2M},$$

with P_i (where $i = x, y, z$) being the components of the linear momentum of the center of mass and $M = m_1 + m_2$ the total mass of the molecule.

The kinetic energy associated with the relative vibrational motion of the two atoms is:

$$T_{\text{rel}} = \frac{p_r^2}{2\mu},$$

where p_r is the relative radial momentum and $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass.

The rotational kinetic energy components for the polar (θ) and azimuthal (ϕ) angles are expressed as:

$$T_{\text{rot},\theta} = \frac{L_\theta^2}{2I},$$
$$T_{\text{rot},\phi} = \frac{L_\phi^2}{2I \sin^2\theta},$$

where L_θ and L_ϕ are the components of the angular momentum, and $I = \mu R^2$ is the moment of inertia.

The potential energy for the vibrational motion is typically modeled as a harmonic oscillator:

$$V_{\text{vib}} = \frac{1}{2} k (R - R_e)^2,$$

where k is the force constant, R the instantaneous separation between the two atoms, and R_e the equilibrium bond length.

Finally, the internal potential energy V_{int} accounts for the interactions between the atoms, which can be more complex and depend on the specific molecule.

$$V_{\text{int}} = V_{\text{int}}(R, \theta, \phi).$$

Each term in this Hamiltonian represents a specific type of energy corresponding to one of the degrees of freedom of the diatomic molecule.

5.2.2. Limitations. The equipartition theorem assumes that all degrees of freedom are accessible and that energy levels are continuous. In quantum mechanics, this assumption breaks down, especially at low temperatures where the energy levels become discrete, and not all levels are thermally accessible. Thus, quantum corrections are necessary to accurately describe the system's behavior under such conditions.

In conclusion, while the equipartition theorem is a powerful tool in classical statistical mechanics, its limitations must be recognized, and quantum statistical mechanics should be employed for complete and accurate descriptions of microscopic systems.

5.3. The Ideal Monatomic Gas

5.3.1. Atomic Partition Function. The total partition function Z for a system of N particles in an ideal gas is the product of the individual molecular partition functions z for each particle, raised to the power of N and divided by $N!$ to account for the indistinguishability of the particles:

$$Z = \frac{z^N}{N!},$$

where the molecular partition function z is the product of translational (z_{trans}), electronic (z_{elec}), and nuclear (z_{nucl}) partition functions:

$$z = z_{trans} \cdot z_{elec} \cdot z_{nucl}.$$

For a monatomic ideal gas, the electronic and nuclear partition functions are typically close to unity under normal conditions due to the large energy gaps in electronic and nuclear energy levels compared to thermal energy $k_B T$. Therefore, $z \approx z_{trans}$ and the focus is predominantly on the translational degrees of freedom.

5.3.2. Translational Partition Function. The translational partition function z_{trans} for a single particle in a three-dimensional box (representing the volume V) can be derived by considering the energy levels of a particle in a box and summing over all possible states. The kinetic energy E_{n_x,n_y,n_z} of a particle in a three-dimensional box with quantum numbers n_x, n_y, n_z is given by:

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right),$$

where h is Planck's constant, m is the mass of the particle, and L_x, L_y, L_z are the lengths of the box in the x, y, z directions, respectively.

The translational partition function is then the sum over all states:

$$z_{trans} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} e^{-\beta E_{n_x,n_y,n_z}},$$

where $\beta = 1/(k_B T)$.

Since the energy levels are closely spaced for a macroscopic system, we can approximate the sum as an integral:

$$z_{trans} \approx \int_0^{\infty}\int_0^{\infty}\int_0^{\infty} e^{-\beta \frac{h^2}{8m}(n_x^2/L_x^2+n_y^2/L_y^2+n_z^2/L_z^2)} dn_x dn_y dn_z.$$

The closed-form expression for z_{trans} is obtained by performing the Gaussian integrals:

$$z_{trans} = \left(\frac{V}{\lambda^3}\right),$$

where $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ is the thermal de Broglie wavelength and $V = L_x L_y L_z$ is the volume of the box.

This translational partition function is a crucial quantity in statistical mechanics, as it directly relates to the thermodynamic properties of the gas.

5.3.3. Thermodynamic Implications of the Translational Partition Function.

The translational partition function z_{trans} plays a pivotal role in determining the macroscopic thermodynamic properties of a gas. By leveraging the partition function, one can derive expressions for pressure P, internal energy U, and entropy S, which are fundamental in understanding the behavior of an ideal monatomic gas.

5.3.3.1. *Pressure.* The pressure of the gas can be found by applying the thermodynamic relation $P = -\left(\frac{\partial F}{\partial V}\right)_T$, where F is the Helmholtz free energy. For an ideal gas, $F = -k_B T \log Z$, and substituting the expression for the total partition function Z, we obtain:

$$P = -\left(\frac{\partial(-k_B T \log Z)}{\partial V}\right)_T = k_B T \frac{\partial \log Z}{\partial V}.$$

Given that $Z = \frac{z_{trans}^N}{N!}$ and $z_{trans} = \frac{V}{\lambda^3}$, it follows that:

$$P = k_B T \frac{\partial \log(\frac{V^N}{\lambda^{3N} N!})}{\partial V} = \frac{N k_B T}{V},$$

which is the ideal gas law.

5.3.3.2. *Internal Energy.* The internal energy is derived from the partition function using $U = -\frac{\partial \log Z}{\partial \beta}$. For an ideal monatomic gas, where the energy is purely kinetic, U is given by:

$$U = -\frac{\partial \log(\frac{V^N}{\lambda^{3N} N!})}{\partial \beta} = \frac{3}{2} N k_B T,$$

which shows that the internal energy is directly proportional to the temperature and the number of particles, independent of the volume.

5.3.3.3. *Entropy.* Entropy can be calculated using the relationship $S = k_B \log Z + \frac{U}{T}$. Substituting the expressions for Z and U into this equation yields:

$$S = k_B \log \left(\frac{V^N}{\lambda^{3N} N!} \right) + \frac{3}{2} N k_B.$$

Applying Stirling's approximation $\log N! \approx N \log N - N$ for large N, the entropy can be expressed as:

$$S = N k_B \left[\log \left(\frac{V}{N \lambda^3} \right) + \frac{5}{2} \right].$$

This equation reflects the dependence of entropy on the volume and temperature of the gas, as well as the number of particles.

Each of these derived quantities is rooted in the translational partition function, underscoring its significance in the statistical mechanical description of thermodynamic systems. The simplicity of these expressions for an ideal gas serves as a cornerstone for more complex systems where interactions between particles cannot be neglected.

5.4. Electronic Partition Function

5.4.1. Approximations for the Electronic Partition Function. The electronic partition function, z_{elec}, is critical for understanding the distribution of electronic energy levels in atoms and molecules. In the case of an ideal monatomic gas, the electronic energy levels are quantized and the energy required to excite an electron from the ground state to the first excited state is typically on the order of electronvolts (eV).

For simplicity and without loss of generality, we set the ground state energy, E_0, to zero. This is a valid approach because the absolute values of energy are not physically observable; only energy differences are. Given the large energy gap to the excited states, at room temperature, the population of excited states is negligible. Therefore, the electronic partition function can often be approximated as:

$$z_{elec} = \underbrace{\sum_i e^{-\beta E_i}}_{\text{sum over states}} = \underbrace{\sum_E W(E) e^{-\beta E}}_{\text{sum over levels}} = W(E_0) + W(E_1) e^{-\beta E_1} + \cdots \approx 1 + e^{-\beta E_1},$$

where E_1 is the energy of the first excited state and $\beta = \frac{1}{kT}$. (In the last step we assumed non-degenerate levels, $W(E_0) = W(E_1) = 1$, but this assumption is not necessary.) However, for most conditions relevant to an ideal gas, the exponential term is very small and can be neglected, simplifying z_{elec} to unity.

5.4.2. Nuclear Partition Function.

5.4.3. Approximations for the Nuclear Partition Function. Similarly, the nuclear partition function, z_{nuc}, accounts for the distribution of nuclear energy levels. The energy required to excite a nucleus to its first excited state is typically on the order of megaelectronvolts (MeV), which is significantly larger than thermal energies at room temperature.

Again, setting the ground state energy to zero and considering the large energy gap to the first excited state, the nuclear partition function for practical purposes reduces to:

$$z_{nuc} \approx 1.$$

(More precisely, it is equal to the degeneracy of the ground nuclear state, $W(E_0)$.) This approximation is valid since the Boltzmann factor for nuclear excitation, $e^{-\beta E_{nuc}}$, where E_{nuc} is the energy of the nuclear excited state, is exceedingly small for any temperature relevant to chemical and most physical processes.

5.5. Combined Partition Function: Ideal Monatomic Gas

The total partition function for a system of N indistinguishable particles is the product of the individual partition functions for translational, electronic, and nuclear degrees of freedom. Considering the approximations for the electronic and nuclear partition functions, the total partition function Z is given by:

$$Z = \frac{\left(z_{trans} \cdot z_{elec} \cdot z_{nuc}\right)^N}{N!}.$$

Given that $z_{elec} \approx 1$ and $z_{nuc} \approx 1$, the expression simplifies to:

$$Z = \frac{z_{trans}^N}{N!}.$$

This form of the partition function explicitly reflects the indistinguishability of particles by the division by $N!$, a consequence of the quantum statistical nature of identical particles.

The assumptions leading to this simplified expression are well-founded for an ideal monatomic gas, where interactions between particles are negligible, and the energy to excite internal degrees of freedom (electronic and nuclear) is much greater than the thermal energy available in the system.

5.6. The Ideal Diatomic Gas

5.6.1. Rigid Rotor-Harmonic Oscillator Model. The description of the ideal diatomic gas often invokes the rigid rotor-harmonic oscillator approximation. Underpinning this model is the Born-Oppenheimer approximation, which allows us to decouple the nuclear and electronic motions due to the vast difference in their masses. The nuclei are assumed to move on a fixed potential energy surface defined by the electronic states.

The Hamiltonian for a diatomic molecule in this approximation is given by:

$$\hat{\mathcal{H}} = \hat{T}_{trans} + \hat{T}_{rot} + \hat{T}_{vib} + \hat{\mathcal{H}}_{elec} + \hat{\mathcal{H}}_{nuc},$$

where $\hat{T}_{trans}$, $\hat{T}_{rot}$, and $\hat{T}_{vib}$ represent the kinetic energies corresponding to translational, rotational, and vibrational motions, respectively. $\hat{\mathcal{H}}_{elec}$ and $\hat{\mathcal{H}}_{nuc}$ are the Hamiltonians for the electronic and nuclear degrees of freedom.

The energy eigenvalues for the rotational and vibrational degrees of freedom are of particular interest:

- Rotational energy levels: $E_{rot} = BJ(J+1)$,
- Vibrational energy levels: $E_{vib} = \hbar\omega(v + \frac{1}{2})$,

where J is the rotational quantum number, B is the rotational constant, v is the vibrational quantum number, and ω is the angular frequency of vibration.

The total partition function for the system is:

$$Z_{total} = \frac{(z_{trans} \cdot z_{rot} \cdot z_{vib} \cdot z_{elec} \cdot z_{nuc})^N}{N!},$$

reflecting the contributions from all degrees of freedom.

5.7. Rotational Kinetic Energy

Consider the classical kinetic energy term for rotation in a rigid body, which is given by the Hamiltonian:

$$\mathcal{H} = \frac{L^2}{2I},$$

where L is the magnitude of the angular momentum and I is the moment of inertia. The angular momentum $\vec{L}$ is defined as:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p},$$

where $\vec{r}$ is the position vector and $\mathbf{p}$ is the linear momentum vector. For a continuous mass distribution, the moment of inertia is:

$$I = \int |\mathbf{r}|^2 \rho(\mathbf{r}) d^3\mathbf{r},$$

where $\rho(\mathbf{r})$ is the mass density. For a system of point particles, the moment of inertia is:

$$I = \sum_i m_i r_i^2.$$

In quantum mechanics, the classical angular momentum operator $\vec{L}^2$ is replaced by the quantum mechanical operator $\hat{L}^2$, and the energy eigenvalue equation for this operator is:

$$\hat{L}^2 Y_l^m(\theta, \varphi) = \hbar^2 l(l+1) Y_l^m(\theta, \varphi),$$

where $Y_l^m(\theta, \varphi)$ are the spherical harmonics which serve as the eigenfunctions of $\hat{L}^2$. In bra-ket notation, the eigenvalue equation is written as:

$$\hat{L}^2 |l, m_L\rangle = \hbar^2 l(l+1) |l, m_L\rangle.$$

Switching to the rotational quantum number J, we have the eigenvalues:

$$\hat{L}^2 \left|J, m_J\right\rangle = \hbar^2 J(J+1) \left|J, m_J\right\rangle .$$

The energy expression for the quantum mechanical rigid rotor, by substituting the moment of inertia and the quantum mechanical angular momentum, becomes:

$$E_{\text{rot}} = \frac{\hbar^2}{2I} J(J+1),$$

where $B = \frac{\hbar^2}{2I}$ is the rotational constant. Thus, the final expression for the energy levels of a quantum mechanical rigid rotor is:

$$E_{\text{rot}} = BJ(J+1).$$

5.8. Quantum Harmonic Oscillator

The classical energy of a harmonic oscillator is described by the potential:

$$V(x) = \frac{1}{2}kx^2,$$

where k is the force constant of the oscillator and x is the displacement from equilibrium. In quantum mechanics, we replace the displacement x with the quantum operator $\hat{x}$, leading to the quantum Hamiltonian:

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2,$$

where $\hat{p}$ is the momentum operator and m is the mass of the oscillating particle. In the case of a diatomic molecule, m is replaced by the reduced mass μ, which is given by $\mu = \frac{m_1 m_2}{m_1 + m_2}$ for two atoms with masses m_1 and m_2.

To simplify the Hamiltonian, we introduce the creation $\hat{a}^\dagger$ and annihilation $\hat{a}$ operators:

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + \frac{i\hat{p}}{m\omega} \right),$$

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i\hat{p}}{m\omega} \right),$$

where $\omega = \sqrt{\frac{k}{m}}$ is the fundamental frequency of the oscillator.

The Hamiltonian in terms of the number operator $\hat{n} = \hat{a}^\dagger \hat{a}$ is derived as follows:

$$\hat{\mathcal{H}} = \bar{\omega} \left(\hat{n} + \frac{1}{2} \right).$$

When this Hamiltonian acts on the number states $|n\rangle$, which are eigenstates of the number operator $\hat{n}$, we obtain the energy eigenvalues:

$$E_{\text{vib}} = \hbar\omega \left(n + \frac{1}{2} \right),$$

where n are the allowed quantum numbers (non-negative integers) representing the vibrational quantum state of the molecule, and $\frac{1}{2}\hbar\omega$ is the zero-point energy, which is the energy of the ground state of the quantum oscillator ($n = 0$).

The reduced mass μ enters the expression for the fundamental frequency ω in the case of diatomic molecules, whether homonuclear or heteronuclear. The moment of inertia I for a diatomic molecule is related to the reduced mass by $I = \mu r_0^2$, where r_0 is the equilibrium bond length. The force constant k from Hooke's law is related to the vibrational frequency by $k = \mu\omega^2$.

5.9. Vibrational Partition Function

The vibrational partition function for a quantum harmonic oscillator can be derived by considering the quantized energy levels. The energy of a harmonic oscillator in quantum mechanics is given by:

$$E_n = \left(n + \frac{1}{2}\right) h\nu,$$

where n is the quantum number of the vibrational state, h is Planck's constant, and ν is the frequency of the oscillator.

The partition function Z_{vib} is the sum over all possible energy states weighted by the Boltzmann factor $e^{-\beta E_n}$, where $\beta = \frac{1}{k_B T}$ with k_B as the Boltzmann constant and T as the temperature:

$$Z_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta E_n} = e^{-\frac{1}{2}\beta h\nu} \sum_{n=0}^{\infty} \left(e^{-\beta h\nu}\right)^n.$$

This sum is a geometric series with a common ratio $r = e^{-\beta h\nu}$. The sum of a geometric series $\sum_{n=0}^{\infty} r^n$ is $\frac{1}{1-r}$, provided that $|r| < 1$, which is true for all physical temperatures (as $e^{-\beta h\nu} < 1$). Hence, we can write:

$$Z_{\text{vib}} = \frac{e^{-\frac{1}{2}\beta h\nu}}{1 - e^{-\beta h\nu}}.$$

5.9.1. Vibrational Partition Function: Computable Thermodynamic Quantities.

This closed-form expression for Z_{vib} allows us to compute various thermodynamic quantities.

5.9.1.1. *Energy.* For example, the average energy $\langle E_{\text{vib}} \rangle$ can be derived from Z_{vib} as follows:

$$\langle E_{\text{vib}} \rangle = -\frac{\partial \log Z_{\text{vib}}}{\partial \beta} = \frac{h\nu}{2} + \frac{h\nu}{e^{\beta h\nu} - 1}.$$

This equation shows that the average energy is the sum of the zero-point energy $\frac{h\nu}{2}$ and the thermal excitation energy $\frac{h\nu}{e^{\beta h\nu}-1}$.

Similarly, other thermodynamic quantities such as the entropy S and the specific heat C_V can be calculated, providing us with a comprehensive understanding of the role of the vibrational partition function in statistical thermodynamics.

5.9.1.2. *Heat Capacity.* The average energy of a quantum harmonic oscillator, derived from the vibrational partition function, is given by:

$$\langle E_{\text{vib}} \rangle = \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} + \frac{1}{2}\hbar\omega,$$

where $\hbar$ is the reduced Planck constant, ω is the angular frequency of the vibration, k_B is the Boltzmann constant, and T is the temperature.

The heat capacity at constant volume for vibrational modes is the temperature derivative of the average energy:

$$C_{V,\text{vib}} = \left(\frac{\partial \langle E_{\text{vib}} \rangle}{\partial T} \right)_V .$$

Using the chain rule, we compute the derivative as follows:

$$\begin{aligned} C_{V,\text{vib}} &= \frac{\partial}{\partial T} \left(\frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \right) \\ &= \frac{\hbar\omega}{k_B T^2} \frac{e^{\hbar\omega/k_B T}}{\left(e^{\hbar\omega/k_B T} - 1\right)^2}. \end{aligned}$$

This formula represents the heat capacity at constant volume for a single vibrational mode. For a molecule with multiple vibrational modes, the total heat capacity is the sum of the contributions from each individual mode.

5.9.1.3. *Entropy.* The entropy S_{vib} is calculated from:

$$S_{\text{vib}} = k_B \log Z_{\text{vib}} + \frac{\langle E_{\text{vib}} \rangle}{T}.$$

For a harmonic oscillator, the vibrational partition function can be simplified using the geometric series formula, because the exponent in Z_{vib} forms a geometric progression. Therefore, we have:

$$Z_{\text{vib}} = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}}.$$

Using this, the average energy is:

$$\begin{aligned} \langle E_{\text{vib}} \rangle &= -\frac{\partial}{\partial \beta} \log \left(\frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} \right) \\ &= \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right). \end{aligned}$$

The heat capacity can be expressed in closed form by differentiating the average energy with respect to temperature:

$$\begin{aligned} C_{V,\mathrm{vib}} &= \left(\frac{\partial}{\partial T}\hbar\omega\left(\frac{1}{2}+\frac{1}{e^{\beta\hbar\omega}-1}\right)\right)_V \\ &= k_B\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}. \end{aligned}$$

And the entropy is:

$$\begin{aligned} S_{\mathrm{vib}} &= k_B\log\left(\frac{e^{-\frac{\beta\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}\right)+\frac{\hbar\omega\left(\frac{1}{2}+\frac{1}{e^{\beta\hbar\omega}-1}\right)}{T} \\ &= k_B\left(\frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1}-\log(1-e^{-\beta\hbar\omega})\right). \end{aligned}$$

In the context of a harmonic oscillator model, vibrational energy levels are quantized and equally spaced. The vibrational quantum number v can take on any integer value starting from zero, representing the ground state energy level. At low temperatures, most molecules occupy the ground vibrational state, and the contribution to the heat capacity is negligible. As temperature increases, higher vibrational levels become more populated, and the heat capacity rises sharply due to the increased energy storage in vibrational modes.

The entropy reflects the number of accessible vibrational states at a given temperature. At absolute zero, all molecules are in the ground state, resulting in zero entropy. As temperature increases, the number of accessible states increases, leading to an increase in entropy. This is indicative of the greater disorder in the system due to the distribution of populations over more vibrational energy levels.

5.9.2. Rotational Partition Function. For a heteronuclear diatomic molecule, the rotational partition function, z_{rot}, is given by:

$$z_{rot} = \sum_{J=0}^{\infty}(2J+1)e^{-\beta BJ(J+1)},$$

where J is the rotational quantum number and B is the rotational constant.

In the high-temperature limit, the sum over J can be approximated by an integral:

$$z_{rot} \approx \int_0^{\infty}(2J+1)e^{-\beta BJ(J+1)}dJ.$$

Evaluating this integral yields the rotational partition function in terms of temperature and the rotational constant.

From z_{rot}, we can derive the expressions for thermodynamic quantities such as the rotational contribution to the internal energy, entropy, and heat capacity.

This comprehensive analysis provides a foundation for understanding the behavior of an ideal diatomic gas and calculating its thermodynamic properties using the partition functions for its various degrees of freedom.

$$
\begin{aligned}
Z_{\text{rot}} &= \sum_{J=0}^{\infty}(2J+1)e^{-\beta BJ(J+1)} \\
&\approx \int_0^{\infty}(2J+1)e^{-\beta BJ(J+1)}dJ \\
&= \int_0^{\infty} e^{-\beta Bx}dx \quad \text{where } x = J(J+1) \text{ and } dx = (2J+1)dJ \\
&= \frac{1}{\beta B} \quad \text{(in the high-temperature limit).}
\end{aligned}
$$

5.9.3. Rotational Partition Function: Computable Thermodynamic Quantities.

From the rotational partition function Z_{rot}, several thermodynamic properties of a system can be derived. The partition function for a rigid rotor, which models the rotational behavior of a diatomic molecule, is given by:

$$
Z_{\text{rot}} = \sum_{J=0}^{\infty}(2J+1)e^{-\frac{\beta\hbar^2}{2I}J(J+1)},
$$

where J is the rotational quantum number, $\hbar$ is the reduced Planck's constant, I is the moment of inertia of the molecule, and $\beta = \frac{1}{k_BT}$.

5.9.3.1. *Energy.* Given the above rotational partition function, we can compute the average energy $\langle E_{\text{rot}}\rangle$ for rotation by differentiating the natural logarithm of the partition function with respect to $-\beta$:

$$
\begin{aligned}
\langle E_{\text{rot}}\rangle &= -\frac{\partial \log Z_{\text{rot}}}{\partial\beta} \\
&= -\frac{\partial}{\partial\beta}\log\left(\sum_{J=0}^{\infty}(2J+1)e^{-\frac{\beta\hbar^2}{2I}J(J+1)}\right) \\
&= \frac{\hbar^2}{2I}\sum_{J=0}^{\infty}\frac{(2J+1)J(J+1)e^{-\frac{\beta\hbar^2}{2I}J(J+1)}}{Z_{\text{rot}}}.
\end{aligned}
$$

This expression can then be used to calculate the heat capacity and entropy

An even simpler result can be derived if we start from the high-temperature approximation:

$$
Z_{\text{rot}} \approx \frac{2Ik_BT}{\hbar^2}
$$

The average energy is then obtained by taking the temperature derivative:

$$
\langle E_{\text{rot}}\rangle = k_BT^2\frac{\partial}{\partial T}\left(\log\left(\frac{2Ik_BT}{\hbar^2}\right)\right)
$$

Which simplifies to:

$$\langle E_{\text{rot}} \rangle = k_B T$$

This result is valid under the assumption that the rotational levels can be treated as continuous, which is a good approximation at high temperatures.

The result $\langle E_{\text{rot}} \rangle = k_B T$ is a demonstration of the classical equipartition theorem, which states that each quadratic degree of freedom contributes $\frac{1}{2}k_B T$ to the average energy at thermal equilibrium. For a diatomic molecule, there are two such degrees of freedom in rotation (neglecting rotation about the bond axis due to negligible moment of inertia), leading to the total contribution being $k_B T$.

The implications of this result are several-fold:

1. **Equipartition of Energy:** It confirms the equipartition principle, signifying that energy is equally partitioned among each degree of freedom.
2. **Temperature Dependence:** The average rotational energy is directly proportional to the temperature, indicating an increase in energy with temperature.
3. **High-Temperature Behavior:** The result holds in the high-temperature limit, where the spacing between rotational energy levels is small enough to be considered continuous.
4. **Classical Limit:** It corresponds with classical expectations and exemplifies how quantum mechanical systems approach classical behavior at higher temperatures or quantum numbers.
5. **Specific Heat:** This linear relationship implies a constant contribution to the specific heat from rotational degrees of freedom, seen as a plateau at higher temperatures in the specific heat of gases at constant volume.
6. **Quantum Effects:** At lower temperatures, quantum mechanical treatment is necessary as the energy levels are not closely spaced and the average energy would deviate from this linear relationship.

This classical treatment is a simplified model that is particularly accurate at high temperatures where quantum effects can be neglected, and it serves to illustrate the fundamental principles of energy distribution in statistical mechanics.

5.9.3.2. *Heat Capacity.* The heat capacity at constant volume $C_{V,\text{rot}}$ can be determined by differentiating the average energy with respect to temperature:

$$C_{V,\text{rot}} = \left(\frac{\partial \langle E_{\text{rot}} \rangle}{\partial T} \right)_V .$$

5.9.3.3. *Entropy.* The entropy S_{rot} is found by using the relationship:

$$S_{\text{rot}} = k_B \log Z_{\text{rot}} + \frac{\langle E_{\text{rot}} \rangle}{T}.$$

These quantities are computed explicitly below.

Comment. The rotational energy levels are quantized and widely spaced at low temperatures, meaning that the contribution to the heat capacity from rotations is small at low temperatures. As the temperature increases, more rotational levels become accessible, and the heat capacity increases. The entropy calculation reflects the degree of disorder or randomness in the rotational states of the molecules. At low temperatures, fewer rotational states are populated, and the entropy is low. As the temperature increases, more states become populated, and the entropy increases.

These quantities are fundamental for understanding molecular behavior and are particularly important in the context of gases, where rotational motion contributes significantly to the overall thermodynamic properties.

5.10. Rotational partition function: Average Rotational Energy and Heat Capacity

The heat capacity at constant volume, C_V, for an ideal gas can be derived from its molecular partition function. For a diatomic molecule, which can be approximated as a rigid rotor, the rotational partition function, Z_{rot}, is particularly relevant. The rotational energy levels of a diatomic molecule are quantized and given by:

$$E_J = BJ(J+1),$$

where B is the rotational constant and J is the rotational quantum number, which can take on any integer value from zero to infinity.

The rotational partition function is the sum over all possible rotational states, weighted by the Boltzmann factor:

$$Z_{\text{rot}} = \sum_{J=0}^{\infty}(2J+1)e^{-\frac{E_J}{k_BT}},$$

where k_B is the Boltzmann constant and T is the temperature. The factor $(2J+1)$ accounts for the degeneracy of each energy level, i.e., the number of distinct states with the same energy.

In the high-temperature limit, where k_BT is much greater than the spacing between adjacent energy levels, the sum can be approximated by an integral:

$$Z_{\text{rot}} \approx \int_0^{\infty}(2J+1)e^{-\frac{E_J}{k_BT}}dJ.$$

Substituting E_J into the expression, the partition function becomes:

$$Z_{\text{rot}} \approx \int_0^{\infty}(2J+1)e^{-\frac{BJ(J+1)}{k_BT}}dJ.$$

By changing variables to $u = BJ(J+1)/(k_BT)$ and performing the integral, we find:

$$Z_{\text{rot}} \approx \frac{k_BT}{B},$$

which indicates that the partition function is directly proportional to the temperature.

The internal energy U of a system in thermal equilibrium is given by the derivative of the partition function with respect to the inverse temperature $\beta = 1/(k_B T)$:

$$U = -\frac{\partial}{\partial \beta} \log(Z_{\text{rot}}).$$

Substituting Z_{rot} into this expression and differentiating gives:

$$U = k_B T^2 \frac{\partial}{\partial T} \left(\log \left(\frac{k_B T}{B} \right) \right).$$

After carrying out the differentiation, we arrive at a simplified form for the internal energy:

$$U = k_B T.$$

The heat capacity at constant volume C_V is the temperature derivative of the internal energy:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V.$$

Thus, we find that the heat capacity at constant volume for a diatomic molecule treated as a rigid rotor is:

$$C_V = k_B.$$

This result, derived under the assumption of high temperature, indicates that each degree of rotational freedom contributes an amount k_B to the heat capacity, which is consistent with the equipartition theorem.

5.10.0.1. *Entropy.* The entropy S of a thermodynamic system in the canonical ensemble can be derived from the partition function Z and the internal energy U. The relationship between these quantities is given by the following equation:

$$S = k_B \left(\log Z + \frac{U}{k_B T} \right)$$

Here, k_B is the Boltzmann constant, T is the absolute temperature, and Z is the partition function of the system. The internal energy U can be obtained from the partition function by taking the derivative of $\log Z$ with respect to the inverse temperature $\beta = \frac{1}{k_B T}$.

For a diatomic molecule, considering only its rotational degrees of freedom, the partition function Z_{rot} can be written as:

$$Z_{rot} = \frac{k_B T}{\sigma h B}$$

In this expression, σ represents the symmetry number of the molecule, h is Planck's constant, and B is the rotational constant. The internal energy U_{rot} is the derivative of $\log Z_{rot}$ with respect to β:

$$U_{rot} = -\frac{\partial}{\partial \beta} \log \left(\frac{\beta}{\sigma h B} \right)$$

Carrying out the differentiation, we obtain:

$$U_{rot} = \frac{\partial}{\partial \beta} \log \beta = \frac{1}{\beta} = k_B T$$

Substituting U_{rot} back into the expression for entropy, we get:

$$S = k_B \left(\log Z_{rot} + \frac{U_{rot}}{k_B T} \right)$$

$$S = k_B \log \left(\frac{k_B T}{\sigma h B} \right) + k_B$$

This final expression gives us the entropy of a diatomic molecule considering only the rotational degrees of freedom. It is important to note that in a complete description of the molecule, contributions from vibrational, translational, and possibly electronic degrees of freedom would also need to be considered to obtain the total entropy of the system.

The first term of S is the thermal contribution to the entropy. It is dependent on the temperature T and reflects the increased disorder and number of accessible rotational states at higher temperatures. This term increases logarithmically with temperature, capturing the effect of temperature on the rotational state distribution.

The second term, k_B, represents the zero-point entropy. This term arises due to the quantum mechanical nature of the molecule and indicates that there is an inherent amount of disorder present in the molecule's rotational state even at the limit of zero temperature. This term is significant because it suggests an intrinsic level of randomness in the quantum state of the molecule, which is not accounted for in classical descriptions of entropy. The presence of zero-point energy in quantum systems leads to this non-zero entropy contribution at absolute zero, illustrating a departure from the classical third law of thermodynamics.

5.10.0.2. *Rotational, Vibrational and Rovibrational Degrees of Freedom.* The Hamiltonian $\hat{\mathcal{H}}$ for a diatomic molecule that includes both rotational and vibrational energies, and their coupling, is:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{vib}} + \hat{\mathcal{H}}_{\text{rot}} + \hat{\mathcal{H}}_{\text{rovib}},$$

where:

- $\hat{\mathcal{H}}_{\text{vib}}$ is the vibrational Hamiltonian, which for a harmonic oscillator is given by:

  $$\hat{\mathcal{H}}_{\text{vib}} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}\mu\omega^2\hat{q}^2,$$

  where μ is the reduced mass of the diatomic molecule, ω is the angular frequency of vibration, $\hat{p}$ is the momentum operator, and $\hat{q}$ is the displacement operator from the equilibrium bond length.

- $\hat{\mathcal{H}}_{\text{rot}}$ is the rotational Hamiltonian, represented by the rigid rotor model:

  $$\hat{\mathcal{H}}_{\text{rot}} = \frac{\hat{L}^2}{2I},$$

where $\hat{L}$ is the angular momentum operator, and I is the moment of inertia of the molecule about the axis of rotation.

- $\hat{\mathcal{H}}_{\text{rovib}}$ is the Hamiltonian representing the coupling between vibration and rotation, which can be derived as follows:
$$\hat{\mathcal{H}}_{\text{rovib}} = -\frac{\hat{L}^2}{2\mu^2 r^3}\hat{q},$$
where r is the internuclear distance. This term arises due to the change in the moment of inertia as the molecule vibrates.

The derivation of the rovibrational coupling term, $\hat{\mathcal{H}}_{\text{rovib}}$, involves considering the changes in the moment of inertia I as a function of the internuclear distance r, which itself is a function of the vibrational motion. The moment of inertia is given by $I = \mu r^2$, and when the molecule vibrates, r changes, thus affecting I and subsequently the rotational energy levels. The coupling term reflects how the rotational motion is affected by the vibrational motion through this changing moment of inertia.

5.11. Couplings that Prevent Factorization of the Partition Function

So far we have only seen the case where the partition factors out because there is no interaction between the different degrees of freedom. When interactions are present, the partition function no longer factorizes into a product of partition functions corresponding to the different degrees of freedom. In this section we discuss examples of interactions that would typically be encountered in real-life situations.

5.11.1. Rovibrational Coupling in Diatomic Molecules. In the quantum mechanical treatment of diatomic molecules, the Hamiltonian must account for both rotational and vibrational energies. When these two motions are considered independently, the moment of inertia is assumed to be fixed for rotational motion, and the internuclear distance remains constant for vibrational motion. However, in a more accurate picture, these two types of motion are coupled because the internuclear distance, and hence the moment of inertia, changes with vibration.

The kinetic energy part of the molecular Hamiltonian without an external field is given by
$$\hat{T} = \frac{\hat{P}_R^2}{2\mu} + \frac{\hat{L}^2}{2I(r)},$$
where $\hat{P}_R$ is the radial momentum operator, μ is the reduced mass of the molecule, $\hat{L}$ is the angular momentum operator, and $I(r)$ is the moment of inertia as a function of the internuclear distance r. The internuclear distance can be expanded about the equilibrium bond length r_e:
$$r = r_e + \hat{q},$$

with $\hat{q}$ representing the displacement from equilibrium. Consequently, the moment of inertia can be expressed as a Taylor series around r_e:

$$I(r) \approx I(r_e) + \left(\frac{\partial I}{\partial r}\right)_{r=r_e} \hat{q} + \frac{1}{2}\left(\frac{\partial^2 I}{\partial r^2}\right)_{r=r_e} \hat{q}^2 + \dots$$

For small vibrational motions, higher-order terms can be neglected, leading to an approximation of the moment of inertia by its value at the equilibrium bond length, $I(r) \approx I(r_e)$. This simplification, however, introduces a coupling between rotational and vibrational motions through the $\hat{q}$ dependence of the rotational kinetic energy:

$$\frac{\hat{L}^2}{2I(r)} \approx \frac{\hat{L}^2}{2I(r_e)} - \frac{\hat{L}^2}{2I(r_e)^2}\left(\frac{\partial I}{\partial r}\right)_{r=r_e} \hat{q}.$$

The first term is the standard rotational kinetic energy, while the second term represents the rovibrational coupling. Upon substituting $\left(\frac{\partial I}{\partial r}\right)_{r=r_e} = 2\mu r_e$, the rovibrational coupling term in the Hamiltonian can be written as

$$\hat{\mathcal{H}}_{\text{rovib}} = -\frac{\hat{L}^2}{2\mu^2 r_e^3}\hat{q}.$$

This term is added to the rotational and vibrational Hamiltonians to account for the rovibrational coupling. It should be noted that this derivation assumes harmonic vibrations and a rigid rotor for rotations. In a more rigorous treatment, anharmonicities and non-rigid rotor effects would introduce additional terms into the Hamiltonian.

5.11.2. Different Types of Couplings in Diatomic Molecules. In diatomic molecules, the internal motions such as rotation and vibration are not always independent. There are several couplings between different mechanical modes of motion, which can influence the energy levels and spectroscopic transitions. Here, we discuss the most significant couplings and their contributions to the molecular Hamiltonian.

5.11.2.1. *Rovibrational Coupling.* Rovibrational coupling arises from the interaction between rotational and vibrational motions. The rotational-vibrational Hamiltonian can be expressed as:

$$\hat{\mathcal{H}}_{\text{rovib}} = \hat{\mathcal{H}}_{\text{vib}} + \hat{\mathcal{H}}_{\text{rot}} + \hat{\mathcal{H}}_{\text{rovib-coupling}},$$

where $\hat{\mathcal{H}}_{\text{vib}}$ is the vibrational Hamiltonian, $\hat{\mathcal{H}}_{\text{rot}}$ is the rotational Hamiltonian, and $\hat{\mathcal{H}}_{\text{rovib-coupling}}$ represents the rovibrational coupling term.

5.11.2.2. *Spin-Orbit Coupling.* Spin-orbit coupling occurs due to the interaction between the spin of the electron and its orbital angular momentum, leading to fine structure in electronic transitions. The Hamiltonian for spin-orbit coupling is:

$$\hat{\mathcal{H}}_{\text{spin-orbit}} = \zeta \hat{\mathbf{L}} \cdot \hat{\mathbf{S}},$$

where ζ is the spin-orbit coupling constant, $\hat{\mathbf{L}}$ is the orbital angular momentum operator, and $\hat{\mathbf{S}}$ is the spin angular momentum operator.

5.11.2.3. *Spin-Rotation Coupling.* Spin-rotation coupling is the interaction between the rotational motion of the molecule and the spin of the electrons. Its Hamiltonian is given by:

$$\hat{\mathcal{H}}_{\text{spin-rotation}} = \gamma \hat{\mathbf{J}} \cdot \hat{\mathbf{S}},$$

where γ is the spin-rotation coupling constant and $\hat{\mathbf{J}}$ is the total angular momentum operator excluding spin.

5.11.2.4. *Spin-Spin Coupling.* In molecules with multiple unpaired electrons, the spins can interact with each other. The Hamiltonian for spin-spin coupling is:

$$\hat{\mathcal{H}}_{\text{spin-spin}} = \lambda \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2,$$

where λ is the spin-spin coupling constant, and $\hat{\mathbf{S}}_1$, $\hat{\mathbf{S}}_2$ are the spin angular momentum operators for the two electrons.

5.11.2.5. *Coriolis Coupling.* Coriolis coupling is the result of the Coriolis force acting on the nuclei in a rotating molecule, coupling the vibrational and rotational motions. The Hamiltonian for Coriolis coupling is:

$$\hat{\mathcal{H}}_{\text{Coriolis}} = -\xi(\hat{\mathbf{J}} \cdot \hat{\mathbf{p}}),$$

where ξ is the Coriolis coupling coefficient, $\hat{\mathbf{J}}$ is the rotational angular momentum operator, and $\hat{\mathbf{p}}$ is the vibrational angular momentum operator.

5.11.2.6. *Anharmonic Coupling.* The anharmonic coupling accounts for the deviations from the ideal harmonic oscillator model. The anharmonic terms in the vibrational Hamiltonian are necessary to describe the real molecular vibrations more accurately. The anharmonic Hamiltonian can be expanded as:

$$\hat{\mathcal{H}}_{\text{anharmonic}} = \hat{H}_{\text{vib}} + x_e \hat{Q}^3 + y_e \hat{Q}^4 + \dots,$$

where $\hat{Q}$ is the vibrational coordinate, x_e and y_e are the anharmonic constants for the cubic and quartic terms, respectively. These terms become significant for large amplitude vibrations and are particularly important for understanding the vibrational spectra of molecules at high energy levels.

5.11.2.7. *Centrifugal Distortion.* Centrifugal distortion occurs due to the stretching of the molecular bond as the molecule rotates. Its Hamiltonian is:

$$\hat{\mathcal{H}}_{\text{centrifugal}} = \delta J^2,$$

where δ is the centrifugal distortion constant and J is the rotational quantum number.

Each of these Hamiltonian contributions must be considered to accurately describe the energy levels of diatomic molecules, particularly in high-resolution spectroscopic investigations.

5.11.3. Can These Couplings Lead to Breakdown of the Born-Oppenheimer Approximation? The breakdown of the Born-Oppenheimer approximation is most directly related to non-adiabatic couplings. The Born-Oppenheimer approximation simplifies molecular Hamiltonians by assuming that the electronic motion and the nuclear motion can be separated due to their large difference in mass. This leads to the treatment of electronic states without considering the nuclear kinetic energy operator.

However, when there are close-lying electronic states or when the nuclei are moving rapidly (which can happen at higher energies), the electronic and nuclear motions can no longer be considered independent. This results in non-adiabatic couplings, where transitions between different electronic states can occur due to the influence of nuclear motion.

In contrast, rovibrational coupling is still within the realm of the Born-Oppenheimer approximation but considers the interaction between rotational and vibrational motions of the nuclei. Anharmonic coupling, similarly, involves higher-order corrections to the vibrational motion but doesn't necessarily imply a breakdown of the Born-Oppenheimer approximation.

Non-adiabatic coupling necessitates a more sophisticated treatment where both electronic and nuclear degrees of freedom are solved simultaneously, or where corrections to the Born-Oppenheimer approximation are included to account for the coupling between electronic states induced by nuclear motion.

5.12. Spectral Decomposition in Quantum Mechanics

Quantum mechanics fundamentally relies on the mathematical framework of linear algebra, particularly the properties of Hermitian operators. A key result in this context is the spectral theorem, which provides a method for expressing Hermitian operators, representing observable quantities, as a sum of projection operators scaled by their eigenvalues. This theorem has profound implications in quantum mechanics, especially in the analysis of quantum states and the probabilistic interpretation of quantum measurements.

5.12.1. Spectral Theorem. Let $\hat{A}$ be a Hermitian operator on a finite-dimensional Hilbert space. The spectral theorem states that $\hat{A}$ can be decomposed as:

$$\hat{A} = \sum_i \lambda_i \hat{P}_i \tag{5.2}$$

where λ_i are the eigenvalues of $\hat{A}$, and $\hat{P}_i$ are the orthogonal projection operators onto the eigenspaces associated with each λ_i. These projection operators satisfy $\hat{P}_i^2 = \hat{P}_i$ and $\hat{P}_i^\dagger = \hat{P}_i$, with † denoting the Hermitian conjugate.

5.12.2. Decomposition of the Density Matrix. In the realm of quantum mechanics, the density matrix ρ describes the state of a quantum system, accommodating both pure and mixed states. Applying the spectral theorem to ρ, a Hermitian operator, yields:

$$\rho = \sum_i p_i |\psi_i\rangle\langle\psi_i| \tag{5.3}$$

Here, $|\psi_i\rangle$ are the orthonormal eigenstates of ρ, and p_i are the corresponding eigenvalues, representing the probabilities of the system being in each of these states. This form is essential for various applications in quantum mechanics.

5.12.3. Trivial (Already in Diagonal Form) Example. Consider a quantum system of a single spin-1/2 particle, where the density matrix ρ describes a mixed state. Assume the system is in a superposition of spin-up and spin-down states along the z-axis. The density matrix in this case can be represented as:

$$\rho = p|\uparrow\rangle\langle\uparrow| + (1-p)|\downarrow\rangle\langle\downarrow| \tag{5.4}$$

where $|\uparrow\rangle$ and $|\downarrow\rangle$ are the eigenstates of the spin operator $\hat{S}_z$, and $0 \leq p \leq 1$.

To find the spectral decomposition of ρ, we observe that the eigenvalues are directly p and $1-p$, with the corresponding eigenstates being $|\uparrow\rangle$ and $|\downarrow\rangle$ respectively. Therefore, the spectral decomposition of ρ is already achieved in its given form.

This example illustrates the practical use of the spectral theorem in analyzing quantum states, particularly in understanding mixed states in terms of probabilities associated with different quantum states.

5.12.4. Less Trivial Example: Two-Level Quantum System (Qubit). Consider a two-level quantum system represented by a spin-1/2 particle or qubit. The Hilbert space of this system is two-dimensional, spanned by the basis vectors $|\psi_1\rangle$ and $|\psi_2\rangle$. Let's consider a density matrix ρ for this system, which is not diagonal in this basis:

$$\rho = \begin{pmatrix} a & b \\ b^* & 1-a \end{pmatrix} \tag{5.5}$$

where $0 \leq a \leq 1$ and $|b|^2 \leq a(1-a)$ for the matrix to be positive and have a trace of 1.

To perform the spectral decomposition of ρ, we first find its eigenvalues and eigenvectors. The eigenvalues $\lambda_{1,2}$ are found by solving the characteristic equation $\det(\rho - \lambda I) = 0$, yielding:

$$\lambda_{1,2} = \frac{1 \pm \sqrt{(2a-1)^2 + 4|b|^2}}{2} \tag{5.6}$$

The corresponding eigenvectors, $|v_1\rangle$ and $|v_2\rangle$, can be found by solving $(\rho - \lambda_{1,2} I)|v_{1,2}\rangle = 0$. The normalized eigenvectors will be:

$$|v_1\rangle = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \quad |v_2\rangle = \begin{pmatrix} -\beta^* \\ \alpha^* \end{pmatrix} \tag{5.7}$$

where α and β are complex numbers determined by the above equations and normalization conditions.

Finally, the spectral decomposition of ρ is given by:

$$\rho = \lambda_1|v_1\rangle\langle v_1| + \lambda_2|v_2\rangle\langle v_2| \tag{5.8}$$

This example demonstrates the process of spectral decomposition in a scenario where the density matrix represents a mixed state in a two-level system. Such a decomposition is fundamental in understanding the statistical properties of quantum systems, particularly in contexts where the basis states are not immediately apparent.

5.13. Comparison of Canonical Density Matrix and Classical Probability Density Measure

In statistical mechanics, understanding the distinctions and parallels between quantum and classical systems is fundamental. The canonical density matrix in quantum mechanics and the classical probability density measure in the context of the canonical ensemble are pivotal concepts in this regard.

5.13.1. Canonical Density Matrix in Quantum Mechanics. The canonical density matrix ρ in quantum mechanics describes the state of a quantum system in thermal equilibrium with a heat bath at temperature T. It is given by:

$$\rho = \frac{\exp(-\beta\mathcal{H})}{\mathrm{Tr}[\exp(-\beta\mathcal{H})]} \tag{5.9}$$

where $\mathcal{H}$ is the Hamiltonian operator of the system, $\beta = \frac{1}{k_B T}$, and Tr denotes the trace. This matrix encapsulates both the probabilistic nature of quantum states and the statistical distribution over these states due to thermal fluctuations.

We note that the denominator is a sum over states:

$$\mathrm{Tr}[\exp(-\beta\mathcal{H})] = \sum_n \langle n| \exp(-\beta\mathcal{H})|n\rangle \,,$$

where n is a set of quantum numbers that labels all possible microstates. The trace can be computed using any[1] basis. And if the wavefunctions are chosen to be energy eigenstates, i.e.

$$\mathcal{H}\,|\phi_i\rangle = E_i\,|\phi_i\rangle \,,$$

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[1] It is a theorem of linear algebra that change of basis does not change the value of the trace, i.e. take $\mathrm{Tr}A = \sum_n \langle n|A|n\rangle$ and insert the unit matrix $B^\dagger B = \mathbb{I}$ as follows $\sum_n \langle n|AB^\dagger B|n\rangle = \sum_n \langle n|BAB^\dagger|n\rangle = \sum_n \langle \psi_n|A|\psi_n\rangle$, where $|\psi_n\rangle = B^\dagger\,|n\rangle$.

the sum over states can be computed using the "good quantum numbers" that label this stationary state:

$$\mathrm{Tr}[\exp(-\beta\mathcal{H})] = \sum_i \langle\phi_i|\exp(-\beta\mathcal{H})|\phi_i\rangle = \sum_i \exp(-\beta E_i) = \sum_E W(E)\exp(-\beta E).$$

where the last expression is a sum over energy levels ϵ and the previous one is a sum over states i. $W(E)$ is the degeneracy of level E.

5.13.2. Classical Probability Density Measure. In classical statistical mechanics, the probability density in phase space for a system in thermal equilibrium is described by:

$$f(p,q) = \frac{1}{Z}\exp(-\beta\mathcal{H}(p,q)) \tag{5.10}$$

Here, $\mathcal{H}(p,q)$ is the classical Hamiltonian as a function of momenta p and coordinates q, and Z is the classical partition function. This function represents the probability density of finding the system in a particular state in phase space.

5.13.3. Similarities. Both formulations serve to describe the statistical distribution of states in thermal equilibrium. They both act as probability measures, where the numerator, $e^{-\beta E_i}$ vs $e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q})}$, is a weight factor determined by the ratio of microstate energy, E_i vs $\mathcal{H}(\mathbf{p},\mathbf{q})$, to the thermal energy, k_BT. In classical mechanics the microstates are labeled by $(\mathbf{p},\mathbf{q}) \in \mathbb{R}^{6N}$. In quantum mechanics, i is a multi-index. For example, $i = (n, l, m_l, m_S)$ for the hydrogen atom. In both cases, the denominator Z is a sum over states, $Z = \sum_i e^{-\beta E_i}$ vs $\int_\Gamma e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q})}\, d^{3N}\mathbf{p}\, d^{3N}\mathbf{q}$. The canonical densities are derived from the principle of maximizing entropy subject to the constraint of a fixed average energy, embodying the Boltzmann factor $\exp(-\beta\mathcal{H})$. This factor plays a central role in both the quantum and classical descriptions, dictating the likelihood of system states based on their energy.

5.13.4. Differences. The key differences arise from the underlying frameworks:

- **State Representation**: In quantum mechanics, states are represented by operators in Hilbert space. We label them using a set of quantum numbers. For example, the spins on a lattice (up, down) are labeled by microstates such as $i = (s_1, s_2, \ldots, s_N)$, where $s_j = \pm 1$. In classical mechanics, they are points in phase space.
- **Statistical Interpretation**: The quantum density matrix provides probabilities for observing various states upon measurement, a concept absent in classical mechanics. This is because of the inherently probabilistic nature of measurement in quantum mechanics. In classical mechanics the trajectories are deterministic.
- **Computation of Averages**: In quantum mechanics, averages of observables are computed using the trace operation with the density matrix, whereas in classical mechanics, averages are computed as integrals over phase space. Of course, integrals are summations (Riemannian sums). In quantum mechanics, the trace symbol stands for "'summation" over the discrete indices and "integration" over the continuous variables (e.g. $\mathbf{x}$ or $\mathbf{p}$).

5.13.5. Examples. Quantum Harmonic Oscillator: The canonical density matrix for a quantum harmonic oscillator can be derived using its Hamiltonian, leading to a description of the energy level populations at different temperatures.

Classical Ideal Gas: The classical probability density measure for an ideal gas can be computed using the Hamiltonian of particles in a box, providing insights into the distribution of particle velocities and positions.

While the canonical density matrix and classical probability density measure both describe systems in thermal equilibrium, they reflect the fundamental differences between quantum and classical mechanics. Understanding these concepts is crucial in the study of statistical mechanics, bridging the gap between microscopic and macroscopic phenomena.

5.14. Canonical Density Matrix of a Spin-1/2 Qubit in a Magnetic Field

The canonical density matrix is a fundamental concept in statistical mechanics, especially in the quantum regime. It describes the statistical state of a quantum system in thermal equilibrium with a heat bath at temperature T. For a spin-1/2 particle in a magnetic field, the Hamiltonian typically includes the Zeeman interaction, leading to an interesting exploration of quantum statistical mechanics.

5.14.1. Hamiltonian of the System. Consider a spin-1/2 particle in a magnetic field $\vec{B}$. The Hamiltonian $\mathcal{H}$ of this system, considering only the Zeeman interaction, is given by:

$$\mathcal{H} = -\gamma \vec{S} \cdot \vec{B}$$

where γ is the gyromagnetic ratio, and $\vec{S}$ is the spin operator. For simplicity, let's assume the magnetic field is oriented along the z-axis, $\vec{B} = B\hat{z}$. Then, the Hamiltonian simplifies to:

$$\mathcal{H} = -\gamma S_z B.$$

Using the Pauli matrices, S_z can be expressed as $\frac{\hbar}{2}\sigma_z$, leading to:

$$\mathcal{H} = -\frac{\gamma \hbar B}{2}\sigma_z.$$

5.14.2. Canonical Density Matrix. The canonical density matrix ρ for a quantum system in thermal equilibrium is defined as:

$$\rho = \frac{\exp(-\beta H)}{\mathrm{Tr}[\exp(-\beta \mathcal{H})]}$$

where $\beta = \frac{1}{k_B T}$, with k_B being the Boltzmann constant and T the temperature. Given our Hamiltonian $\mathcal{H} = -\frac{\gamma \hbar B}{2}\sigma_z$, the exponential term in the density matrix becomes:

$$\exp(-\beta \mathcal{H}) = \exp\left(\frac{\beta \gamma \hbar B}{2}\sigma_z\right) = \begin{pmatrix} e^{\frac{\beta \gamma \hbar B}{2}} & 0 \\ 0 & e^{-\frac{\beta \gamma \hbar B}{2}} \end{pmatrix} \tag{5.11}$$

This direct computation of the exponential of the Hamiltonian leverages the diagonal nature of σ_z.

5.14.3. Exponential of the Hamiltonian.

The exponential of the Hamiltonian, involving the Pauli σ_z matrix, can be simplified due to the diagonal nature of σ_z. The σ_z matrix is given by:

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{5.12}$$

Since σ_z is diagonal, exponentiating it is straightforward and involves exponentiating its diagonal elements. Thus, the exponential of a scalar multiplied by σ_z is:

$$\exp\left(\frac{\beta\gamma\hbar B}{2}\sigma_z\right) = \exp\left(\frac{\beta\gamma\hbar B}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right) = \begin{pmatrix} \exp\left(\frac{\beta\gamma\hbar B}{2}\right) & 0 \\ 0 & \exp\left(-\frac{\beta\gamma\hbar B}{2}\right) \end{pmatrix} \tag{5.13}$$

This result is obtained simply by taking the exponential of each of the diagonal elements. In matrix form, it appears as:

$$\exp\left(\frac{\beta\gamma\hbar B}{2}\sigma_z\right) = \begin{pmatrix} e^{\frac{\beta\gamma\hbar B}{2}} & 0 \\ 0 & e^{-\frac{\beta\gamma\hbar B}{2}} \end{pmatrix} \tag{5.14}$$

This matrix clearly demonstrates the simplicity of the operation due to the diagonal structure of σ_z. Exponentiating a diagonal matrix in this way is a powerful yet deceptively simple method often used in quantum mechanics and statistical physics, particularly when dealing with spin systems and their interactions with external fields.

5.14.4. Partition Function and Final Form of ρ.

The partition function Z, which is the denominator in the expression for ρ, is the trace of the exponential of the Hamiltonian. It can be computed as:

$$Z = \mathrm{Tr}\left[\exp\left(\frac{\beta\gamma\hbar B}{2}\sigma_z\right)\right] = \mathrm{Tr}\begin{pmatrix} e^{\frac{\beta\gamma\hbar B}{2}} & 0 \\ 0 & e^{-\frac{\beta\gamma\hbar B}{2}} \end{pmatrix} = e^{\frac{\beta\gamma\hbar B}{2}} + e^{-\frac{\beta\gamma\hbar B}{2}} \tag{5.15}$$

This leads to $Z = 2\cosh\left(\frac{\beta\gamma\hbar B}{2}\right)$, as $\cosh(x) = \frac{e^x+e^{-x}}{2}$.

Thus, the canonical density matrix ρ becomes:

$$\rho = \frac{1}{2\cosh\left(\frac{\beta\gamma\hbar B}{2}\right)}\begin{pmatrix} e^{\frac{\beta\gamma\hbar B}{2}} & 0 \\ 0 & e^{-\frac{\beta\gamma\hbar B}{2}} \end{pmatrix} \tag{5.16}$$

This form of ρ clearly demonstrates the distribution of the spin states in thermal equilibrium, influenced by the external magnetic field. The simplicity of the result, derived from the diagonal nature of the Hamiltonian, provides an elegant illustration of the interplay between quantum mechanics and statistical mechanics in the study of quantum systems.

The canonical density matrix for a quantum system, as demonstrated with the spin-1/2 particle in a magnetic field, elegantly connects the microscopic quantum properties with macroscopic thermodynamic quantities. This approach is central to the understanding of quantum statistical mechanics and provides a powerful tool for analyzing quantum systems in equilibrium.

5.15. Third Law - Nernst Theorem

We first need to recast the entropy in the language of quantum mechanics. In thermal equilibrium we have the canonical density matrix:

$$\rho = \frac{e^{-\beta \mathcal{H}}}{\mathrm{Tr}[e^{-\beta \mathcal{H}}]}.$$

In general, we may have an arbitrary density matrix ρ. A density matrix is defined as a matrix with unit trace that is positive semi-definite and Hermitian. In practice, we check that it is Hermitian, we find the eigenvalues of the matrix and check if they are non-negative and add up to 1. The unit trace requirement is identical to the requirement that a probability mass function $\{p_i\}$ add up to 1, $\sum_i p_i = 1$. Semi-positive definitiveness requires $p_i \geq 0$.

In quantum mechanics the entropy S is defined by (von Neumann):

$$S = -k_B \mathrm{Tr}[\rho \log \rho] = -k_B \langle \log \rho \rangle.$$

The second equality follows from the definition of average in quantum mechanics, $\langle A \rangle = \mathrm{Tr}[\rho A]$. You can easily check that it has the same form as the Gibbs-Shannon formula:

$$S = -k_B \sum_i p_i \log p_i.$$

Indeed, take an arbitrary density matrix ρ. For an ensemble that is a mixture of states $|\psi_j\rangle$ each with probability p_j, ρ is usually constructed from:

$$\rho = \sum_j p_j \left|\psi_j\right\rangle \left\langle\psi_j\right|.$$

According to the spectral theorem for operators (see Section 5.12.1), such a density matrix can be decomposed as a sum of projectors $|\phi_j\rangle \langle\phi_j|$:

$$\rho = \sum_j \lambda_j \left|\phi_j\right\rangle \left\langle\phi_j\right|,$$

where $|\phi_j\rangle$ are orthonormal vectors that are eigenvectors of ρ:

$$\rho \left|\phi_j\right\rangle = \lambda_j \left|\phi_j\right\rangle$$

and $\lambda_i \geq 0$, $\sum \lambda_i = 1$. Then,

$$S = -k_B \langle \log \rho \rangle = -k - B\mathrm{Tr}[\rho \log \rho] = -k_B \sum_j \langle \phi_j | \rho \log \rho | \phi_j \rangle = -k_B \sum_i \lambda_i \log \lambda_i.$$

This definition implies that the von Neumann entropy of any pure state is zero.

Theorem 5.2. *For the canonical ensemble,* $\rho = Z^{-1}e^{-\beta\mathcal{H}}$*, and the entropy is*

$$S = -k_B\langle\log\rho\rangle = \frac{1}{T}U + k_B\log Z$$

with $U = \langle\mathcal{H}\rangle$*.*

Proof. The statement is obvious by inspection and requires no proof. However, a detailed step-by-step explanation may be useful to some. Recall the definition of the canonical partition function:

$$Z = \sum_n e^{-E_n/k_BT} = \mathrm{Tr}e^{-\mathcal{H}/k_BT}$$

Using the energy eigenstates:

$$\mathcal{H}\left|n\right\rangle = E_n\left|n\right\rangle,$$

and the Gibbs distribution

$$p_n = \frac{1}{Z}e^{-E_n/k_BT},$$

we have:

$$\rho = \sum_m \left|m\right\rangle\left\langle m\right| Z^{-1}e^{-\mathcal{H}/k_BT}\sum_n \left|n\right\rangle\left\langle n\right| = \sum_n p_n\left|n\right\rangle\left\langle n\right|$$

Using the definition of average, we then find:

$$S = -k_B\langle\log\rho\rangle = -k_B\sum_m\langle m|\rho\log\rho|m\rangle$$

whereas substitution of $\rho = Z^{-1}e^{-\beta\mathcal{H}}$ gives:

$$\begin{aligned}S =& -k_B\sum_m\langle m|Z^{-1}e^{-\beta\mathcal{H}}\log(Z^{-1}e^{-\beta\mathcal{H}})|m\rangle\\ =&\frac{k_B}{Z}\sum_m\langle m|e^{-\beta\mathcal{H}}(\log Z + \beta\mathcal{H})|m\rangle\\ =&\frac{k_B}{Z}\sum_m e^{-\beta E_m}(\log Z + \beta E_m)\\ =&k_B\log Z + \frac{1}{T}U\end{aligned}$$

where $U = \frac{1}{Z}\sum_m e^{-\beta E_m}E_m = \sum_m p_mE_m = \langle\mathcal{H}\rangle$. □

Definition 5.3 (Nernst Theorem)**.** The determination of entropy as a function of temperature, denoted as $S(T)$, involves measuring the specific heat $C_X(T)$, where $X \in \{P, V\}$ represents either constant pressure (C_P) or constant volume (C_V). This measurement is carried out over the temperature interval $[T_0, T]$. The entropy is then obtained by integrating the relationship $TdS = \delta Q$ with $\delta Q = C_XdT$, leading to the expression:

$$S(T) = S_0 + \int_{T_0}^{T}\frac{C_X(T')}{T'}\,dT', \tag{5.17}$$

where S_0 is the value of entropy at the initial temperature T_0. This integration assumes reversible thermodynamic processes.

Nernst's theorem, often regarded as the Third Law of Thermodynamics, is formulated as:

$$\lim_{T\to 0} \frac{S(T)}{N} = 0, \tag{5.18}$$

where N denotes the number of particles or lattice sites. This theorem states that the entropy per particle approaches zero as the temperature approaches absolute zero, under ideal conditions such as a perfect crystal. In the context of statistical mechanics, this theorem is supported by quantum mechanics, which provides a microscopic explanation for the behavior of systems at very low temperatures, highlighting the role of quantum effects and imperfections in real materials.

According to statistical mechanics, the value of the entropy at absolute zero, $T = 0$, depends on the degeneracy of the ground state. We assume that the ground state energy E_0 is $W(E_0)$-fold degenerate. Let $P_0 = \sum_i |0_i\rangle\langle 0_i|$ be the projection operator[2] onto states with $E = E_0$. Here, $|0_i\rangle$ are the kets for which $\mathcal{H}|0_i\rangle = E_0|0_i\rangle$ and i is the index of degeneracy. (There can be several wavefunctions associated with the ground state energy, if that level is degenerate.) Then the density matrix of the canonical ensemble can be cast in the form

$$\rho = \frac{e^{-\beta\mathcal{H}}}{\mathrm{Tr}[e^{-\beta\mathcal{H}}]} = \frac{\sum_n e^{-\beta E_n}|n\rangle\langle n|}{\sum_n e^{-\beta E_n}} = \frac{\sum_i |0_i\rangle\langle 0_i| + \sum_{n>0} e^{-\beta(E_n-E_0)}|n\rangle\langle n|}{W(E_0) + \sum_{n>0} e^{-\beta(E_n-E_0)}},$$

where: 1) we have divided numerator and denominator by $e^{-\beta E_0}$, 2) in the numerator and denominator we used a sum over states (denoted as $\sum_n$).

Theorem 5.4. *For $T = 0$, this leads to $\rho(T=0) = \frac{P_0}{W(E_0)}$, and thus for the entropy, to*

$$S(T=0) = -k_B\langle\log\rho\rangle = k_B \log W(E_0).$$

---

[2] An operator P is a projection operator when $P^2 = P$.

Proof. Substituting the definition, $P_0 = \sum_i |0_i\rangle \langle 0_i|$ into

$$\begin{aligned}
S(T=0) = &- k_B \langle \log \rho \rangle = -k_B \mathrm{Tr}[\rho \log \rho] = -k_B \sum_m \langle m | \frac{P_0}{W(E_0)} (\log P_0 - \log W(E_0)) | m \rangle \\
= &- \frac{k_B}{W(E_0)} \sum_m \langle m | \sum_i |0_i\rangle \langle 0_i| (\log \sum_k |0_k\rangle \langle 0_k| - \log W(E_0)) | m \rangle \\
= &- \frac{k_B}{W(E_0)} \sum_i \langle 0_i | (\log 1 - \log W(E_0)) | 0_i \rangle \\
= &\frac{k_B}{W(E_0)} \sum_i \langle 0_i | \log W(E_0) | 0_i \rangle = \frac{k_B}{W(E_0)} \log W(E_0) \underbrace{\sum_i \langle 0_i | 0_i \rangle}_{W(E_0)} \\
= &\frac{k_B}{\cancel{W(E_0)}} \log W(E_0) \cdot \cancel{W(E_0)} = k_B \log W(E_0).
\end{aligned}$$

□

The general opinion in mathematical physics is that the ground state of interacting systems should not be degenerate, or that the degree of degeneracy in any case should be considerably less than the number of particles. If $W(E_0) = \mathcal{O}(1)$ or even if $W(E_0) = \mathcal{O}(N)$, we find

$$\lim_{T \to 0} \frac{S(T=0)}{k_B N} = 0,$$

i.e. for such degrees of degeneracy, Nernst's theorem follows from quantum statistics.

Problem 134. Consider a non-interacting system of N spins, where the only interaction is of the Zeeman type. The Hamiltonian is $\mathcal{H} = -B \sum_{i=1}^{N} \sigma_i$, where $\sigma_i = \pm 1$. The microstates are denoted by N-tuples $(\sigma_1, \sigma_2, \ldots, \sigma_N)$. The macrostates are defined by the numbers of particles in each state, N_1 and N_2. These two numbers are constrained by the condition, $N_1 + N_2 = N$. The number of microstates in one macrostate (that is, the number of different microstates that belong to the same macrostate) is given by the binomial distribution

$$W(N_1) = \frac{N!}{N_1!(N-N_1)!} = \binom{N}{N_1}.$$

Show that the degeneracy of a macrostate when N is large is of order

$$S \sim \mathcal{O}(N).$$

Does this violate the Third Law?

Solution. Using the Stirling formula:

$$N! \approx \sqrt{2\pi N} \left(\frac{N}{e} \right)^N,$$

and substituting

$$\begin{aligned} W(N_1) =& \frac{N!}{N_1!(N-N_1)!} \\ \approx& \frac{\sqrt{2\pi N}(N/e)^N}{\sqrt{2\pi N_1}(N_1/e)^{N_1}\sqrt{2\pi(N-N_1)}((N-N_1)/e)^{N-N_1}} \end{aligned}$$

The binomial coefficient $\binom{n}{k}$ reaches a maximum when $k = n/2$. Therefore, we focus on this particular macrostate:

$$\begin{aligned} W(N/2) \approx& \frac{\sqrt{2\pi N}(N/e)^N}{\sqrt{2\pi(N/2)}((N/2)/e)^{N/2}\sqrt{2\pi(N/2)}((N/2)/e)^{N/2}} \\ \sim& \frac{1}{\sqrt{N}}2^N \end{aligned}$$

Thus,

$$S = -k_B \log W = -k_B(N\log 2 - \frac{1}{2}\log N).$$

This certainly appears to violate the law

$$\lim_{T\to 0}\frac{S(T=0)}{k_B N} = 0.$$

However, the state $k = N/2$ is only found in the high-temperature limit. (At high temperatures, the thermal energy dominates, so that half the spins point up and half point down along the axis of quantization.) In the limit $T \to 0$, only the ground state $(1, 1, 1, \ldots, 1)$ exists. You can “prove” this by writing down the density matrix in the zero and high-temperature temperature limits. (A useful exercise, if you have never done it.) In the ground state of the non-interacting spin system, the degeneracy is 1 (a finite number), and in this case, $\lim_{T\to 0}\frac{S(T=0)}{k_B N} = 0$, is satisfied. ■

Problem 135. Derive the canonical density matrix ρ for a non-interacting spin system in the high-temperature approximation and show that we get a maximally mixed state, $\rho(T \to \infty) = \frac{1}{2^N}\mathbb{I}$, where $\mathbb{I}$ is the $2^N \times 2^N$ unit matrix. Conversely, obtain ρ in the zero temperature limit and show that it is a projector $\rho(T = 0) = |0\rangle\langle 0|$, where $|0\rangle$ is the ground state wavefunction, i.e. $|0\rangle \equiv |111\ldots 1\rangle$.

It is best to formulate the Third Law taking into account the possibility of a residual entropy. This is in practice necessary for the following reasons: (i) there are model systems with greater ground-state degeneracies (ice, non-interacting magnetic moments); (ii) a very weak lifting of the degeneracy might make itself felt only at extremely low temperatures; (iii) a disordered metastable state can be ‘frozen in’ by rapid cooling and retains a finite residual entropy.

5.16. Planck's Law of Radiation

Planck's law of radiation describes the spectral density of electromagnetic radiation at a specific frequency for a black body in thermal equilibrium. A black body is an idealized physical body that absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence. In thermodynamics and quantum mechanics, a black body is a perfect emitter and absorber of radiation. Planck's law of radiation, derived from the quantization of energy and the statistical distribution of photons, provides a fundamental understanding of the electromagnetic radiation emitted by a black body. This law explains the spectral distribution of radiation and is crucial in fields like astrophysics, climate science, and the study of thermal radiation in various materials.

Energy States of Photons: Consider a black body at temperature T. The energy of a photon in the black body is given by $\epsilon = \hbar\omega$, where $\hbar$ is the reduced Planck constant and ω is the angular frequency of the photon.

Bose-Einstein Distribution: The average number of photons $\langle n_\omega \rangle$ in a state with energy ϵ is given by the Bose-Einstein distribution:

$$\langle n_\omega \rangle = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

where k_B is the Boltzmann constant.

Spectral Energy Density: The spectral energy density $u(\omega, T)$ in units of J/m^3/rad is the energy per unit volume per unit frequency. It can be obtained by multiplying the average number of photons (dimensionless) by the energy of each photon ($\hbar\omega$, in units of J) and the density of states $g(\omega)$ in units of states/m^3/rad:

$$u(\omega, T) = \langle n_\omega \rangle \cdot \hbar\omega \cdot g(\omega)$$

where $g(\omega)$ is the density of states function.

Density of States: The density of states for photons in three dimensions is given by:

$$g(\omega) = \frac{\omega^2 V}{\pi^2 c^3}$$

where ω is the angular frequency in rad/s, V is the volume of the black body in m^3, and c is the speed of light in m/s. The resulting density of states $g(\omega)$ has units of states/m^3/rad.

Planck's Radiation Formula: Substituting the Bose-Einstein distribution and the density of states into the expression for spectral energy density, we obtain Planck's radiation formula:

$$u(\omega, T) = \frac{\hbar\omega^3 V}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

where $\hbar$ (reduced Planck's constant) has units of J$\cdot$ s, ω (angular frequency) is in rad/s, V (volume) is in m^3, c (speed of light) is in m/s, k_B (Boltzmann's constant) is in J/K, and T (temperature) is in Kelvin (K). The spectral energy density $u(\omega, T)$ is given in J/m^3/rad.

Bose-Einstein Distribution from the Partition Function: Starting with the canonical partition function, which recognize to be a geometric series:

$$Z = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega_k n} = \frac{1}{1 - e^{-\beta\hbar\omega_k}}$$

Differentiating both sides with respect to β to introduce a factor of n:

Left-hand side:

$$\frac{d}{d\beta}\left(\sum_{n=0}^{\infty} e^{-\beta\hbar\omega_k n}\right) = \sum_{n=0}^{\infty}(-\hbar\omega_k n)e^{-\beta\hbar\omega_k n}.$$

Right-hand side:

$$\frac{d}{d\beta}\left(\frac{1}{1 - e^{-\beta\hbar\omega_k}}\right) = \frac{\hbar\omega_k e^{-\beta\hbar\omega_k}}{(1 - e^{-\beta\hbar\omega_k})^2}$$

Equating these, we find:

$$\sum_{n=0}^{\infty}(-\hbar\omega_k n)e^{-\beta\hbar\omega_k n} = \frac{\hbar\omega_k e^{-\beta\hbar\omega_k}}{(1 - e^{-\beta\hbar\omega_k})^2}.$$

Simplifying, we obtain:

$$\sum_{n=0}^{\infty} n e^{-\beta\hbar\omega_k n} = \frac{e^{-\beta\hbar\omega_k}}{(1 - e^{-\beta\hbar\omega_k})^2}.$$

Substituting this result back into the expression for $\langle n_{\mathbf{k},\lambda}\rangle$ yields the Planck distribution:

$$\langle n_{\mathbf{k},\lambda}\rangle = \frac{1}{e^{\beta\hbar\omega_k} - 1}.$$

5.17. Stefan-Boltzmann Law

The Stefan-Boltzmann law describes the power radiated from a black body in terms of its temperature. To derive this law, we start with Planck's law for black-body radiation and integrate over all frequencies and solid angles. Planck's law gives the energy density of electromagnetic radiation at a specific frequency ω and temperature T:

$$u(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

where $\hbar$ is the reduced Planck constant, c is the speed of light, k_B is the Boltzmann constant, and T is the temperature. The total energy density $U(T)$ is obtained by integrating $u(\omega, T)$ over all frequencies:

$$U(T) = \int_0^{\infty} u(\omega, T)\, d\omega = \int_0^{\infty} \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}\, d\omega$$

Introduce a dimensionless variable $x = \frac{\hbar\omega}{k_B T}$ to simplify the integral. The integral becomes:

$$U(T) = \int_0^\infty \frac{(k_B T)^4}{\pi^2 c^3 \hbar^3} \frac{x^3}{e^x - 1} \, dx$$

The integral of $\frac{x^3}{e^x-1}$ over x from 0 to ∞ is a standard integral in statistical mechanics, equal to $\frac{\pi^4}{15}$. Substituting the integral value, we find:

$$U(T) = \frac{(k_B T)^4}{\pi^2 c^3 \hbar^3} \cdot \frac{\pi^4}{15} = \frac{\pi^2 k_B^4}{15 c^3 \hbar^3} T^4$$

The power radiated per unit area P is given by $P = cU(T)$, leading to:

$$P = \sigma T^4$$

where σ is the Stefan-Boltzmann constant, given by $\sigma = \frac{\pi^2 k_B^4}{60 c^2 \hbar^3}$. The Stefan-Boltzmann law states that the total power radiated per unit area by a black body is proportional to the fourth power of its absolute temperature. It is useful in astronomy, where measurement of the power radiated (light intensity) from a celestial body can be used to infer its temperature.

5.18. Quantum Mechanical Derivation of Planck Distribution

The Hamiltonian for the radiation field in the second quantized form is typically expressed as a sum over all modes of the field. Each mode is characterized by a wave vector $\mathbf{k}$ and a polarization index λ. The Hamiltonian is

$$\hat{\mathcal{H}} = \sum_{\mathbf{k},\lambda} \hbar\omega_{\mathbf{k}} \left(\hat{a}^\dagger_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda} + \frac{1}{2} \right).$$

Here $\hat{a}^\dagger_{\mathbf{k},\lambda}$ and $\hat{a}_{\mathbf{k},\lambda}$ are the creation and annihilation operators for a photon in the mode $(\mathbf{k}, \lambda)$, and $\omega_{\mathbf{k}}$ is the angular frequency of that mode. These operators obey the commutation relations of bosonic particles. The term $\frac{1}{2}\hbar\omega_{\mathbf{k}}$ represents the zero-point energy of each mode.

In this formulation, the number operator $\hat{n}_{\mathbf{k},\lambda} = \hat{a}^\dagger_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda}$ measures the number of photons in the mode $(\mathbf{k}, \lambda)$. The Hamiltonian can thus be interpreted as a sum over the energies of all the photons in the field, with each mode contributing its energy quantized in units of $\hbar\omega_{\mathbf{k}}$.

The term $\frac{1}{2}\hbar\omega_{\mathbf{k}}$ in the Hamiltonian represents the zero-point energy of each mode of the field. This is the energy that each mode possesses even in its ground state, due to the Heisenberg uncertainty principle. In many physical situations, especially when dealing with phenomena like the interaction of light with matter, only differences in energy are physically observable, not the absolute energy values. Therefore, the zero-point energy, being a constant for each mode, can often be omitted without affecting the physics of such phenomena.

The Hamiltonian without the zero-point energy term is given by:

$$\hat{\mathcal{H}} = \sum_{\mathbf{k},\lambda} \hbar\omega_{\mathbf{k}} \hat{a}^{\dagger}_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda}.$$

In this form, the Hamiltonian simply sums the energies of all the photons present in the field, and it's particularly convenient in contexts where zero-point energies are not relevant, such as in many calculations involving light-matter interactions or in situations where relative energies are the main focus.

The canonical partition function Z at temperature T for the radiation field is defined as the trace over the Fock space of the Boltzmann exponential:

$$Z = \mathrm{Tr}\left(e^{-\beta \hat{H}}\right),$$

where $\beta = \frac{1}{k_B T}$.

The Fock space for the radiation field is spanned by the states. $|\{n_{\mathbf{k},\lambda}\}\rangle$, where $\{n_{\mathbf{k},\lambda}\}$ denotes a set of occupation numbers for all modes $(\mathbf{k}, \lambda)$. This set is usually infinite, because in general there are an infinite number of modes. The partition function can be separated into a sum over the total occupation number N and a sum over the microstates for each value of N:

$$Z = \sum_{N=0}^{\infty} \sum_{\{n_{\mathbf{k},\lambda}\}\to N} \langle\{n_{\mathbf{k},\lambda}\}|e^{-\beta\hat{H}}|\{n_{\mathbf{k},\lambda}\}\rangle\,.$$

Since photons are bosons, the occupation number $n_{\mathbf{k},\lambda}$ for each mode can range from 0 to ∞. The Hamiltonian acts diagonally in this basis, giving

$$Z = \sum_{N=0}^{\infty} \sum_{\{n_{\mathbf{k},\lambda}\}\to N} e^{-\beta\hbar\omega_{\mathbf{k}}\hat{n}_{\mathbf{k},\lambda}}.$$

Simplifying further, since each mode is independent, the partition function can be written as a product of partition functions for each mode:

$$Z = \prod_{\mathbf{k},\lambda} \sum_{n_{\mathbf{k},\lambda}=0}^{\infty} e^{-\beta\hbar\omega_{\mathbf{k}}\hat{n}_{\mathbf{k},\lambda}}.$$

This is a geometric series for each mode, which sums to:

$$Z = \prod_{\mathbf{k},\lambda} \frac{1}{1 - e^{-\beta\hbar\omega_{\mathbf{k}}}}.$$

This final form of the partition function shows the contribution of each mode of the radiation field, with the product running over all possible modes characterized by wave vector $\mathbf{k}$ and polarization λ. Each term in the product is a geometric series representing the sum over the occupation number for that particular model.

To compute the average occupation number $\langle \hat{n}_{\mathbf{k},\lambda} \rangle$ for a given mode $(\mathbf{k}, \lambda)$ in the radiation field, we use the definition:

$$\langle \hat{n}_{\mathbf{k},\lambda} \rangle = \mathrm{Tr}[\hat{\rho}\, \hat{n}_{\mathbf{k},\lambda}] = \frac{\mathrm{Tr}[e^{-\beta \hat{\mathcal{H}}} \hat{n}_{\mathbf{k},\lambda}]}{Z},$$

where $\hat{\rho} = Z^{-1} e^{-\beta \hat{\mathcal{H}}}$ is the canonical density matrix and $\hat{n}_{\mathbf{k},\lambda} = \hat{a}^\dagger_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda}$ is the number operator for mode $(\mathbf{k}, \lambda)$.

Given that the Hamiltonian $\hat{\mathcal{H}} = \sum_{\mathbf{k},\lambda} \hbar\omega_{\mathbf{k}} \hat{a}^\dagger_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda}$ is the sum over all modes and acts diagonally in the Fock space, the trace operation can be decomposed over the states $|\{n_{\mathbf{k}',\lambda'}\}\rangle$:

$$\langle \hat{n}_{\mathbf{k},\lambda} \rangle = \frac{1}{Z} \sum_{\{n_{\mathbf{k}',\lambda'}\}} \langle \{n_{\mathbf{k}',\lambda'}\} | e^{-\beta \hat{\mathcal{H}}} \hat{n}_{\mathbf{k},\lambda} | \{n_{\mathbf{k}',\lambda'}\} \rangle \,.$$

The expression $e^{-\beta \hat{\mathcal{H}}}$ commutes with $\hat{n}_{\mathbf{k},\lambda}$ because they are diagonal in the same basis. Therefore, we can rewrite the expression as

$$\langle \hat{n}_{\mathbf{k},\lambda} \rangle = \frac{1}{Z} \sum_{\{n_{\mathbf{k}',\lambda'}\}} e^{-\beta \sum_{\mathbf{k}',\lambda'} \hbar\omega_{\mathbf{k}'} n_{\mathbf{k}',\lambda'}} n_{\mathbf{k},\lambda}.$$

Alternative Expression of Summation Over $\{n_{\mathbf{k}',\lambda'}\}$. In the formula

$$\langle \hat{n}_{\mathbf{k},\lambda} \rangle = \frac{1}{Z} \sum_{\{n_{\mathbf{k}',\lambda'}\}} e^{-\beta \sum_{\mathbf{k}',\lambda'} \hbar\omega_{\mathbf{k}'} n_{\mathbf{k}',\lambda'}} n_{\mathbf{k},\lambda}$$

we can express the summation over all configurations more explicitly. The formula becomes:

$$\langle \hat{n}_{\mathbf{k},\lambda} \rangle = \frac{1}{Z} \prod_{(\mathbf{k}'',\lambda'') \neq (\mathbf{k},\lambda)} \left(\sum_{n_{\mathbf{k}'',\lambda''}=0}^{\infty} \right) e^{-\beta\left(\hbar\omega_{\mathbf{k}} n_{\mathbf{k},\lambda} + \sum_{\mathbf{k}'',\lambda''} \hbar\omega_{\mathbf{k}''} n_{\mathbf{k}'',\lambda''}\right)} n_{\mathbf{k},\lambda}$$

Here, each summation $\sum_{n_{\mathbf{k}'',\lambda''}=0}^{\infty}$ runs over all possible occupation numbers for modes other than $(\mathbf{k}, \lambda)$, and the product $\prod_{(\mathbf{k}'',\lambda'') \neq (\mathbf{k},\lambda)}$ combines these for all other modes. The term $\hbar\omega_{\mathbf{k}} n_{\mathbf{k},\lambda}$ is separated to specifically account for the mode $(\mathbf{k}, \lambda)$.

Transformation of the Average Occupation Number Expression

We provide a detailed proof of transforming the expression for the average occupation number in Fock space from its original form to a product over modes. The starting point is the expression:

$$\langle \hat{n}_{\mathbf{k},\lambda} \rangle = \frac{1}{Z} \sum_{\{n_{\mathbf{k}',\lambda'}\}} e^{-\beta \sum_{\mathbf{k}',\lambda'} \hbar\omega_{\mathbf{k}'} n_{\mathbf{k}',\lambda'}} n_{\mathbf{k},\lambda}$$

The exponential of a summation can be decomposed:

$$e^{-\beta \sum_{\mathbf{k}',\lambda'} \hbar\omega_{\mathbf{k}'} n_{\mathbf{k}',\lambda'}} = \prod_{\mathbf{k}',\lambda'} e^{-\beta\hbar\omega_{\mathbf{k}'} n_{\mathbf{k}',\lambda'}}$$

Rewriting to isolate the mode $(\mathbf{k}, \lambda)$:

$$\prod_{\mathbf{k}',\lambda'} e^{-\beta\hbar\omega_{\mathbf{k}'} n_{\mathbf{k}',\lambda'}} = e^{-\beta\hbar\omega_{\mathbf{k}} n_{\mathbf{k},\lambda}} \prod_{(\mathbf{k}'',\lambda'')\neq(\mathbf{k},\lambda)} e^{-\beta\hbar\omega_{\mathbf{k}''} n_{\mathbf{k}'',\lambda''}}$$

Substituting back into the original expression and expressing the summation as a product:

$$\langle \hat{n}_{\mathbf{k},\lambda} \rangle = \frac{1}{Z} \left(\sum_{n_{\mathbf{k},\lambda}=0}^{\infty} \right) n_{\mathbf{k},\lambda} e^{-\beta\hbar\omega_{\mathbf{k}} n_{\mathbf{k},\lambda}} \prod_{(\mathbf{k}'',\lambda'')\neq(\mathbf{k},\lambda)} \left(\sum_{n_{\mathbf{k}'',\lambda''}=0}^{\infty} e^{-\beta\hbar\omega_{\mathbf{k}''} n_{\mathbf{k}'',\lambda''}} \right)$$

Remark 5.5. If you are seeing this type of expression for the first time, you should think about the use of summation indices in this formula. *Outer Summation.* The outer summation in the formula

$$\langle \hat{n}_{\mathbf{k},\lambda} \rangle = \frac{1}{Z} \sum_{\{n_{\mathbf{k}',\lambda'}\}} \langle \{n_{\mathbf{k}',\lambda'}\} | e^{-\beta\hat{\mathcal{H}}} \hat{n}_{\mathbf{k},\lambda} | \{n_{\mathbf{k}',\lambda'}\} \rangle$$

runs over all possible sets of occupation numbers $\{n_{\mathbf{k}',\lambda'}\}$ for each mode $(\mathbf{k}', \lambda')$ in the system. It represents a summation over all possible states in Fock space.
Inner Summation. The inner summation within the exponential, $e^{-\beta \sum_{\mathbf{k}',\lambda'} \hbar\omega_{\mathbf{k}'} n_{\mathbf{k}',\lambda'}}$, is over the energy contribution of each individual mode $(\mathbf{k}', \lambda')$ to the total Hamiltonian. For each state in the outer sum, this inner sum calculates the total energy of that state by summing up the energy contributions of each occupied mode.
The indices $n_{\mathbf{k}',\lambda'}$ are consistently used in both sums because we are summing over the same set of quantum numbers (modes). In each term of the outer sum, the inner sum calculates the total energy for that specific set of occupation numbers. The occupation number $n_{\mathbf{k},\lambda}$ outside the exponential is the specific occupation number for which the average is being calculated.

Since $n_{\mathbf{k},\lambda}$ is just a number, the occupation number for the state $|\{n_{\mathbf{k}',\lambda'}\}\rangle$, it can be taken out of the summation over other modes. The expression simplifies to:

$$\langle \hat{n}_{\mathbf{k},\lambda} \rangle = \frac{1}{Z} \sum_{n_{\mathbf{k},\lambda}=0}^{\infty} n_{\mathbf{k},\lambda} e^{-\beta\hbar\omega_{\mathbf{k}} n_{\mathbf{k},\lambda}} \prod_{(\mathbf{k}',\lambda')\neq(\mathbf{k},\lambda)} \sum_{n_{\mathbf{k}',\lambda'}=0}^{\infty} e^{-\beta\hbar\omega_{\mathbf{k}'} n_{\mathbf{k}',\lambda'}}.$$

Remark 5.6. Let's take a look at why the summation $\sum_{n_{\mathbf{k},\lambda}=0}^{\infty} n_{\mathbf{k},\lambda} e^{-\beta\hbar\omega_{\mathbf{k}} n_{\mathbf{k},\lambda}}$ arises in this context.

Decomposition in Fock Space. Initially, we sum over all possible sets of occupation numbers for all modes in the entire Fock space, covering all possible quantum states.

Isolating a Single Mode. Focusing on a specific mode $(\mathbf{k}, \lambda)$, we isolate the contribution of this mode from the entire set of occupation numbers.

Summing Over $n_{\mathbf{k},\lambda}$. For the mode $(\mathbf{k}, \lambda)$, the occupation number $n_{\mathbf{k},\lambda}$ can take any non-negative integer value. Therefore, we sum over all these possible values to account for every possible state of this mode:

$$\sum_{n_{\mathbf{k},\lambda}=0}^{\infty} n_{\mathbf{k},\lambda} e^{-\beta\hbar\omega_{\mathbf{k}} n_{\mathbf{k},\lambda}}$$

Product Over Other Modes. The product term accounts for the contribution of all other modes, summing over their possible occupation numbers separately.

This summation represents the statistical behavior of the mode $(\mathbf{k}, \lambda)$, considering all possible ways it can be populated under the given temperature conditions. It is a key principle in statistical mechanics to consider the contributions of all possible configurations to a statistical average.

5.19. Explicit Representation of Summation in Fock Space

The summation $\sum_{\{n_{\mathbf{k},\lambda}\}}$ over all states in Fock space can be explicitly represented as an infinite series of nested summations over occupation numbers for each mode.

5.19.1. Case 1: Bosonic Fock Space. The summation is represented as:

$$\sum_{\{n_{\mathbf{k},\lambda}\}} = \sum_{n_{\mathbf{k}_1,\lambda_1}=0}^{\infty} \sum_{n_{\mathbf{k}_2,\lambda_2}=0}^{\infty} \cdots \sum_{n_{\mathbf{k}_j,\lambda_j}=0}^{\infty} \cdots = \prod_{(\mathbf{k},\lambda)} \left(\sum_{n_{\mathbf{k},\lambda}=0}^{\infty} \right)$$

where each summation is over the occupation number $n_{\mathbf{k}_i,\lambda_i}$ for a specific mode $(\mathbf{k}_i, \lambda_i)$, running from 0 to ∞. The dots "..." indicate the continuation of this pattern for all modes in the system.

Each term in the overall summation corresponds to a specific configuration of particles across all modes, encompassing all possible states in the Fock space.

5.19.2. Case 2: Fermionic Fock Space. For fermionic systems, the Pauli exclusion principle restricts each mode in Fock space to be occupied by at most one fermion. Therefore, the summation over Fock space states for fermions is different from that for bosons. For a fermionic mode characterized by a wavevector $\mathbf{k}$ and a polarization λ, the occupation number $n_{\mathbf{k},\lambda}$ can only take the values 0 or 1. The summation for each fermionic mode is thus $\sum_{n_{\mathbf{k},\lambda}=0}^{1}$. The overall summation over fermionic Fock space is the product of these individual summations for each mode:

$$\prod_{(\mathbf{k},\lambda)}\left(\sum_{n_{\mathbf{k},\lambda}=0}^{1}\right)$$

This represents all possible configurations of fermions in the system.

5.19.3. Derivation of the Gibbs Distribution: Classical Case. We derive the Gibbs distribution by maximizing the Gibbs-Shannon entropy under the constraint of fixed total energy. The Gibbs-Shannon entropy is given by:

$$S = -k_B \sum_i p_i \log p_i$$

We have two constraints: 1) normalization: $\sum_i p_i = 1$. 2) fixed total energy: $\sum_i p_i E_i = \langle E\rangle$. Introducing Lagrange multipliers α and β, the function to maximize is:

$$\mathcal{L} = -k_B \sum_i p_i \log p_i - \alpha\left(\sum_i p_i - 1\right) - \beta\left(\sum_i p_i E_i - \langle E\rangle\right).$$

Setting the derivative to zero yields:

$$-k_B(1+\log p_i) - \alpha - \beta E_i = 0.$$

Solving for p_i we find $p_i = e^{-(1+\frac{\alpha}{k_B})}e^{-\frac{\beta E_i}{k_B}}$. We may absorb k_B into the definition of β. The factor $e^{-(1+\frac{\alpha}{k_B})}$ ends up being $1/Z$ due to normalization. Using normalization, we find:

$$p_i = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}.$$

5.19.4. Derivation of the Gibbs Distribution: Quantum Case. We derive the quantum Gibbs distribution by maximizing the von Neumann entropy in quantum statistical mechanics, $S = -k_B \mathrm{Tr}(\hat{\rho}\log\hat{\rho})$ subjected to two constraints: 1) normalization: $\mathrm{Tr}(\hat{\rho}) = 1$. 2) Fixed average energy: $\mathrm{Tr}(\hat{\rho}\hat{H}) = \langle E\rangle$. To deal with constraints we introduce Lagrange multipliers α and β. The function to maximize is then:

$$\mathcal{L} = -k_B \mathrm{Tr}(\hat{\rho}\log\hat{\rho}) - \alpha\left(\mathrm{Tr}(\hat{\rho}) - 1\right) - \beta\left(\mathrm{Tr}(\hat{\rho}\hat{H}) - \langle E\rangle\right)$$

Maximizing with respect to $\hat{\rho}$ yields $-k_B(\log\hat{\rho} + I) - \alpha I - \beta\hat{H} = 0$. Solving for $\hat{\rho}$ gives $\hat{\rho} = e^{-(1+\frac{\alpha}{k_B})I}e^{-\frac{\beta\hat{H}}{k_B}}$. We may absorb k_B into the definition of β. Also, the term $e^{-(1+\frac{\alpha}{k_B})}$ ends up being Z due to the requirement for normalization $\mathrm{Tr}[\hat{\rho}] = 1$. Using normalization, we find:

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{\mathrm{Tr}(e^{-\beta\hat{H}})}.$$

β is related to the temperature T: $\beta = \frac{1}{k_B T}$.

5.19.5. Derivation of the Grand Canonical Distribution: Quantum Case. Statistical operators such as

$$\hat{\rho} = \frac{e^{-\beta(\hat{\mathcal{H}}-\mu\hat{N})}}{\mathrm{Tr}[e^{-\beta(\hat{\mathcal{H}}-\mu\hat{N})}]}, \tag{5.19}$$

are required when our knowledge of the state of the system is incomplete. Here $\beta = \frac{1}{k_B T}$. The trace is performed in Fock space, i.e.

$$\mathrm{Tr}[\dots] = \sum_{n_1,\dots,n_\infty} \langle n_1,\dots,n_\infty|\dots|n_1,\dots,n_\infty\rangle\,.$$

The statistical operator can be derived from the principle of maximum entropy, which states that the entropy

$$S = -k_B \mathrm{Tr}[\hat{\rho}\log\hat{\rho}]$$

should reach a maximum for the true statistical operator, provided that the average energy and particle number are determined by

$$E = \mathrm{Tr}[\hat{\rho}\hat{\mathcal{H}}], \qquad N = \mathrm{Tr}[\hat{\rho}\hat{N}]. \tag{5.20}$$

This is obviously true if we minimize the thermodynamic potential

$$\Omega = \mathrm{Tr}\left[\hat{\rho}\left(\frac{1}{\beta}\log\hat{\rho} + \hat{\mathcal{H}} - \mu\hat{N}\right)\right]. \tag{5.21}$$

where the constraints (5.20) are taken into account by means of Lagrange multipliers, i.e., β and the chemical potential μ. Their meaning becomes clear when we rewrite (5.21) in the familiar form

$$\Omega = E - \mu N - TS.$$

One can easily check that (5.19) minimizes the thermodynamic potential,

$$\frac{\partial\Omega}{\partial\hat{\rho}} = \frac{\partial}{\partial\hat{\rho}}\mathrm{Tr}\left[\hat{\rho}\left(\frac{1}{\beta}\log\hat{\rho} + \hat{\mathcal{H}} - \mu\hat{N}\right)\right] = \beta^{-1}(\log\hat{\rho} + I) + \hat{\mathcal{H}} - \mu\hat{N} = 0,$$

$$\to \quad \hat{\rho} = e^{-I-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}} \quad \to \quad \hat{\rho} = \frac{e^{-\beta(\hat{\mathcal{H}}-\mu\hat{N})}}{\mathrm{Tr}[e^{-\beta(\hat{\mathcal{H}}-\mu\hat{N})}]},$$

which is obtained as

$$\begin{aligned}
\Omega =&\mathrm{Tr}\left[\hat\rho\left(\frac{1}{\beta}\log\hat\rho+\hat{\mathcal{H}}-\mu\hat N\right)\right]\\
=&\mathrm{Tr}\left[\frac{e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}}{\mathrm{Tr}[e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}]}\left(\frac{1}{\beta}\log\frac{e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}}{\mathrm{Tr}[e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}]}+\hat{\mathcal{H}}-\mu\hat N\right)\right]\\
=&\mathrm{Tr}\left[\frac{e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}}{\mathrm{Tr}[e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}]}\left(\frac{1}{\beta}(-\beta(\hat{\mathcal{H}}-\mu\hat N)-\log\mathrm{Tr}[e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}])+\hat{\mathcal{H}}-\mu\hat N\right)\right]\\
=&\mathrm{Tr}\left[\frac{e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}}{\mathrm{Tr}[e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}]}\left(-\frac{1}{\beta}\log\mathrm{Tr}[e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}]\right)\right]\\
=&\left(-\frac{1}{\beta}\log\mathrm{Tr}[e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}]\right)\mathrm{Tr}\left[\frac{e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}}{\mathrm{Tr}[e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}]}\right]\\
=&-\beta^{-1}\log\mathcal{Z}
\end{aligned}$$

where the grand partition function is

$$\mathcal{Z}=\mathrm{Tr}\left[e^{-\beta(\hat{\mathcal{H}}-\mu\hat N)}\right].$$

Chapter 6

Quantum Statistics

Quantum statistics is an important framework for comprehending systems where quantum effects are non-negligible. Quantum effects typically manifest themselves at very low temperatures. Classical statistical mechanics, with its roots in the Boltzmann distribution, serves well for a wide range of macroscopic systems where quantum effects are marginal. However, at the microscopic level, particularly for systems at low temperatures or high densities, quantum effects become significant, necessitating a quantum statistical approach. This approach accounts for the intrinsic quantum nature of particles, encapsulated in the principles of indistinguishability and quantum state occupation.

The foundational distributions in quantum statistics are the Bose-Einstein (BE) and Fermi-Dirac (FD) distributions. They emerge from considering the quantum characteristics of bosons and fermions, respectively. Bosons, governed by BE statistics, are particles that do not obey the Pauli exclusion principle, allowing multiple particles to occupy the same quantum state. In contrast, fermions, described by FD statistics, are subject to the Pauli exclusion principle, which prohibits more than one particle from occupying the same quantum state. The profound implications of these quantum statistical distributions are evident in a range of phenomena, from the behavior of electrons in metals and semiconductors to the properties of photons in blackbody radiation.

The transition from quantum to classical statistics is not merely a theoretical curiosity but a bridge connecting quantum behavior with classical observations. In the high-temperature or low-density limit, both BE and FD statistics smoothly converge to the classical Boltzmann distribution, underscoring the universality and interconnectedness of statistical mechanical principles across scales and regimes.

6.1. Bose-Einstein, Fermi-Dirac and Boltzmann Distributions

The derivation of the BE and FD distributions enables us to understand the difference between different types of quantum particles, as well as the transition to classical mechanics. This derivation begins with the grand canonical partition function, a tool that allows for the consideration of systems in thermal equilibrium with a reservoir, where both energy and particle number can fluctuate. The grand canonical partition function encapsulates the probabilistic nature of the system's state and is a powerful framework for exploring quantum statistics.

The grand canonical ensemble (GCE), represented by its partition function, serves as a comprehensive framework in statistical mechanics, particularly advantageous for analyzing systems in thermal and particle exchange equilibrium with a reservoir. This partition function not only encapsulates the probabilistic distribution of system states but also accommodates variations in particle number and energy levels, a feature crucial for studying quantum gases and condensed matter systems. Its formulation allows for the precise calculation of thermodynamic properties, such as pressure and chemical potential, and offers a robust approach for deriving quantum statistical distributions like the Bose-Einstein and Fermi-Dirac distributions. The GCE is particularly effective in situations where particle number fluctuations are significant, providing insights into phase transitions and critical phenomena, which are essential in understanding many-body quantum systems.

From this starting point, we compute the average occupation numbers. The average occupation number represents the expected number of particles in a given quantum state, and its determination is fundamental for understanding the statistical behavior of quantum systems. By taking the derivative of the grand canonical partition function with respect to the chemical potential, we extract these average occupation numbers. This process unveils the distinct statistical behaviors of bosons and fermions, leading to the BE and FD distributions, respectively.

These distributions are not just mathematical constructs; they are the key to unlocking a deeper understanding of the quantum world. They explain a myriad of physical phenomena, from the unique characteristics of superconductors and superfluids to the distribution of electrons in atoms and the characteristics of blackbody radiation. The derivation of these distributions is more than a theoretical exercise; it's a journey through the heart of quantum mechanics, revealing how fundamental quantum principles manifest in the macroscopic properties of materials and phenomena we observe.

6.1.1. Derivation.

$$\begin{aligned}
\mathcal{Z}(V,T,\mu) &= \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N,V,T) \\
&= \sum_{N} \lambda^{n} \sum_{\{n_k\}}^{*} e^{-\beta\sum_i \epsilon_i n_i} \\
&= \sum_{N} \sum_{\{n_k\}}^{*} \lambda^{\sum_i n_i} e^{-\beta\sum_i \epsilon_i n_i} \\
&= \sum_{N} \sum_{\{n_k\}}^{*} \prod_{k} \left(\lambda e^{-\beta\epsilon_k}\right)^{n_k} \\
&= \sum_{n_1=0}^{n_1(max)} \sum_{n_2=0}^{n_2(max)} \cdots \prod_{k} \left(\lambda e^{-\beta\epsilon_k}\right)^{n_k} \\
&= \prod_{k} \sum_{n_k=0}^{n_k(max)} \left(\lambda e^{-\beta\epsilon_k}\right)^{n_k}
\end{aligned}$$

Fermions

$$\mathcal{Z}_{FD} = \prod_{k} (1 + \lambda e^{-\beta\epsilon_k})$$

Bosons

$$\mathcal{Z}_{BE} = \prod_{k} \sum_{n_k=0}^{\infty} (\lambda e^{-\beta\epsilon_k})^{n_k} = \prod_{k} (1 - \lambda e^{-\beta\epsilon_k})^{-1}$$

Combining the two results:

$$\mathcal{Z}_{\substack{FD \\ BE}} = \prod_{k} (1 \pm \lambda e^{-\beta\epsilon_k})^{\pm 1}.$$

From this we compute the average number of particles:

$$\langle N \rangle = \sum_{k} \overline{n}_k = k_B T \left(\frac{\partial}{\partial \mu} \log \mathcal{Z} \right) V,T = \lambda \left(\frac{\partial}{\partial \lambda} \log \mathcal{Z} \right)_{V,T} = \sum_{k} \frac{\lambda e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}}$$

so that

$$\langle n_k \rangle = \frac{\lambda e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}}$$

Average energy:

$$\langle E\rangle = N\langle\epsilon\rangle = \sum_k \langle n_k\rangle \epsilon_k = \sum_k \frac{\lambda\epsilon_k e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}}$$

Equation of state:

$$PV = k_B T \log \mathcal{Z}(V,T,\mu) = \pm k_B T \sum_k \log\left(1 \pm \lambda e^{-\beta\epsilon_k}\right)$$

The positive (+) sign indicates Fermi-Dirac statistics. The negative (-) sign indicates Bose-Einstein statistics.

The Boltzmann (classical) limit is obtained at high temperatures, where the occupation number is vanishingly small. To accomplish this (small occupation number) we take the limit $\lambda \to 0$ and obtain

$$\langle n_k\rangle = \lambda e^{-\beta\epsilon_k}$$

6.2. Fermi-Dirac Distribution

The advantage of introducing the statistical operator by means of a variational principle is that it allows one to construct upper bounds for the thermodynamic potential. Let us apply this method to derive the Hartree-Fock equation for finite temperature and obtain an effective one-particle equation. We start with trial form of the statistical operator

$$\hat{\rho} = \frac{e^{-\beta\hat{\mathcal{H}}_{tr}}}{\mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}_{tr}}]}$$

and associated Hamiltonian containing only one-body operators:

$$\hat{\mathcal{H}}_{tr} = \sum_j (E_j - \mu)\hat{n}_j,$$

where the E_j may be unknowns (variational parameters). Using

$$\log\hat{\rho} = -\beta\hat{\mathcal{H}}_{tr} - \log \mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}_{tr}}],$$

we have, according to

$$\Omega = \mathrm{Tr}\left[\hat{\rho}\left(\frac{1}{\beta}\log\hat{\rho} + \hat{\mathcal{H}} - \mu\hat{N}\right)\right]$$

to minimize

$$\Omega = -\frac{1}{\beta}\log \mathrm{Tr}(e^{-\beta\hat{\mathcal{H}}_{tr}}) + \frac{\mathrm{Tr}\left(e^{-\beta\hat{\mathcal{H}}_{tr}}(\hat{\mathcal{H}} - \hat{\mathcal{H}}_{tr})\right)}{\mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}_{tr}}]}. \tag{6.1}$$

Using the Fock space representation of the trace, the traces of one-particle operators can easily be evaluated. First we consider the trace of the trial statistical operator

$$\begin{aligned}\mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}_{tr}}] &= \sum_{n_1,\ldots,n_\infty} \langle n_1,\ldots,n_\infty|e^{-\beta\sum_j(E_j-\mu)\hat{n}_j}|n_1,\ldots,n_\infty\rangle \\ &= \prod_{j=1}^{\infty}\sum_{n_j=0,1} e^{-\beta(E_j-\mu)n_j} = \prod_{j=1}^{\infty}(1+e^{-\beta(E_j-\mu)}).\end{aligned}$$

Correspondingly, we obtain, for the trace containing the trial Hamiltonian,

$$\begin{aligned}\mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}_{tr}}\hat{\mathcal{H}}_{tr}] &= \sum_{n_1,\ldots,n_\infty} \langle n_1,\ldots,n_\infty|\sum_i(E_i-\mu)\hat{n}_i e^{-\beta\sum_j(E_j-\mu)\hat{n}_j}|n_1,\ldots,n_\infty\rangle \\ &= \sum_{i,n_i}(E_i-\mu)n_i e^{-\beta(E_i-\mu)n_i}\prod_{j\neq i}^{\infty}\sum_{n_j=0,1} e^{-\beta(E_j-\mu)n_j} \\ &= \sum_{i,n_i}(E_i-\mu)n_i e^{-\beta(E_i-\mu)n_i}\prod_{j\neq i}^{\infty}(1+e^{-\beta(E_j-\mu)}) \\ &= \sum_i \frac{(E_i-\mu)e^{-\beta(E_i-\mu)}}{1+e^{-\beta(E_i-\mu)}}\prod_{j=1}^{\infty}(1+e^{-\beta(E_j-\mu)}).\end{aligned}$$

Combining the last two results we obtain

$$\frac{\mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}_{tr}}\hat{\mathcal{H}}_{tr}]}{\mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}_{tr}}]} = \sum_i(E_i-\mu)f_i,$$

where

$$f_i = \frac{1}{1+e^{\beta(E_i-\mu)}}.$$

Thus, the statistical average in Fock space is reduced to a trace of one-particle energies, weighted with the one-particle distribution function, i.e. the *Fermi-Dirac* distribution function, f_i. This also follows directly from the general definition of the one-particle distribution function

$$f_i = \mathrm{Tr}[\hat{\rho}\hat{n}_i],$$

if the statistical operator is approximated by $\hat{\rho} = \frac{e^{-\beta\hat{\mathcal{H}}_{tr}}}{\mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}_{tr}}]}$. We now proceed to evaluate (6.1) and calculate the contribution of the many-particle Hamiltonian. As before, the trace in Fock space of the one-particle contribution yields a trace in one-particle Hilbert space, i.e.

$$\frac{\mathrm{Tr}\left(\sum_i \langle i|\hat{h}|i\rangle\,\hat{n}_i e^{-\beta\hat{\mathcal{H}}_{tr}}\right)}{\mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}_{tr}}]} = \sum_i \langle i|\hat{h}|i\rangle\, f_i = \sum_i h_i f_i.$$

The trace over the interaction contribution is obtained by applying the Hartree-Fock factorization ($|\Phi_0\rangle$ is a single Slater determinant)

$$\begin{aligned}\langle\Phi_0|c_j^\dagger c_{j'}^\dagger c_{k'}c_k|\Phi_0\rangle =&\delta_{jk}\delta_{j'k'}\langle\Phi_0|c_j^\dagger c_k|\Phi_0\rangle\langle\Phi_0|c_{j'}^\dagger c_{k'}|\Phi_0\rangle\\ &-\delta_{jk'}\delta_{j'k}\langle\Phi_0|c_j^\dagger c_{k'}|\Phi_0\rangle\langle\Phi_0|c_{j'}^\dagger c_k|\Phi_0\rangle\\ =&(\delta_{jk}\delta_{j'k'}-\delta_{jk'}\delta_{j'k})n_k n_{k'}\end{aligned}\tag{6.2}$$

as follows:

$$\begin{aligned}\mathrm{Tr}\left(\sum_{ij}v_{ij}\hat{n}_i\hat{n}_j e^{-\beta\hat{\mathcal{H}}_{tr}}\right)&=\sum_{n_1,\ldots,n_\infty}\langle n_1,\ldots,n_\infty|\sum_{ij}v_{ij}\hat{n}_i\hat{n}_j e^{-\beta\sum_k(E_k-\mu)\hat{n}_k}|n_1,\ldots,n_\infty\rangle\\ &=\sum_{ij}v_{ij}\prod_{k\neq i,j}(1+e^{-\beta(E_k-\mu)})=\sum_{ij}v_{ij}f_i f_j\mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}_{tr}}],\end{aligned}$$

where we have used the abbreviation

$$v_{ij}=\langle ij|v|ij\rangle-\langle ij|v|ji\rangle\,.$$

Thus the statistical average of the Hamiltonian (invoking 6.2):

$$\begin{aligned}\hat{\mathcal{H}}&=\sum_j\langle j|h|j\rangle\,c_j^\dagger c_j+\frac{e^2}{2}\sum_{jklm}\langle jk|v|lm\rangle\,c_j^\dagger c_k^\dagger c_m c_l\\ &=\sum_j\langle j|h|j\rangle\,\hat{n}_j+\frac{e^2}{2}\sum_{jklm}(\langle jj'|v|jj'\rangle-\langle jj'|v|j'j\rangle)\hat{n}_j\hat{n}_{j'}\end{aligned}$$

takes the form

$$\frac{\mathrm{Tr}\left(e^{-\beta\hat{\mathcal{H}}_{tr}}\hat{\mathcal{H}}\right)}{\mathrm{Tr}[e^{-\beta\hat{\mathcal{H}}_{tr}}]}=\sum_i h_i f_i+\frac{e^2}{2}\sum_{ij}v_{ij}f_i f_j.$$

Lumping these results together, we see that the *thermodynamic potential* is given by

$$\Omega=-\frac{1}{\beta}\sum_i\log\left(1+e^{-\beta(E_i-\mu)}\right)+\sum_i(h_i-E_i)f_i+\frac{e^2}{2}\sum_{ij}(\langle ij|v|ij\rangle-\langle ij|v|ji\rangle)f_i f_j.$$

Evaluating the derivative with respect to the variational parameter E_i, we obtain, as a condition for the stationarity of the thermodynamic potential,

$$h_i+e^2\sum_j(\langle ij|v|ij\rangle-\langle ij|v|ji\rangle)f_j=E_i,$$

which shows that we have solved the problem if the one-particle energies are determined from a Hartree-Fock equation similar to ($\mathbf{q}=\{\mathbf{r},s\}$)

$$h(\mathbf{r})\varphi_n(\mathbf{r})+e^2\sum_j\int d^3\mathbf{q}'\left(v(\mathbf{r}-\mathbf{r}')\varphi_j^*(\mathbf{q}')\varphi_j(\mathbf{q}')\varphi_n(\mathbf{q})-v(\mathbf{r}-\mathbf{r}')\varphi_j^*(\mathbf{q}')\varphi_n(\mathbf{q}')\varphi_j(\mathbf{q})\right)=E_n\varphi_n(\mathbf{q})$$

in which, however, the occupation numbers have been replaced by Fermi functions. The resulting equation constitutes a rather complicated problem of self-consistency, which we shall now rewrite in a more compact form:

$$[h(\mathbf{r}) + \phi_{eff}(\mathbf{r})]\varphi_i(\mathbf{r}) + \int d^3\mathbf{r}'\Sigma(\mathbf{r}, \mathbf{r}')\varphi_i(\mathbf{r}') = E_i\varphi_i(\mathbf{r}),$$

where φ_i are occupied one-particle states, ϕ_{eff} is the Hartree potential

$$\phi_{eff}(\mathbf{r}) = e^2 \sum_i \int d^3\mathbf{r}' v(\mathbf{r} - \mathbf{r}')|\varphi_i(\mathbf{r}')|^2, \qquad \rho(\mathbf{r}) = -e \sum_i |\varphi_i(\mathbf{r})|^2,$$

and we have introduced the so-called *exchange self-energy*

$$\Sigma(\mathbf{r}, \mathbf{r}') = e^2 \sum_j v(\mathbf{r} - \mathbf{r}')\varphi_j^*(\mathbf{r})\varphi_j(\mathbf{r}')f_j.$$

6.3. Electron Gas Model

The electron gas model is a theoretical framework used to understand the behavior of electrons in a solid, particularly metals. It simplifies the complex interactions in a solid by considering the electrons as a gas of non-interacting particles confined within a potential well, typically a box-like potential.

In this model, the key quantum mechanical property is the Pauli exclusion principle, which states that no two electrons can occupy the same quantum state. This leads to the filling of energy levels up to a certain point, known as the Fermi level, at absolute zero temperature. The distribution of electrons across energy states at higher temperatures is described by the Fermi-Dirac distribution.

This electron gas model is fundamental in solid-state physics and helps explain various properties of materials, such as electrical conductivity, heat capacity, and magnetic behavior. It serves as the starting point for more complex models that incorporate electron-electron and electron-lattice interactions.

In this section, we shall give a brief overview of the electron gas model in metals and discuss its importance in solid-state physics and quantum statistical mechanics. The key assumptions for the electron gas model are that: electrons are non-interacting electrons, and placed in an infinite potential well. From this, we easily obtain the quantum states of electrons in a box (three-dimensional well). This differs from the gas of classical particles in that we must apply the Pauli exclusion principle. We will assume that the reader is already familiar with the derivation of energy Levels, which are obtained from a quantum mechanical treatment using the Schrödinger equation for particles in a box. Quantization of momentum leads to: $p = \hbar k$. The energy levels are: $E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$.

6.3.1. Density of States Derivation. Consider a three-dimensional box with length L in each dimension, containing electrons that behave as a free electron gas. First, we recognize that the wavevectors of the electrons are quantized due to the boundary conditions of the box. The wavevector components are given by:

$$k_x = \frac{n_x \pi}{L}, \quad k_y = \frac{n_y \pi}{L}, \quad k_z = \frac{n_z \pi}{L} \tag{6.3}$$

where n_x, n_y, n_z are integers. In k-space, each quantum state occupies a volume of $\left(\frac{2\pi}{L}\right)^3$. The number of states within a spherical shell of radius k and thickness dk in k-space is:

$$dn = 2 \times \frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3} = \frac{V}{2\pi^2} k^2 dk \tag{6.4}$$

The factor of 2 accounts for the two possible spin states of each electron.

The energy of an electron in a free electron gas is given by $E = \frac{\hbar^2 k^2}{2m}$. Rearranging this, we get $k = \sqrt{\frac{2mE}{\hbar^2}}$. Substituting this into our expression for dn, we get:

$$dn = \frac{V}{2\pi^2} \left(\sqrt{\frac{2mE}{\hbar^2}} \right)^2 d\left(\sqrt{\frac{2mE}{\hbar^2}} \right) \tag{6.5}$$

The density of states $g(E)$ is then given by the number of states per unit energy interval, which is $\frac{dn}{dE}$:

$$g(E) = \frac{dn}{dE} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} \tag{6.6}$$

This is the density of states for a three-dimensional electron gas. It shows that the density of states increases as the square root of the energy.

6.3.2. Density of States Derivation. Starting from the equation for the number of states dn in a differential volume of energy space:

$$dn = \frac{V}{2\pi^2} \left(\sqrt{\frac{2mE}{\hbar^2}} \right)^2 d\left(\sqrt{\frac{2mE}{\hbar^2}} \right) \tag{6.7}$$

we proceed to find the density of states $\frac{dn}{dE}$. First, simplify the expression inside the square brackets:

$$\left(\sqrt{\frac{2mE}{\hbar^2}} \right)^2 = \frac{2mE}{\hbar^2} \tag{6.8}$$

Thus, the equation becomes:

$$dn = \frac{V}{2\pi^2} \frac{2mE}{\hbar^2} d\left(\sqrt{\frac{2mE}{\hbar^2}} \right) \tag{6.9}$$

Next, differentiate the square root term:

$$d\left(\sqrt{\frac{2mE}{\hbar^2}} \right) = \frac{1}{2\sqrt{\frac{2mE}{\hbar^2}}} dE = \frac{\hbar}{2\sqrt{2mE}} dE \tag{6.10}$$

Substituting this back into the equation for dn gives:

$$dn = \frac{V}{2\pi^2}\frac{2mE}{\hbar^2}\cdot\frac{\hbar}{2\sqrt{2mE}}dE \tag{6.11}$$

Simplifying this expression, we obtain:

$$dn = \frac{V}{2\pi^2}\frac{m}{\hbar\sqrt{2mE}}EdE \tag{6.12}$$

Finally, computing $\frac{dn}{dE}$ gives the density of states $g(E)$:

$$\frac{dn}{dE} = \frac{V}{2\pi^2}\frac{m}{\hbar\sqrt{2mE}}\cdot\frac{3}{2} = \frac{3V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}E^{1/2} \tag{6.13}$$

This is the density of states for a three-dimensional electron gas.

6.3.3. Fermi Energy and Fermi-Dirac Distribution. The Fermi energy E_F is defined as the highest occupied energy level at absolute zero temperature. For an electron gas, the total number of electrons N is given by integrating the density of states $g(E)$ up to the Fermi energy:

$$N = \int_0^{E_F} g(E)dE \tag{6.14}$$

Substituting the expression for $g(E)$ in a three-dimensional electron gas:

$$N = \int_0^{E_F} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}dE \tag{6.15}$$

Solving this integral, we find:

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \tag{6.16}$$

The Fermi-Dirac distribution function $f(E)$ describes the probability that an energy state at energy E is occupied by an electron at finite temperature T:

$$f(E) = \frac{1}{e^{(E-\mu)/k_BT}+1} \tag{6.17}$$

Here, μ is the chemical potential, which approaches E_F at absolute zero. At $T = 0\,\mathrm{K}$, this distribution becomes a step function, with all states below E_F filled and those above empty. At temperatures above absolute zero, the occupation of energy levels near E_F starts to spread out due to thermal excitation:

- For $E < E_F$, $f(E)$ decreases from 1.
- For $E > E_F$, $f(E)$ increases from 0.

This thermal smearing effect is crucial for understanding the behavior of electrons in metals and semiconductors at finite temperatures.

6.3.4. Thermodynamic Properties.

6.3.4.1. *Internal Energy.* The internal energy U of the electron gas can be calculated by summing the energies of all electrons, each weighted by the probability of being in a given energy state, provided by the Fermi-Dirac distribution:

$$U = \int_0^\infty E \cdot g(E) \cdot f(E)\, dE \tag{6.18}$$

Substituting the expressions for $g(E)$ and $f(E)$:

$$U = \int_0^\infty E \cdot \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E} \cdot \frac{1}{e^{(E-\mu)/k_B T} + 1}\, dE \tag{6.19}$$

This integral does not have a simple analytical solution and is typically evaluated numerically, especially at finite temperatures. This expression for U represents the total energy of the electron gas, taking into account the quantum mechanical nature of the electrons and the statistical distribution of their energies at a given temperature.

6.3.4.2. *Specific Heat.* The specific heat at constant volume C_V can be derived from the temperature derivative of the internal energy:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{6.20}$$

Evaluating this derivative involves differentiating under the integral, which is complex but can be approximated under certain conditions (e.g., low temperatures). The resulting expression provides insight into the temperature dependence of the specific heat.

At temperatures much lower than the Fermi temperature ($T \ll T_F$), the specific heat of the electron gas is linear in T:

$$C_V \approx \gamma T \tag{6.21}$$

where γ is a constant that depends on the electron density and the effective mass of electrons. This linear behavior is a characteristic feature of metals and is in contrast to the T^3 dependence observed for lattice vibrations (phonons).

6.3.5. Heat Capacity of Electron Gas at Low Temperatures.

Starting from the expression for the internal energy U of the electron gas:

$$U = \int_0^\infty E \cdot g(E) \cdot f(E)\, dE \tag{6.22}$$

where $g(E)$ is the density of states and $f(E)$ is the Fermi-Dirac distribution.

6.3.5.1. *Density of States and Fermi-Dirac Distribution.* For a three-dimensional electron gas, the density of states is given by:

$$g(E) = \frac{3V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \tag{6.23}$$

The Fermi-Dirac distribution at low temperatures ($T \ll T_F$) can be approximated as:

$$f(E) \approx \theta(E_F - E) \tag{6.24}$$

where θ is the Heaviside step function, and E_F is the Fermi energy.

6.3.5.2. *Internal Energy at Low Temperatures.* At low temperatures, the internal energy simplifies to:

$$U \approx \int_0^{E_F} E \cdot g(E)\, dE \tag{6.25}$$

Substituting $g(E)$ and integrating gives:

$$U \approx \frac{3V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{E_F} E^{3/2}\, dE \tag{6.26}$$

Evaluating the integral results in:

$$U \approx \frac{3V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \frac{2}{5} E_F^{5/2} \tag{6.27}$$

6.3.5.3. *Heat Capacity.* The heat capacity at constant volume C_V is the temperature derivative of the internal energy:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{6.28}$$

Since E_F is a function of temperature, we differentiate U with respect to T:

$$C_V \approx \frac{\partial}{\partial T} \left[\frac{3V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \frac{2}{5} E_F^{5/2} \right] \tag{6.29}$$

At low temperatures, it can be shown that:

$$C_V \propto T \tag{6.30}$$

Therefore, at low temperatures, the heat capacity of the electron gas is linearly dependent on the temperature, which is a characteristic feature of metals.

6.3.5.4. *Electronic Contribution to Heat Capacity.* In a metal, the total heat capacity has contributions from both the electron gas and the lattice (phonons). However, at low temperatures, the electronic contribution (linear in T) dominates over the lattice contribution (T^3 dependence).

6.3.5.5. *High-Temperature Limit.* At high temperatures ($T \gg T_F$), the specific heat approaches the classical limit set by the Dulong-Petit law, indicating a saturation in the contribution of electrons to the heat capacity.

6.3.6. High-Temperature Limit: Dulong-Petit Law.

6.3.6.1. *Classical Model of Lattice Vibrations.* In a solid, atoms vibrate about their equilibrium positions. At high temperatures, where $k_BT \gg \hbar\omega$ (with ω being the vibrational frequency of the atoms), these vibrations can be treated classically.

6.3.6.2. *Equipartition Theorem.* The equipartition theorem states that each degree of freedom contributes $\frac{1}{2}k_BT$ to the internal energy per particle. In a solid, each atom has 3 degrees of freedom for kinetic energy and 3 for potential energy, totaling 6 degrees of freedom.

6.3.6.3. *Internal Energy.* The internal energy U per mole of a solid is then given by:

$$U = 3N_Ak_BT \tag{6.31}$$

where N_A is Avogadro's number, representing the number of atoms per mole.

6.3.6.4. *Heat Capacity at Constant Volume.* The molar heat capacity at constant volume C_V is the derivative of the internal energy with respect to temperature:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\right)_V (3N_Ak_BT) = 3N_Ak_B \tag{6.32}$$

Since $R = N_Ak_B$ (where R is the gas constant), this simplifies to:

$$C_V = 3R \tag{6.33}$$

The Dulong-Petit law, $C_V = 3R$, is thus derived, predicting the molar heat capacity at constant volume for solid elements at high temperatures. This law is a result of classical considerations of lattice vibrations and does not directly apply to the electronic heat capacity of an electron gas.

6.3.7. Electrical and Thermal Conductivities.

6.3.7.1. *Electrical Conductivity.* The electrical conductivity (σ) in metals can be understood through the Drude model, extended by quantum considerations of the electron gas. The conductivity is given by:

$$\sigma = ne\mu \tag{6.34}$$

where n is the electron density, e is the elementary charge, and μ is the electron mobility.

6.3.7.2. *Drude Model Revisited.* In the quantum context, the electron mobility can be expressed as:

$$\mu = \frac{e\tau}{m} \tag{6.35}$$

where τ is the mean free time between collisions, and m is the electron mass.

6.3.7.3. *Mean Free Path.* The mean free path (λ) of electrons, which is the average distance traveled between collisions, can be linked to the conductivity:

$$\lambda = v_F\tau \tag{6.36}$$

where v_F is the Fermi velocity.

6.3.7.4. *Thermal Conductivity.* The Wiedemann-Franz law relates the thermal conductivity (k) to the electrical conductivity:

$$k = L\sigma T \tag{6.37}$$

where L is the Lorenz number and T is the absolute temperature.

6.3.7.5. *Lorenz Number.* The Lorenz number is a key constant in the Wiedemann-Franz law, which relates the thermal conductivity (k) to the electrical conductivity (σ) of a material. The Lorenz number is given by:

$$L = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 \tag{6.38}$$

where k_B is the Boltzmann constant and e is the elementary charge. This relation is a consequence of the fact that the same free electrons contribute to both electrical and thermal conduction. The Lorenz number, approximately $2.44 \times 10^{-8}\,\mathrm{W\Omega K^{-2}}$, indicates a fundamental relationship between electrical and thermal conductivities in metals, suggesting a profound connection between these properties and the electronic structure of the material.

6.3.7.6. *Temperature Dependence.* Both electrical and thermal conductivities are temperature-dependent. The resistivity (inverse of conductivity) in metals typically increases with temperature due to increased scattering of electrons.

6.3.7.7. *Quantum Corrections.* In more advanced treatments, quantum corrections to the Drude model are considered, taking into account the Fermi-Dirac statistics and the Pauli exclusion principle. These corrections lead to a more accurate description of conductivities in metals, especially at low temperatures.

6.4. Bose-Einstein Condensation

Bose-Einstein Condensation (BEC), a concept initially proposed in the early 1920s by Satyendra Nath Bose and further developed by Albert Einstein, represents a unique state of matter where bosons occupy the same quantum state at extremely low temperatures. However, the experimental realization of BEC was a challenge for many decades due to the requirement of ultra-low temperatures.

The breakthrough came in the 1990s with the advent of innovative cooling techniques, including laser cooling and evaporative cooling. In 1995, independent experiments by Eric A. Cornell, Carl E. Wieman, and Wolfgang Ketterle successfully observed BEC in dilute gases of alkali atoms like Rubidium-87 and Sodium-23, marking a significant advancement in quantum physics and leading to the 2001 Nobel Prize in Physics.

The phenomenon of BEC is distinct from Fermi-Dirac statistics, which govern the behavior of fermions (particles with half-integer spin), such as electrons and protons. Bosons, including photons and helium-4 atoms, adhere to Bose-Einstein statistics, allowing multiple particles to occupy the same quantum state. This fundamental distinction underpins various quantum phenomena, including superfluidity, superconductivity, and laser properties.

The realization of BEC has profound implications for both fundamental physics and practical applications. It provides an experimental platform to explore quantum macroscopic phenomena and serves as a testing ground for quantum theories. BECs are crucial in understanding quantum phenomena on a macroscopic scale, such as superfluidity, quantized vortices, and Josephson junctions.

In terms of applications, BECs offer potential in quantum computing, where their coherence properties make them suitable for developing quantum bits. They are also ideal for precision measurements, enhancing the accuracy of devices like atomic clocks and gravitational wave detectors. Furthermore, BECs are instrumental in condensed matter physics research and have potential applications in optics and photonics.

6.4.1. Wavefunction of Bose-Einstein Condensates. In the context of Bose-Einstein Condensates (BECs), the treatment of the wavefunction as a simple product of single-particle wavefunctions, rather than a symmetrized permanent, merits explanation. Under normal circumstances, for a system of bosons, the many-body wavefunction should be symmetric under the exchange of any two particles, necessitating the use of a permanent. The permanent of a matrix is similar to the determinant but without alternating signs:

$$\text{Permanent}(A) = \sum_{\sigma \in S_N} \prod_{i=1}^{N} a_{i,\sigma(i)}, \tag{6.39}$$

where S_N is the set of all permutations of N elements, and $a_{i,\sigma(i)}$ are the elements of matrix A. This is in contrast to the Slater determinant used for fermions, which incorporates alternating signs to ensure antisymmetry:

$$\text{Determinant}(A) = \sum_{\sigma \in S_N} \text{sgn}(\sigma) \prod_{i=1}^{N} a_{i,\sigma(i)}, \tag{6.40}$$

where $\text{sgn}(\sigma)$ denotes the sign of the permutation σ. In BECs, however, the many-body wavefunction simplifies due to the macroscopic occupation of the same quantum state by bosons. The wavefunction can be expressed as:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \prod_{i=1}^{N} \psi(\mathbf{r}_i). \tag{6.41}$$

This simplification from a symmetrized permanent to a product form in BECs is justified by the following:

- **Indistinguishability and Identical State**: In a BEC, all particles are in the same quantum state, making any exchange of two particles redundant as it returns the same state.
- **Simplification in the Mean-Field Approximation**: The product form of the wavefunction provides a practical and accurate description of the BEC state, especially under the mean-field approximation.

- **Macroscopic Quantum State**: The overlapping and indistinguishable nature of the wavefunction of each particle in a BEC validates the use of the product form.

In conclusion, while the permanent is essential for ensuring symmetry in a general bosonic system, the unique properties of BECs allow for the simplification to a product form of the wavefunction, effectively capturing the essential physics of BECs without the computational complexity of a fully symmetrized wavefunction.

6.4.2. Important Facts About Bose-Einstein Condensation. Bose-Einstein Condensation (BEC), along with superconductivity and superfluidity, marks a significant chapter in the study of quantum phenomena manifesting at macroscopic scales. Unlike many quantum effects that are confined to atomic or subatomic scales, these phenomena demonstrate the influence of quantum mechanics on the bulk properties of matter, representing a bridge between the microscopic and macroscopic worlds.

The concept of BEC, theorized in the 1920s, was only experimentally confirmed in the mid-1990s, marking a pivotal moment in quantum physics. This delay highlights the challenges associated with creating conditions necessary for BEC, notably the extremely low temperatures required for its observation. The successful realization of BEC in the laboratory was not just a triumph in cooling techniques but also a testament to the persistent efforts of the scientific community in exploring the frontiers of quantum mechanics.

Research in this domain continues to evolve rapidly, with significant strides being made in both atomic BEC systems and high-temperature superconductors. Atomic BEC systems are now being studied at nano-Kelvin temperatures, pushing the boundaries of low-temperature physics. Meanwhile, the field of high-temperature superconductors has witnessed substantial advancements, with materials like $HgBa_2Ca_2Cu_3O_{8+\delta}$ exhibiting superconducting transition temperatures (T_c) as high as 133 K under room pressure. Under high-pressure conditions (approximately 30 GPa), these temperatures can be further increased, reaching up to 164 K. These developments not only expand our understanding of quantum phenomena but also hold promise for future technological applications, driving research towards the elusive goal of a room-temperature superconductor.

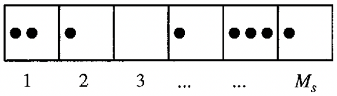
6.4.2.1. *Bose-Einstein Statistics.* In 1924, the Indian physicist S.N. Bose proposed a novel approach to derive the Planck black-body radiation formula, marking a significant development in quantum theory. During this period, Albert Einstein, renowned for his contributions to quantum mechanics and the recipient of the Nobel Prize for his explanation of the photoelectric effect, was a towering figure in the world of physics. Bose, then a relatively unknown scientist based in Dacca (now in Bangladesh), had faced challenges in gaining recognition for his work, with previous correspondence to European journals going unnoticed. However, Einstein recognized the innovative aspect of Bose's approach and played a pivotal role in facilitating the publication of Bose's results.

Bose's breakthrough idea was to treat the electromagnetic waves in black-body radiation as a gas of indistinguishable particles. This approach provided a novel perspective on the nature of 'light quanta', a concept introduced by Max Planck in 1900 and employed by Einstein in 1905 for his photoelectric effect theory. For the first time, it suggested that these quanta could be considered actual particles of light, now known as photons. Einstein extended Bose's method to ideal gases composed of particles with mass, leading to the first quantum mechanical generalization of the classical ideal gas theory developed by Boltzmann, Maxwell, and Gibbs. This foundation paved the way for the distinction between two types of quantum ideal gases, defined by Bose-Einstein and Fermi-Dirac statistics.

At the heart of Bose-Einstein statistics is the principle that identical quantum particles can be enumerated using combinatorial methods. If there are N_s indistinguishable Bose particles distributed across M_s quantum states, the number of possible distributions is given by:

$$W_s = \frac{(N_s + M_s - 1)!}{N_s!(M_s - 1)!}, \tag{6.42}$$

This formula arises from envisioning each quantum state as a 'box' capable of containing any number of identical 'balls', representing the particles. Such a representation simplifies the understanding of quantum state distribution for bosonic particles, such as photons or ^{4}He atoms.



N_s boson particles in M_s available quantum states. We can count the number of possible configurations by considering that the N_s identical particles and the $M_s - 1$ walls between boxes and can be arranged along a line in any order. For bosons each box can hold any number of particles, 0, 1, 2 . . . .

We can determine the number of possible arrangements by considering both the N_s particles (balls) and the $M_s - 1$ partitions (walls between boxes). Conceptually, this involves arranging $N_s + M_s - 1$ objects in a sequence, where N_s objects represent particles and $M_s - 1$ objects represent partitions. If each of these $N_s + M_s - 1$ objects were distinct, they could be arranged in $(N_s + M_s - 1)!$ ways. However, since the N_s particles and the $M_s - 1$ partitions are indistinguishable within their groups, this count must be adjusted. The indistinguishability of the particles and partitions reduces the number of unique arrangements, leading to the division by $N_s!(M_s - 1)!$, thereby yielding the total number of configurations as given in the previous equation.

In applying this combinatorial principle to the thermodynamics of an ideal gas consisting of N boson particles within a volume V, we consider each atom to be in a plane-wave quantum state represented by

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{-i\mathbf{k}\cdot\mathbf{r}},$$

where the permissible wave vectors are defined as

$$\mathbf{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right),$$

with L_x, L_y, and L_z denoting the dimensions of the volume in each respective direction. The total volume $V = L_x L_y L_z$ implies that an infinitesimally small volume element $d^3k = dk_x dk_y dk_z$ in k-space encompasses

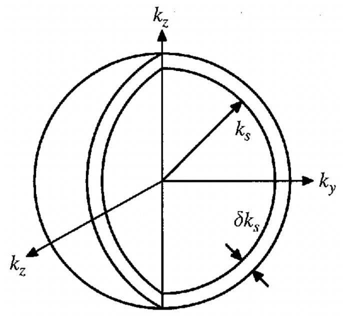
$$\frac{V}{(2\pi)^3} d^3k$$

quantum states.

The energy associated with each of these single-particle quantum states is given by

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m},$$

where m is the mass of the particle. Consequently, we can categorize the available single-particle quantum states into a series of thin spherical shells of states, as illustrated below:



A thin shell of states of wave vector between k_s and $k_s + \delta k_s$. The shell has volume $4\pi k_s^2 \delta k_s$ and so there are $4\pi k_s^2 \delta k_s V/(2\pi)^3$ quantum states in the shell.

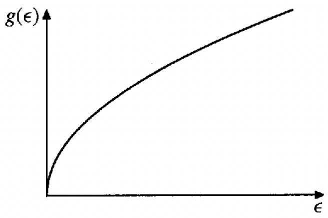
A shell of radius k_s, and thickness δk_s contains

$$M_s = 4\pi k_s^2 \delta k_s \frac{V}{(2\pi)^3}$$

single particle states. The number of available states between energy ϵ_s and $\epsilon_s + \delta\epsilon_s$ is therefore

$$M_s = \frac{V m^{3/2} \epsilon^{1/2}}{\sqrt{2}\pi^2 \hbar^3} \delta\epsilon_s = V g(\epsilon_s) \delta\epsilon_s, \quad \text{where} \quad g(\epsilon) = \frac{m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \epsilon^{1/2}$$

is the density of states per unit volume, shown below:



The single particle density of states $g(\epsilon)$, of a three dimensional gas of particles.

The fundamental tenets of statistical mechanics assert that the total entropy of a gas is given by $S = k_B \log W$, where k_B represents Boltzmann's constant and W signifies the number of microstates corresponding to a given total energy E. To ascertain W, it is essential to analyze the distribution of the N atoms in the gas among the various k-space shells, each characterized by distinct energy levels. Suppose a specific shell s contains N_s atoms. Given that this shell encompasses M_s quantum states, we can employ Eq. (6.42) to calculate the total number of feasible quantum states for this shell. Consequently, the overall number of microstates for the entire gas is the product of the number of available states in each k-space shell:

$$W = \prod_s W_s = \prod_s \frac{(N_s + M_s - 1)!}{N_s!(M_s - 1)!}.$$

By applying Stirling's approximation, $\log N! \approx N \log N - N$, and under the assumption that both N_s and M_s are considerably large, we derive the entropy as

$$S = k_B \log W = k_B \sum_s [(N_s + M_s) \log(N_s + M_s) - N_s \log N_s - M_s \log M_s]. \tag{6.43}$$

In a state of thermal equilibrium, particles rearrange themselves such that the numbers N_s in each energy shell are optimized to maximize the total entropy. This optimization occurs while maintaining constant the total number of particles and the total internal energy of the gas:

$$N = \sum_s N_s, \quad U = \sum_s \epsilon_s N_s.$$

Maximizing entropy under these constraints, via the method of Lagrange multipliers, leads to the condition:

$$\frac{\partial S}{\partial N_s} - k_B \beta \frac{\partial U}{\partial N_s} + k_B \beta \mu \frac{\partial N}{\partial N_s} = 0, \tag{6.44}$$

where we define the Lagrange multiplier constants as $k_B \beta$ and $-k_B \beta \mu$. The differentiation process yields:

$$\log(N_s + M_s) - \log N_s - \beta \epsilon_s + \beta \mu = 0.$$

Rearranging, we arrive at the Bose-Einstein formula for N_s:

$$N_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1} M_s. \tag{6.45}$$

Hence, the average occupation number of a single quantum state with energy $\epsilon_{\mathbf{k}}$ is described by the Bose-Einstein distribution:

$$f_{BE}(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} - 1}.$$

The constants β and μ, initially introduced as Lagrange multipliers, can be interpreted via the first law of thermodynamics for a gas of N particles:

$$dU = TdS - PdV + \mu dN,$$

where T is the temperature, P is the pressure, and μ is the chemical potential. Rearranging, we get:

$$dS = \frac{1}{T}(dU + PdV - \mu dN). \tag{6.46}$$

From Eq. (6.44), we deduce:

$$dS = k_B \beta \sum_s \left(\frac{\partial U}{\partial N_s} - \mu \frac{\partial N}{\partial N_s} \right) dN_s = k_B \beta (dU - \mu dN).$$

Comparing with Eq. (6.46), we affirm that:

$$\beta = \frac{1}{k_B T},$$

and thus, the constant μ introduced is indeed the chemical potential of the gas.

The derivation of the Bose-Einstein distribution formula above utilizes the thermodynamics of a gas with a fixed total number of particles, N, and fixed total energy, U. This approach corresponds to the microcanonical ensemble, which is well-suited for systems with a constant number of particles, such as a gas confined within a magnetic trap. However, for many practical situations, particularly those involving an effectively infinite number of atoms, a different approach is warranted. In such cases, we consider the thermodynamic limit, $V \to \infty$, while keeping the atom density, $n = N/V$, constant. Here, the grand canonical ensemble becomes a more expedient framework, allowing for fluctuations in both total energy and particle number. The system is assumed to be in equilibrium with an external heat bath, ensuring a constant temperature T, and a particle reservoir, maintaining a constant chemical potential μ.

In the grand canonical ensemble, the probability of each N-body quantum state, with energy $E_i^{(N)}$ for $i = 1, 2, \ldots$, is given by:

$$P^{(N)}(i) = \frac{1}{\mathcal{Z}} \exp\left[-\beta (E_i^{(N)} - \mu N) \right], \tag{6.47}$$

where $\mathcal{Z}$, the grand partition function, is defined as:

$$\mathcal{Z} = \sum_{N,i} \exp\left[-\beta (E_i^{(N)} - \mu N) \right].$$

The grand potential, which is a pivotal thermodynamic quantity, is calculated from $\mathcal{Z}$:

$$\Omega(T, V, \mu) = -k_B T \log \mathcal{Z},$$

and is related to other thermodynamic variables via the differential relation:

$$d\Omega = -SdT - PdV - Nd\mu.$$

Employing this grand canonical framework, rather than the microcanonical ensemble used previously, simplifies the derivation of the Bose-Einstein distribution. The grand canonical approach is particularly advantageous for systems with a large number of particles, where fluctuations in particle number and energy are significant.

6.4.2.2. *Condensation.* The Bose-Einstein ideal gas exhibits a unique thermodynamic phase transition, known as BEC, which distinguishes it from both the classical ideal gas and the Fermi-Dirac gas. Remarkably, this phase transition occurs in a system of non-interacting particles and is driven solely by particle statistics rather than interparticle interactions. At the phase transition, thermodynamic observables undergo a distinct and abrupt change in behavior, defining the critical temperature, T_c.

The term “condensation” in this context is analogous to the liquid-gas phase transition observed in the van der Waals theory of gases, where liquid droplets condense from the gas, forming a saturated vapor. Similarly, in the BEC, below the critical temperature T_c, particles in the “normal gas” phase coexist in equilibrium with ”condensed” particles. However, this condensation differs significantly from the classical liquid-gas transition. In BEC, the “condensed” particles are not spatially segregated from the “normal” particles. Instead, they are differentiated in momentum space. Below T_c, the condensed particles occupy a single quantum state with zero momentum, while the normal particles possess finite momentum.

Using the Bose-Einstein distribution (6.47), the total number of particles in the box is

$$N = \sum_{\mathbf{k}} \frac{1}{e^{\beta(\epsilon_{\mathbf{k}})} - 1}. \tag{6.48}$$

In the thermodynamic limit, $V \to \infty$, the possible $\mathbf{k}$ values become a continuum and so we should normally expect to be able to replace the summation in Eq. (6.48) with an integration

$$\sum_{\mathbf{k}} \to \int \frac{V}{(2\pi)^3} d^3k.$$

If this is valid, then Eq. (6.48) becomes

$$N = \frac{V}{(2\pi)^3} \int \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} - 1} d^3k,$$

and so the particle density is

$$n = \frac{1}{(2\pi)^3} \int \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} - 1} d^3k,$$

or, in terms of the density of states per unit volume $g(\epsilon)$ from Eq. (2.9),

$$n = \int_0^\infty \frac{1}{e^{\beta(\epsilon_{\mathbf{k}}-\mu)} - 1} g(\epsilon) d\epsilon. \tag{6.49}$$

This equation defines the particle density $n(T\mu)$ as a function of the temperature and chemical potential. But, of course, usually we have a known particle density, n, and wish to find the corresponding chemical potential μ. Therefore we must view Eq. (6.49) as an equation which implicitly determines the chemical potential, $\mu(T,n)$, a function of temperature and the particle density n.

Rewriting Eq. (6.49) in terms of the dimensionless variables $z = e^{\beta\mu}$ (called the fugacity), and $x = \beta\epsilon$ gives

$$n = \frac{(mk_BT)^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{ze^{-x}}{1 - ze^{-x}} x^{1/2} dx. \tag{6.50}$$

To calculate this integral we can expand

$$\frac{ze^{-x}}{1 - ze^{-x}} = ze^{-x}\left(1 + ze^{-x} + z^2e^{-2x} + \dots\right) = \sum_{p=1}^\infty z^p e^{-px}.$$

This expansion is clearly convergent provided that z is smaller than 1. Inserting this into Eq. (6.50) we can now carry out the integral over x using

$$\int_0^\infty e^{-px} x^{1/2} dx = \frac{1}{p^{3/2}} \int_0^\infty e^{-y} y^{1/2} dy = \frac{1}{p^{3/2}} \frac{\sqrt{\pi}}{2},$$

where the dimensionless integral is a special case of the Gamma function,

$$\Gamma(t) = \int_0^\infty y^{t-1} e^{-y} dy$$

with the value $\Gamma(3/2) = \sqrt{\pi}/2$. Combining the numerical constants, the particle density is therefore given as a function of the fugacity, z, by

$$n = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} g_{3/2}(z), \tag{6.51}$$

where the function $g_{3/2}(z)$ is defined by the series

$$g_{3/2}(z) = \sum_{p=1}^\infty \frac{z^p}{p^{3/2}}. \tag{6.52}$$

In order to evaluate the particle density in Eq. (6.51), we must consider the shape of the function $g_{3/2}(z)$. Using the ratio test for convergence, one can easily show that the series Eq. 6.52 converges when $|z| < 1$, but diverges if $|z| > 1$. At $z = 1$ the series is just convergent,

$$g_{3/2}(1) = \sum_{p=1}^\infty \frac{1}{p^{3/2}} = \zeta\left(\frac{3}{2}\right) = 2.612,$$

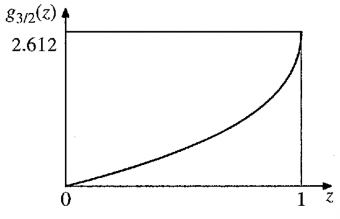


Figure 6.1. The function $g_{3/2}(z)$ as defined in Eq. (6.52). At $z = 1$ the function is finite but its derivative is infinite.

where

$$\zeta(s) = \sum_{p=1}^{\infty} \frac{1}{p^s}$$

is the Riemann zeta function. On the other hand, the function has infinite derivative at $z = 1$, since

$$\frac{dg_{3/2}(z)}{dz} = \frac{1}{z} \sum_{p=1}^{\infty} \frac{z^p}{p^{1/2}},$$

which diverges at $z = 1$. With these limiting values we can make a sketch of the function $g_{3/2}(z)$ between $z = 0$ and $z = 1$, as shown in Fig. 6.1.

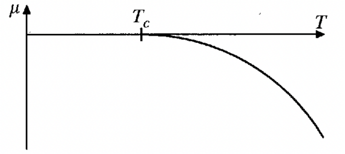
Equation (6.51) gives the density, n in terms of $g_{3/2}(z)$. Turning it around, we can say that the value of z, and hence the chemical potential μ, is determined by

$$g_{3/2}(e^{\beta\mu}) = \left(\frac{2\pi\hbar^2}{mk_BT} \right)^{3/2} n.$$

If we are at high temperature T or low density n, then the right-hand side of this equation is small, and we can use the small z expansion $g_{3/2}(z) \approx z + \ldots$ to obtain,

$$\mu \approx -\frac{3}{2} k_BT \log \left(\frac{mk_BT}{2\pi\hbar^2 n^{2/3}} \right).$$

This gives a negative chemical potential, as sketched below:



Chemical potential μ, of a Bose gas as a function of temperature, T. At $T = 0$ all the particles are in the condensate and $n_0 = n$. On the other hand, above the critical temperature T_c all the particles are in the normal component, and $n_0 = 0$.

As the gas is cooled to lower temperatures, the fugacity, z, gradually increases until it reaches unity. At this juncture, the chemical potential, μ, becomes zero. The temperature at which this occurs, for a fixed density n, defines the critical temperature T_c,

$$T_c = \frac{2\pi\hbar^2}{k_B m}\left(\frac{n}{2.612}\right)^{2/3}, \tag{6.53}$$

where $g_{3/2}(z)$ attains its maximum finite value of 2.612. This T_c is the characteristic temperature of BEC.

Below T_c, an intriguing phenomenon occurs, as Einstein first realized: the number of particles in the lowest energy quantum state (with $\epsilon_{\mathbf{k}} = 0$) becomes macroscopically significant. Specifically, out of N total particles in the gas, a macroscopic number N_0 occupy this ground state. Here, "macroscopic number" implies that N_0 is proportional to the system volume, such that a finite fraction, N_0/N, of all particles occupy this single quantum state. This is particularly relevant in the thermodynamic limit, $V \to \infty$. The Bose-Einstein distribution predicts the occupation of the $\epsilon_{\mathbf{k}} = 0$ state as

$$N_0 = \frac{1}{e^{-\beta\mu} - 1}. \tag{6.54}$$

Rewriting Eq. (6.54), we have

$$\mu = -k_B T \log\left(1 + \frac{1}{N_0}\right) \approx -k_B T \frac{1}{N_0}.$$

If a finite fraction of the particles reside in the ground state, then as $V \to \infty$, $N_0 \to \infty$ and consequently, $\mu \to 0$. Therefore, below the BEC temperature T_c, the chemical potential effectively becomes zero.

Below T_c, the $\mathbf{k} = 0$ state must be considered separately, leading to the modification of Eq. (6.48) to

$$N = N_0 + \sum_{\mathbf{k}\neq 0} \frac{1}{e^{\beta\epsilon_{\mathbf{k}} - 1}},$$

with the chemical potential μ being zero. Replacing the summation over $\mathbf{k}$ with an integral (excluding the $\mathbf{k} = 0$ point), the particle density can be expressed as

$$n = n_0 + \frac{(mk_B T)^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{e^{-x}}{1 - e^{-x}} x^{1/2} dx,$$

where the integral evaluates to $\Gamma(3/2)\zeta(3/2)$. For $T < T_c$, we obtain

$$n = n_0 + 2.612\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}.$$

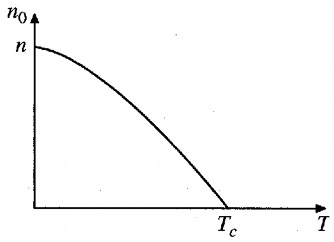
Thus, the particle density n is composed of a condensate density n_0 and a normal density n_n,

$$n = n_0 + n_n.$$

The proportion of particles in the condensate is succinctly described by

$$\frac{n_0}{n} = 1 - \left(\frac{T}{T_c}\right)^{3/2},$$

as depicted below:



BEC density, n_0, as a function of temperature T.

It is evident from this formulation that at $T = 0$, all particles reside in the ground state, implying $n_0 = n$. However, as the temperature increases, n_0 gradually decreases. It reaches zero at the critical temperature T_c, and remains zero for temperatures above T_c.

Utilizing these insights, other thermodynamic properties of the Bose gas can be precisely calculated. For instance, the total internal energy of the gas is given by:

$$U = V\int_0^\infty \frac{\epsilon}{e^{\beta(\epsilon-\mu)}-1} g(\epsilon)d\epsilon = V(k_BT)^{5/2}\frac{m^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty \frac{ze^{-x}}{1-ze^{-x}}x^{3/2}dx.$$

The average energy per particle, for temperatures above T_c, is determined by dividing the total internal energy by the particle number:

$$u = \frac{U}{N} = \frac{3}{2}k_BT\frac{g_{5/2}(z)}{g_{3/2}(z)}$$

Below T_c, this average energy per particle is:

$$u = \frac{3}{2}k_B\frac{T^{5/2}}{T_c^{3/2}}\frac{g_{5/2}(1)}{g_{3/2}(1)},$$

where $g_{5/2}(z)$ is defined as:

$$g_{5/2}(z) = \sum_{p=1}^{\infty}\frac{z^p}{p^{5/2}},$$

and the numerical constant $g_{5/2}(1)$ equals $\zeta(5/2) = 1.342$.

In the high-temperature limit, significantly above T_c, the gas behaves as a normal Bose gas, with

$$u \sim \frac{3}{2}k_BT$$

(since both $g_{5/2}(z) \approx z$ and $g_{3/2}(z) \approx z$ for small z). This result coincides with the energy per particle in a classical monatomic ideal gas, indicating that at high temperatures ($T \gg T_c$), the Bose-Einstein statistics of the particles become negligible.

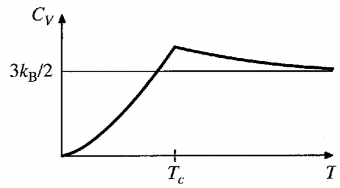
The examination of the gas's heat capacity reveals that T_c represents a bona fide thermodynamic phase transition. The heat capacity at constant volume, C_V, per particle, is obtained by differentiating the internal energy with respect to temperature while maintaining a constant density n:

$$C_V = \frac{\partial u}{\partial T}$$

For temperatures well above T_c, we find $C_V \sim \frac{3}{2}k_B$, mirroring the behavior of a classical ideal gas. Below T_c, however, C_V is given by:

$$C_V = \frac{15}{4}\frac{g_{5/2}(1)}{g_{3/2}(1)}\left(\frac{T}{T_c}\right)^{3/2} k_B.$$

This relationship is illustrated below:



Heat capacity of a Bose-Einstein ideal gas as a function of temperature T. The cusp at T_c implies that BEC is a thermodynamic phase transition.

At the critical temperature T_c, the heat capacity exhibits a distinctive cusp, characterized by a discontinuity in its slope. This behavior indicates that the free energy of the system is non-analytic at T_c, affirming that BEC indeed constitutes a thermodynamic phase transition. Other thermodynamic quantities, such as entropy or pressure, can also be derived using similar considerations.

Further reflection on the origin of BEC reveals additional insights. Initially, the summation over the discrete k-space plane wave states was replaced by a continuum integral. However, the realization that the $\mathbf{k} = 0$ state requires special treatment prompted a more nuanced approach, treating this state distinctly while approximating the remaining states as a continuum. Why is this approximation justified? Let us consider the occupation number of the first states with a finite wave vector $\mathbf{k}$. In a cubic box with side length L, the lowest energy states correspond to $k \approx 2\pi/L$, leading to an energy $\epsilon_{\mathbf{k}} \approx h^2/mL^2 = V^{-2/3}h^2/m$. The occupation number of these states is given by:

$$N_1 = \frac{1}{e^{\beta(\epsilon_{\mathbf{k}})} - 1} \approx \frac{1}{e^{\beta V^{-2/3}h^2/m} - 1} = O(V^{2/3}),$$

where the notation $O(n)$ signifies "of order n" in the limit $V \to \infty$. Although the occupation numbers of finite $\mathbf{k}$ states increase with V, they do so at a rate significantly slower than that of N_0. In fact, the ratio N_1/N_0 is $O(V^{-1/3})$ and tends to zero as $V \to \infty$. Consequently, in the limit of an infinitely large system, the occupations of any individual single-particle plane wave state with $\mathbf{k} \neq 0$ are negligible compared to the occupation of the unique state at $\mathbf{k} = 0$. Thus, in the thermodynamic limit, the continuum approximation for all $\mathbf{k}$ states, except for $\mathbf{k} = 0$, is indeed accurate and introduces no significant error.

6.4.2.3. *BEC in ultra-cold atomic gases.* In the late 1930s, shortly after Einstein's theoretical prediction of BEC, it was observed that liquid ^{4}He transitions into a superfluid state below the lambda point, at approximately 2.2 K. Considering the composition of a ^{4}He atom—two electrons, two protons, and two neutrons—it effectively behaves as a boson, characterized by a total spin of zero. This prompted the hypothesis of a connection between BEC and the superfluidity observed in ^{4}He. An interesting observation arises when calculating the critical temperature T_c for BEC in ^{4}He, using its density ($\rho \approx 145$ kg.m^{-3}) and atomic mass ($m \approx 4m_p$), which yields a value of approximately 3.1 K using Eq. (6.53). This is notably close to the superfluid transition temperature of ^{4}He.

However, the BEC theory primarily concerns an ideal gas and neglects particle interactions, which are significant in liquid helium due to its high particle density. As a result, liquid helium is not an ideal test case for validating BEC theory. Indeed, there are notable differences between the properties of superfluid ^{4}He and the predictions for an ideal Bose gas.

It was not until 1995 that BEC was experimentally realized in dilute gases of alkali metal atoms, rather than in helium. Advances in the techniques for trapping and cooling atoms in magnetic and laser traps over the previous two decades made this possible. Despite the seemingly unfavorable conditions—extremely low atomic densities in the traps (approximately $10^{11} - 10^{15}$ cm^{-3}, far less than the atomic density of ^{4}He) and the larger atomic masses of alkalis compared to ^{4}He—BEC was achieved. Employing Eq. (6.53) suggests critical temperatures (T_c) for alkali atoms would be significantly lower than for ^{4}He, in the range of 10 nK to 1 K. The ability to reach such low temperatures in laboratory settings is a remarkable feat of modern atomic physics. A detailed explanation of these cooling and trapping techniques is beyond the scope of this text, but a brief overview of the fundamental principles is provided.

A key question is how large atoms, such as rubidium, can be classified as bosons. In quantum mechanics, particles with integer spins are bosons. Alkali metal atoms, with a single valence electron in their outermost s-orbital, have their other electrons in completely filled shells, resulting in zero net orbital angular momentum and spin. The nucleus's spin then determines the atom's overall spin. Isotopes like ^{7}Li, ^{23}Na, and ^{87}Rb, with $S = 3/2$ nuclei, combined with the valence electron's spin ($S = 1/2$), result in total spin states of either $S = 2$ or $S = 1$. In quantum mechanics, the sum of two spins S_1 and S_2 leads to total spin values ranging from $|S_1 - S_2|$ to $S_1 + S_2$. If a gas is prepared such that only atoms in one of these spin states are present, it behaves as a Bose gas. However, if both $S = 1$ and $S = 2$ states coexist, the gas effectively becomes a mixture of two distinguishable boson species.

To understand how these atoms can be magnetically trapped, one must consider the atom's energy levels and their response to a magnetic field. Assuming an alkali atom with an $S = 3/2$ nucleus, the explicit spin wave functions for different quantum states can be deduced. The maximum total spin states ($S = 2$) comprise five states, with z-components of total spin given by quantum numbers $M_s = 2, 1, 0, -1, -2$. The state with $M_s = 2$ is represented as $|S = 2, M_s = 2\rangle = |\frac{3}{2}, \frac{1}{2}\rangle$, using the notation $|m_{s_1}, m_{s_2}\rangle$ for the nuclear state m_{s_1} and the electron state m_{s_2}. The other M_s quantum states with total spin $S = 2$ are generated using the spin lowering operator $\hat{S}^- = \hat{S}_1^- + \hat{S}_2^-$ and the identity $\hat{S}^- |k\rangle = \sqrt{s(s+1) - m(m-1)}\, |m-1\rangle$ to obtain the states $M_s = 2, 1, 0, -1, -2$:

$$\begin{aligned}
|S = 2, M_s = 2\rangle =& |\frac{3}{2}, \frac{1}{2}\rangle\,, \\
|S = 2, M_s = 1\rangle =& \frac{1}{2}\left(\sqrt{3}\,|\frac{1}{2}, \frac{1}{2}\rangle + |\frac{3}{2}, -\frac{1}{2}\rangle\right), \\
|S = 2, M_s = 0\rangle =& \frac{1}{\sqrt{2}}\left(|\frac{1}{2}, -\frac{1}{2}\rangle + |\frac{1}{2}, \frac{1}{2}\rangle\right), \\
|S = 2, M_s = -1\rangle =& \frac{1}{2}\left(\sqrt{3}\,|-\frac{1}{2}, -\frac{1}{2}\rangle + |-\frac{3}{2}, \frac{1}{2}\rangle\right), \\
|S = 2, M_s = -2\rangle =& |-\frac{3}{2}, -\frac{1}{2}\rangle\,.
\end{aligned}$$

The three states with total spin $S = 1$ and $M_s = 1, 0, -1$ must be orthogonal to the corresponding $S = 2$ states, and this requirement determines them uniquely to be

$$\begin{aligned}
|S = 1, M_s = 1\rangle =& \frac{1}{2}\left(|\frac{1}{2}, \frac{1}{2}\rangle - \sqrt{3}\,|\frac{3}{2}, -\frac{1}{2}\rangle\right), \\
|S = 1, M_s = 0\rangle =& \frac{1}{\sqrt{2}}\left(|\frac{1}{2}, -\frac{1}{2}\rangle - |-\frac{1}{2}, \frac{1}{2}\rangle\right), \\
|S = 1, M_s = -1\rangle =& \frac{1}{2}\left(|-\frac{1}{2}, -\frac{1}{2}\rangle - \sqrt{3}\,|-\frac{3}{2}, \frac{1}{2}\rangle\right).
\end{aligned}$$

The effective potential energy of the trap, as depicted in Fig. 6.2, facilitates a natural mechanism for cooling the trapped gas. Atoms with higher kinetic energies are likely to escape the trap, taking their energy with them. This process, akin to cooling by evaporation, results in a reduction of the average kinetic energy of the remaining atoms. By carefully controlling the barrier height, one can regulate the rate of cooling and, consequently, the final temperature of the system. Employing this method, temperatures below 1 pK can be attained.

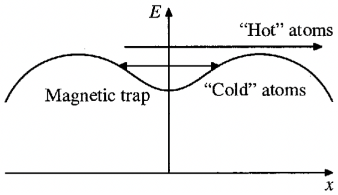


Figure 6.2. A magnetic trap provides a local minimum in energy. Atoms which are too energetic can escape, while atoms with lower kinetic energy are trapped. Also atoms in a quantum state M_s whose energy decreases with $|\mathbf{B}|$ will see a local maximum in potential energy, not a minimum, and so will be expelled from the trap.

In contrast to the ideal Bose gas discussed earlier in this chapter, the alkali atoms in a magnetic trap do interact with each other. These interactions can be quite pronounced, particularly due to strong repulsion at short distances and van der Waals attraction at larger distances. Without these interactions, atoms in the trap would likely form tightly bound clusters. However, the rate of such clustering is considerably slow. The primary reason is that collisions in the trap are predominantly two-body elastic collisions, which do not lead to binding. The formation of bound states would require three-body collisions, where a pair of atoms could form a bound state while the excess kinetic energy is carried away by the third atom. Given the low density of atoms in the trap (typically around $n \sim 10^{11} - 10^{15}$ cm^{-3}), corresponding to interatomic spacings of $r_s \sim 50 - 600$ nm (where r_s is defined by $n = 1/(4\pi r_s^3/3)$), the likelihood of simultaneous three-body collisions is minimal. Therefore, the atoms can be maintained in the trap for extended periods (seconds or even minutes), allowing sufficient time for experimental observations.

Nevertheless, two-body collisions between particles in the trap are not entirely inconsequential. First, it is essential to recognize that these collisions do not induce transitions between different hyperfine quantum states, as shown in Fig. 6.1. This holds true for atoms in low field-seeking states like $S = 2$, $M_s = 2$ or $S = 1$, $M_s = -1$. Consequently, atoms prepared in one of these states will remain in that state. Second, inter-particle interactions contribute significantly to the overall potential energy within the trap and must be considered. Pairwise interactions are also crucial for establishing thermal equilibrium within the experimental timeframe. These collisions lead to an energy redistribution, a necessary condition for the system to reach thermal equilibrium. An approximate treatment of the interatomic pair interactions involves considering the interaction to act over a very short range compared to the typical inter-particle separation. Consequently, we can model the pair interaction as a Dirac delta-function.

$$V(\mathbf{r}_1 - \mathbf{r}_2) \approx g\delta(\mathbf{r}_1 - \mathbf{r}_2). \tag{6.55}$$

The interaction can therefore be characterized by a single constant, g. Using scattering theory this can also be expressed as a two-body s-wave scattering length, a_s, defined by

$$g = \frac{4\pi a_s \hbar^2}{m}.$$

Usually g and a_s, are positive, corresponding to a net repulsive interaction. On average the effects of this interactions can be represented as an additional potential felt by each particle, resulting from the average interaction with the other particles. This mean-field contribution to the potential can be written

$$V_{eff}(\mathbf{r}) = gn(\mathbf{r}), \tag{6.56}$$

where $n(\mathbf{r})$ is the density of atoms at point r in the trap. In this approximation the atoms in the magnetic trap obey an effective Schödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{trap}(\mathbf{r}) + V_{eff}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \tag{6.57}$$

where $V_{trap}(\mathbf{r})$ is the effective potential of the magnetic trap, as in Fig. 6.2, including both the magnetic field energy and gravity. Equation 6.57 is effectively a nonlinear Schrödinger equation, since the potential depends on the particle density which in turn depends on the wave functions via the Bose-Einstein distribution

$$n(\mathbf{r}) = \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} |\psi_i(\mathbf{r})|^2. \tag{6.58}$$

As usual, the chemical potential μ, is determined from the constraint of the constant total number of atoms in the trap, N,

$$N = \int n(\mathbf{r}) d^3\mathbf{r} = \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \tag{6.59}$$

These equations (Eqs 6.56-6.59) are a closed set, which must be solved self-consistently. At zero temperature all of the particles are in the condensate, and

$$n(\mathbf{r}) = N|\psi_0(\mathbf{r})|^2,$$

where $\psi_0(\mathbf{r})$ is the ground state wave function. These coupled equations must be solved self-consistently to find the wavefunctions, density $n(\mathbf{r})$ and the effective potential $V_{eff}(\mathbf{r})$. They are known as the Gross-Pitaevskii equations.

Solving the coupled set of nonlinear equations inherent in this context necessitates numerical methods. Despite this complexity, the solution once again reveals a form of BEC. If the lowest energy state in the potential well is denoted as ϵ_0, a critical temperature T_c can be identified where the occupation number of this state, N_0, transitions abruptly from a small value (of the order of 1) to a large value (comparable to N). According to the principles of statistical mechanics, this phenomenon, strictly speaking, cannot be classified as a thermodynamic phase transition due to the finite number of particles involved, precluding a thermodynamic limit. However, in practical terms, the atom numbers in traps are often large (ranging from 10^4 to 10^6), making the critical temperature T_c quite distinct and well-defined.

The first observation of BEC in trapped ultra-cold gases occurred in 1995, leading to the awarding of the 2001 Nobel Prize in Physics to Cornell, Ketterle, and Wieman for this breakthrough. This discovery was the culmination of decades of work by numerous research groups dedicated to developing and refining the technology of trapping and cooling atoms using magnetic and laser traps. In 1995, three separate research teams achieved BEC using different alkali atoms: ^{87}Rb, ^{23}Na, and ^{7}Li. The experimental setups incorporated both magnetic and laser trapping methods, although the specifics of laser trapping and cooling are beyond the scope of this discussion. The temperatures at which BEC was observed varied depending on the alkali atom and the achieved atomic density in the trap, typically in the range of 0.5-2 pK.

Following the successful realization of BEC in atomic gases, a wide array of experiments has been conducted. The system presents an ideal experimental platform due to the controllability of all physical parameters and the versatility in manipulating the BEC. Similar experiments have been conducted with Fermi-Dirac atoms, although they do not exhibit BEC. It has been found that the interatomic interactions, as described in Eq. 6.55, play a crucial role in the behavior of atomic BEC, meaning the system represents weakly interacting bosons rather than an ideal Bose gas. These weak but significant two-body interactions are pivotal. For instance, an ideal BEC, in the absence of interactions, does not exhibit superfluidity, as the critical velocity for superfluid flow is zero.

However, when interactions are present, even if minimal, they enable the sustenance of a genuine superfluid state. This encompasses phenomena such as zero-viscosity flow or the maintenance of persistent currents impervious to external disturbances. In experimentally obtained atomic BECs, the small yet finite residual interactions mean these systems effectively function as superfluids, with observed phenomena including persistent currents and superfluid vortices.

Finally, experiments have also addressed the implications of macroscopic quantum coherence in BECs. These studies have demonstrated quantum superpositions and interference effects in systems with macroscopically large numbers of particles (on the order of 10^5 to 10^6). Such macroscopic superposition states serve as a physical embodiment of the Schrödinger cat paradox in quantum measurement theory. Analogous to placing the Schrödinger cat in a quantum superposition of "dead" and "alive" states, BECs can be manipulated into superpositions of two quantum states, each differing macroscopically in particle coordinates.

Chapter 7

Liquids

In statistical mechanics, the liquid state presents a uniquely challenging and fascinating subject. Liquids, occupying the intermediate phase between the ordered solidity of crystals and the disordered gaseous state, exhibit a complex balance of order and randomness. Understanding this phase from the perspective of statistical mechanics involves delving into the interplay of molecular interactions and thermal motion. Unlike gases, where particles are widely separated and interact weakly, or solids, where particles occupy fixed positions in a lattice, liquids are characterized by short-range order and mobility of particles within a fluid structure.

Central to the statistical mechanical treatment of liquids is the concept of the radial distribution function (RDF), which provides a measure of the probability of finding a pair of particles separated by a certain distance. This function is pivotal in characterizing the microscopic structure of liquids, revealing the balance between thermal motion and intermolecular forces. The RDF in liquids shows peaks corresponding to the preferred distances between particles, indicative of short-range order, but lacks the long-range periodicity seen in solids.

Another cornerstone in the study of liquids is the Mayer expansion, a series expansion of the partition function in terms of the so-called Mayer f-functions. These functions quantify the effect of particle interactions and are instrumental in translating the microscopic interactions into macroscopic thermodynamic properties. The Virial expansion, derived from the Mayer series, expresses the equation of state in terms of the powers of density, providing insights into the behavior of liquids under various conditions.

Additionally, integral equations like the Percus-Yevick equation offer a route to calculate the RDF. These equations, derived from the Ornstein-Zernike relation, incorporate approximations for handling the complex many-body interactions in liquids. The Percus-Yevick approximation, for instance, has been remarkably successful in describing simple liquids, offering a balance between analytical tractability and physical realism.

In summary, the statistical mechanics of liquids involves an intricate blend of theoretical constructs and approximations, each contributing to our understanding of the liquid state. By exploring the microscopic details through these tools, we gain a deeper appreciation of the unique properties of liquids – their structure, dynamics, and the subtle balance of forces that govern their behavior. This understanding is not just theoretical; it has practical implications in fields ranging from material science to biology, where the liquid state plays a crucial role.

7.1. Radial Distribution Function

We first introduce the local density of particles as a random variable

$$N(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{Q}_i).$$

Here $\mathbf{Q}_i$ are random variables whose realizations correspond to the positions of the individual molecules. That the quantity $N(\mathbf{r})$ really is something like a local particle density can easily be seen when we calculate the number of particles in a volume element dV. In this case one finds for the number $n(\mathbf{r})$ of a realization of $N(\mathbf{r})$:

$$\int_{dV} d^3\mathbf{r}\, n(\mathbf{r}) = \sum_{i=1}^{N} \int_{dV} d^3\mathbf{r}\, \delta(\mathbf{r} - \mathbf{q}_i) = \sum_{i=1}^{N} I_{\mathbf{q}_i \in dV},$$

where $I_{\mathbf{q}_i \in dV} = 1$ if $\mathbf{q}_i$ is in dV, and is otherwise zero. So all particles in dV are counted. For a canonical system one has

$$\langle N(\mathbf{r}) = \frac{1}{n! h^{3N} Z} N \int d^{3N}\mathbf{p} \int d^{3N}\mathbf{q}\, \delta(\mathbf{r} - \mathbf{q}_1) e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q})} = N\rho_1(\mathbf{r}) \tag{7.1}$$

with the marginal density

$$\rho_1(\mathbf{r}) = \frac{1}{N! h^{3N} Z} \int d^{3N}\mathbf{p} \int d^3\mathbf{q}_2 \dots d^3\mathbf{q}_N\; e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q})}\Big|_{\mathbf{q}_1 = \mathbf{r}}. \tag{7.2}$$

In a spatially homogeneous system the particle density is independent of position. It is therefore a constant across space. Normalization (integration over all space) requires that it takes the value

$$\rho_1(\mathbf{r}) = \frac{1}{V}$$

and therefore one finds for the local density of particles

$$\langle N(\mathbf{r}) = \frac{N}{V} \equiv n.$$

Next we consider the second moment

$$\begin{aligned}\langle N(\mathbf{r})N(\mathbf{r}')\rangle &= \sum_{i,j=1}^{N}\langle\delta(\mathbf{r}-\mathbf{Q}_i)\delta(\mathbf{r}'-\mathbf{Q}_j)\rangle\\ &=\sum_{i=1}^{N}\langle\delta(\mathbf{r}-\mathbf{Q}_i)\delta(\mathbf{r}'-\mathbf{Q}_i)\rangle+\sum_{i\neq j}^{N}\langle\delta(\mathbf{r}-\mathbf{Q}_i)\delta(\mathbf{r}'-\mathbf{Q}_j)\rangle.\end{aligned}$$

For the first term one obtains immediately

$$\begin{aligned}\sum_{i=1}^{N}\langle\delta(\mathbf{r}-\mathbf{Q}_i)\delta(\mathbf{r}'-\mathbf{Q}_i)\rangle =&\delta(\mathbf{r}-\mathbf{r}')\sum_{i=1}^{N}\langle\delta(\mathbf{r}-\mathbf{Q}_i)\rangle\\ =&\delta(\mathbf{r}-\mathbf{r}')\langle N(\mathbf{r})\rangle\\ =&\frac{N}{V}\delta(\mathbf{r}-\mathbf{r}')=n\delta(\mathbf{r}-\mathbf{r}')\end{aligned}$$

and for the second term

$$\begin{aligned}\sum_{i\neq j}^{N}\langle\delta(\mathbf{r}-\mathbf{Q}_i)\delta(\mathbf{r}'-\mathbf{Q}_j)\rangle =&\frac{N(N-1)}{N!h^{3N}Z}\int d^{3N}\mathbf{p}d^{3N}\mathbf{q}\,\delta(\mathbf{r}-\mathbf{q}_1)\delta(\mathbf{r}'-\mathbf{q}_2)e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q})}\\ =&N(N-1)\rho_2(\mathbf{r},\mathbf{r}')\end{aligned}$$

with the marginal density

$$\rho_2(\mathbf{r},\mathbf{r}')=\frac{1}{N!h^{3N}Z}\int d^{3N}\mathbf{p}d^3\mathbf{q}_3\dots d^3\mathbf{q}_N\;\; e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q})}\Big|_{\mathbf{q}_1=\mathbf{r},\mathbf{q}_2=\mathbf{r}}.$$

Hence, for the second moments of the local density of particles we find

$$\langle N(\mathbf{r}N(\mathbf{r}')\rangle=\frac{N}{V}\delta(\mathbf{r}-\mathbf{r}')+N(N-1)\rho_2(\mathbf{r},\mathbf{r}').$$

For a spatially homogeneous system the second moment function $\langle N(\mathbf{r}N(\mathbf{r}')\rangle$ can depend only on $\mathbf{r}-\mathbf{r}'$. If in addition the system is isotropic, $\langle N(\mathbf{r}N(\mathbf{r}')\rangle$ can depend only on $|\mathbf{r}-\mathbf{r}'|$.

For large distances $|\mathbf{r}-\mathbf{r}'|$ the dependence between the two local densities should vanish such that

$$\langle N(\mathbf{r}N(\mathbf{r}')\rangle\to\langle N(\mathbf{r}\rangle\langle N(\mathbf{r}')\rangle=n^2\quad\text{for}\quad|\mathbf{r}-\mathbf{r}'|\to\infty.$$

This suggests that, in addition to the second moment function, one also introduces a radial distribution function given by

$$\begin{aligned} g_2(\mathbf{r},\mathbf{r}') =& \frac{\langle N(\mathbf{r})N(\mathbf{r}')\rangle - n\delta(\mathbf{r}-\mathbf{r}')}{\langle N(\mathbf{r})\rangle\langle N(\mathbf{r}')\rangle} \\ =& \frac{N(N-1)}{n^2}\rho_2(\mathbf{r},\mathbf{r}') \\ =& \frac{(N-1)V}{n}\rho_2(\mathbf{r},\mathbf{r}'). \end{aligned} \tag{7.3}$$

This function satisfies $g_2(\mathbf{r},\mathbf{r}') \to 1$ for $|\mathbf{r}-\mathbf{r}'| \to \infty$.

From their definition, the second moment function and the radial distribution function are closely related to the interactions between the particles. We clarify this point below.

For an ideal gas we get immediately from (7.2)

$$\rho_2(\mathbf{r},\mathbf{r}') = \frac{1}{V^2}$$

and therefore

$$\langle N(\mathbf{r})N(\mathbf{r}')\rangle = \frac{N}{V}\delta(\mathbf{r}-\mathbf{r}') + \frac{N(N-1)}{V^2}.$$

For the radial distribution function this leads to $g_2(\mathbf{r},\mathbf{r}') = \frac{N-1}{N} \approx 1$.

Note that one always has

$$\int d^3\mathbf{r}\, d^3\mathbf{r}'\, \langle N(\mathbf{r})N(\mathbf{r}')\rangle = N^2.$$

Furthermore, we find

$$n g_2(\mathbf{r},\mathbf{r}') = (N-1)\frac{\rho_2(\mathbf{r},\mathbf{r}')}{\rho_1(\mathbf{r})} = (N-1)\rho_2(\mathbf{r}|\mathbf{r}'),$$

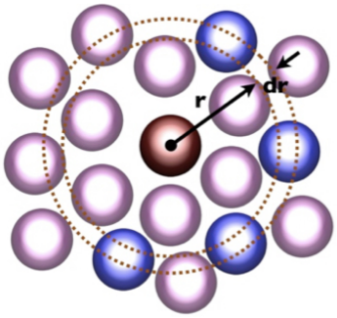
where $\rho_2(\mathbf{r}'|\mathbf{r})d^3\mathbf{r}'$ is the probability of finding a particle in a region around $\mathbf{r}'$ under the condition that a particle is at $\mathbf{r}$. In particular, if $g_2(\mathbf{r},\mathbf{r}')$ only depends on $|\mathbf{r}-\mathbf{r}'|$, one gets

$$\int d^3\mathbf{r}'\, n\, g_2(|\mathbf{r}-\mathbf{r}'|) = \int dr\, r^2\, 4\pi\, n g_2(r) = (N-1)$$

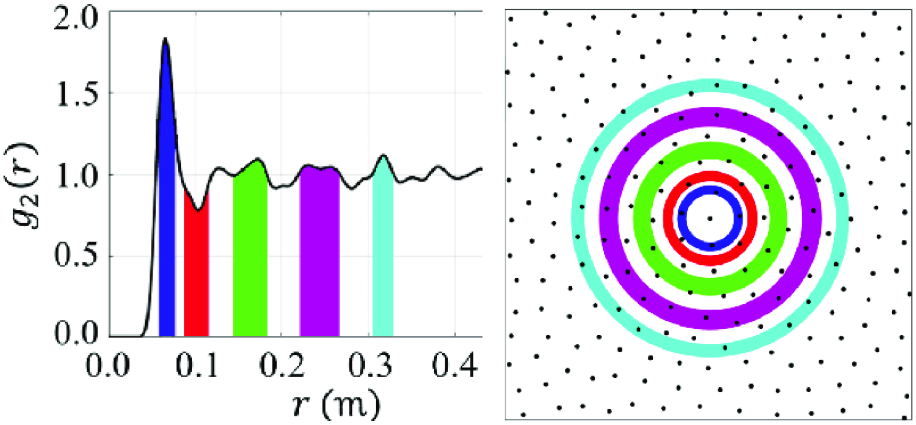
and therefore

$$n\, g_2(r) 4\pi r^2 dr$$

is the average number of molecules in a spherical shell $(r, r+dr)$ around a given molecule in the gas.



In a spatially homogeneous system the origin may be placed at the center of any particle picked at random. Obviously for $r \to 0$ we must have $g_2(\mathbf{r}) \to 0$, as the molecules cannot overlap. $g_2(\mathbf{r})$ assumes its maxima at values which correspond to those distances from the reference particle where other particles are most likely to be found. Consequently, for a crystal $g_2(\mathbf{r})$ not only depends on $|\mathbf{r}|$, but it displays sharp maxima for those vectors that are lattice vectors. In a liquid one would not expect such a sharp structure, but one will find rotational symmetry and a few peaks whose sharpness, however, decreases with increasing distance:



We will now show how certain many-particle quantities can be reduced to two-particle quantities using the radial distribution function.

1) Suppose that the interaction potential $V(\mathbf{q}_1, \ldots, \mathbf{q}_N)$ can be represented as a sum of two-particle potentials

$$V(\mathbf{q}_1, \ldots, \mathbf{q}_N) = \frac{1}{2} \sum_{i \neq j}^{N} V_2(\mathbf{q}_i - \mathbf{q}_j);$$

then $\langle V(\mathbf{q}_1,\ldots,\mathbf{q}_N)\rangle$ is determined by the radial distribution function. Indeed,

$$\begin{aligned}\langle V(\mathbf{q}_1,\ldots,\mathbf{q}_N)\rangle =&\frac{1}{2}\sum_{i\neq j}^{N}\langle V_2(\mathbf{q}_i-\mathbf{q}_j)\rangle\\ =&\frac{1}{2}\frac{N(N-1)}{N!h^{3N}Z}\int d^{3N}\mathbf{p}\int d^{3N}\mathbf{q}V_2(\mathbf{q}_i-\mathbf{q}_j)e^{-\beta H(\mathbf{p},\mathbf{q})}\\ =&\frac{1}{2}N(N-1)\int d^{3N}\mathbf{q}_1\int d^3\mathbf{q}_2V_2(\mathbf{q}_1-\mathbf{q}_2)\rho_2(\mathbf{q}_1,\mathbf{q}_2)\\ =&\frac{1}{2}\frac{N^2}{V}\int d^3\mathbf{q}\,g_2(\mathbf{q})V_2(\mathbf{q}),\end{aligned}$$

where we have used $(N-1)V\rho_2(\mathbf{q})=ng_2(\mathbf{q})$. Therefore, taking into account

$$\langle\mathcal{H}_{kin}\rangle=\frac{3}{2}Nk_BT,$$

one obtains for $\langle\mathcal{H}\rangle$:

$$\langle\mathcal{H}\rangle=\frac{3}{2}Nk_BT+\frac{N^2}{2V}\int d^3\mathbf{q}\,g_2(\mathbf{q})V_2(\mathbf{q}).$$

In classical mechanics the virial is the time average of the quantity

$$\sum_{\alpha=1}^{3N}q_\alpha\frac{\partial V(\mathbf{q}_1,\ldots,\mathbf{q}_N)}{\partial q_\alpha},$$

and a virial theorem holds in the form

$$2\overline{\mathcal{H}_{kin}}=\overline{\sum_{\alpha=1}^{3N}q_\alpha\frac{\partial V(\mathbf{q}_1,\ldots,\mathbf{q}_N)}{\partial q_\alpha}},$$

where $\overline{A}$ denotes the time average of some quantity A.

2) In statistical mechanics the expectation value

$$\mathcal{V}=\left\langle\sum_{\alpha=1}^{3N}q_\alpha\frac{\partial V(\mathbf{q}_1,\ldots,\mathbf{q}_N)}{\partial q_\alpha}\right\rangle$$

is called the virial of the potential $V(\mathbf{q}_1,\ldots,\mathbf{q}_N)$. If the potential can be written as a sum of two-particle potentials, then

$$\mathcal{V}=\left\langle\sum_{k=1}^{N}\mathbf{q}_k\cdot\nabla_kV\right\rangle=\frac{1}{2}\sum_{i\neq j}\langle(\mathbf{q}_i-\mathbf{q}_j)\cdot\nabla V_2(\mathbf{q}_i-\mathbf{q}_j)\rangle. \tag{7.4}$$

All $N(N-1)$ terms in the sum in (7.4) now lead to the same contribution, thus

$$\begin{aligned}\mathcal{V} =&N(N-1)\frac{1}{2}\int d^3\mathbf{q}_1\int d^3\mathbf{q}_2(\mathbf{q}_1-\mathbf{q}_2)\cdot\nabla V_2(\mathbf{q}_1-\mathbf{q}_2)\rho_2(\mathbf{q}_1,\mathbf{q}_2)\\ =&\frac{1}{2}\frac{N^2}{V}\int d^3\mathbf{q}\, g_2(\mathbf{q})\mathbf{q}\cdot\nabla V_2(\mathbf{q}),\end{aligned}$$

where we have again used

$$(N-1)V\rho_2(\mathbf{q}) = ng_2(\mathbf{q}) = \frac{N}{V}g_2(\mathbf{q}). \tag{7.5}$$

Hence, the radial distribution function also determines the virial of the total many-particle potential.

To obtain a virial theorem in statistical mechanics we consider the state density of the canonical system. We consider the identity

$$Z(T,t^3V,N) = \int d^{3N}\mathbf{q}d^33N\mathbf{p}\exp\left(-\beta\left(\sum_{\alpha=1}^{3N}\frac{p_\alpha^2}{2mt^2}+V(tq_1,\ldots,tq_{3N})\right)\right).$$

That this equation holds can easily be seen by the coordinate transformation $p'_\alpha = \frac{1}{t}p_\alpha$, $q'_\alpha = tq_\alpha$, which leaves the measure $d^{3N}\mathbf{q}d^{3N}\mathbf{p}$ invariant but stretches each length by a factor t.

Taking the derivative with respect to t and then setting $t=1$ leads to

$$3V\frac{\partial Z(T,V,N)}{\partial V} = \left(2\beta\langle\mathcal{H}_{kin}\rangle - \beta\left\langle\sum_{\alpha=1}^{3N}q_\alpha\frac{\partial V}{\partial q_\alpha}\right\rangle\right)Z,$$

or, with $\frac{1}{Z}\frac{\partial Z}{\partial V} = \frac{\partial}{\partial V}(-\beta F) = \beta P$ (F: Helmholtz free energy)

$$PV = \frac{2}{3}\langle\mathcal{H}_{kin}\rangle - \frac{1}{3}\left\langle\sum_{\alpha=1}^{3N}q_\alpha\frac{\partial V}{\partial q_\alpha}\right\rangle.$$

Using (7.5) and

$$\langle\mathcal{H}_{kin}\rangle = \frac{3}{2}Nk_BT$$

and within the framework of statistical mechanics one obtains from the virial theorem the general equation of state in the form

$$PV = Nk_BT - \frac{1}{6}\frac{N^2}{N}\int d^3\mathbf{q}g_2(\mathbf{q})\mathbf{q}\cdot\nabla V_2(\mathbf{q}). \tag{7.6}$$

Hence, the radial distribution function plays a key role for the equations of state of real gases. It is even accessible by experiment.

7.2. Elastic Scattering

The radial distribution function in a spatially homogeneous system may also be written as

$$n\,g_2(\mathbf{r}) = \sum_{j=2}^{N} \langle \delta(\mathbf{r} - \mathbf{Q}_1 + \mathbf{Q}_j) \rangle \equiv (N-1) \langle \delta(\mathbf{r} - \mathbf{Q}_1 + \mathbf{Q}_2) \rangle.$$

This is easy to see: since $\rho_2(\mathbf{q}_1, \mathbf{q}_2)$ can only depend on $(\mathbf{q}_1 - \mathbf{q}_2)$, we get

$$(N-1)\langle \delta(\mathbf{r} - \mathbf{Q}_1 + \mathbf{Q}_2) \rangle = (N-1) \int d^3\mathbf{q}_1\, d^3\mathbf{q}_2\, \delta(\mathbf{r} - \mathbf{q}_1 + \mathbf{q}_2) \rho_2(\mathbf{q}_1, \mathbf{q}_2) = (N-1) V \rho_2(\mathbf{r})$$

and a comparison with (7.3) leads to the statement.

Now the Fourier transform of

$$\frac{1}{n}\langle N(0) N(\mathbf{r}) \rangle = \delta(\mathbf{r}) + n\,g_2(\mathbf{r}) = \delta(\mathbf{r}) + \sum_{j=2}^{N} \langle \delta(\mathbf{r} - \mathbf{Q}_1 + \mathbf{Q}_j) \rangle = \sum_{j=1}^{N} \langle \delta(\mathbf{r} - \mathbf{Q}_1 + \mathbf{Q}_j) \rangle$$

is easily calculated and we obtain

$$I(\boldsymbol{\kappa}) = \frac{1}{2\pi} \int d^3\mathbf{r}\, e^{i\boldsymbol{\kappa}\cdot\mathbf{r}} \sum_{j=1}^{N} \langle \delta(\mathbf{r} - \mathbf{Q}_1 + \mathbf{Q}_j) \rangle = \frac{1}{2\pi} \sum_{j=1}^{N} \langle e^{i\boldsymbol{\kappa}\cdot\mathbf{Q}_1} e^{-i\boldsymbol{\kappa}\cdot\mathbf{Q}_j} \rangle = \frac{1}{2\pi}\frac{1}{N} \sum_{i,j=1}^{N} \langle e^{i\boldsymbol{\kappa}\cdot\mathbf{Q}_i} e^{-i\boldsymbol{\kappa}\cdot\mathbf{Q}_j} \rangle.$$

$I(\boldsymbol{\kappa})$ is called the elastic structure function. It can be measured experimentally in the quasi-elastic scattering of neutrons or X-rays at a momentum transfer of $\hbar\boldsymbol{\kappa}$. Thus the Fourier transform of the radial distribution function is a measurable quantity.

Remark 7.1. The static structure function follows from the dynamical structure function $S(\boldsymbol{\kappa}, \omega)$ for general inelastic scattering with momentum transfer $\hbar\boldsymbol{\kappa}$ and energy transfer $\hbar\omega$ by

$$I(\boldsymbol{\kappa}) = \hbar \int d\omega S(\boldsymbol{\kappa}, \omega). \tag{7.7}$$

This dynamical structure function $S(\boldsymbol{\kappa}, \omega)$ is proportional to the cross section for the inelastic scattering of a particle (neutron or photon) with momentum $\hbar\boldsymbol{\kappa}$ and energy E into the state $\hbar\boldsymbol{\kappa}'$, E':

$$\frac{d^2\sigma}{d\Omega dE'} \propto S(\boldsymbol{\kappa}, \omega), \qquad \boldsymbol{\kappa} = \mathbf{k} - \mathbf{k}', \qquad E' - E = \hbar\omega.$$

A scattering process is called quasi-elastic if the energy transfer satisfies $|E' - E| \ll E$; for a given scattering angle $\boldsymbol{\kappa}$ is then independent of E'. If, then, for a given momentum transfer all photons or neutrons are registered regardless of their energies E', this corresponds to the integration of the cross section over ω in (7.7) and therefore

$$I(|\boldsymbol{\kappa}|) \propto \frac{d\sigma}{d\Omega} \equiv \int dE' \frac{d^2\sigma}{d\Omega dE'}.$$

7.3. Approximation Methods

In the previous section we have met a central quantity in the description of nonideal gases, namely the radial distribution function, and we have derived some general statements about the form of the equations of state in terms of this distribution function.

Now we will examine how systematic approximations allow us to calculate the radial distribution function or to obtain the equations of state directly. This is the subject of the statistical theory of fluids. A further approximation method, the mean field approximation, is normally introduced in the context of spin systems.

7.3.1. The Virial Expansion. For the ideal gas it was a straightforward matter to derive the equation of state. We found that the pressure is linear in the particle density $n = N/V$, explicitly $P = k_B T n$. Here for nonideal gases an expansion with respect to powers of the particle density n in the form

$$\frac{P}{nk_BT} = \frac{PV}{Nk_BT} = 1 + b(T)n + c(T)n^2 + \dots$$

will be derived. We proceed from the partition function of the grand canonical system

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z(T,V,N).$$

Here $z = e^{\beta\mu}$, also called fugacity, and $Z(T,V,N)$ is the partition function of the N-particle system. One obtains

$$\log \mathcal{Z} = -\beta\Omega = \frac{PV}{k_BT} = \log(1 + zZ(T,V,1) + z^2 Z(T,V,2) + \dots).$$

Expanding the logarithm

$$\log(1+x) = \sum_{k=1}^{\infty} \frac{(-1)^{k-1}}{k} x^k = x - \frac{x^2}{2} + \frac{x^3}{3} - \cdots,$$

valid for $|x| \le 1$ and $x \ne -1$, one finds

$$\log \mathcal{Z} = \frac{PV}{k_BT} = zZ_1 + z^2 Z_2 + z^3 Z_3 + \dots \tag{7.8}$$

with

$$Z_1 = Z(T,V,1), \quad Z_2 = Z(T,V,2) - \frac{1}{2} Z^2(T,V,1), \quad \text{etc.}$$

Equation (7.8) would have the form of an equation of state if the fugacity z were written as a function of T, V, N. In order to achieve this, we note that the determination of N

$$N = -\frac{\partial\Omega}{\partial\mu} = k_BT\frac{\partial \log\Omega}{\partial\mu} = k_BT\frac{\partial z}{\partial\mu}\frac{\partial\log\Omega}{\partial z} = z\frac{\partial\log\Omega}{\partial z}$$

$$= zZ_1 + 2z^2 Z_2 + 3z^3 Z_3 + \dots \tag{7.9}$$

also leads to a series expansion in z. We now make the ansatz

$$z = \frac{N}{Z_1} + \alpha N^2 + \beta N^3 + \dots \tag{7.10}$$

for z as a function of T, V, N. Inserting this into the expansion (7.9) we can determine the coefficients $\alpha, \beta, \dots$ by comparing the coefficients of powers of N. In general this is a complicated procedure for which a systematic strategy should be developed. For the first two virial coefficients, however, we will go through this procedure explicitly:

The coefficients α and β are determined from

$$\begin{aligned} N = \left(\frac{N}{Z_1} + \alpha N^2 + \beta N^3 + \dots\right) Z_1 + 2\left(\frac{N}{Z_1} + \alpha N^2 + \beta N^3 + \dots\right)^2 Z_2 \\ + 3\left(\frac{N}{Z_1} + \alpha N^2 + \beta N^3 + \dots\right)^3 Z_3 + \dots \end{aligned}$$

The requirement that terms of order N^2 have to vanish on the right-hand size implies

$$\alpha Z_1 + 2\frac{Z_2}{Z_1^2} = 0,$$

and a similar requirement for the terms of order N^3 leads to

$$\beta Z_1 + 4\alpha\frac{Z_2}{Z_1} + 3\frac{Z_3}{Z_1^3} = 0.$$

Thus we find

$$\alpha = -2\frac{Z_2}{Z_1^3}, \qquad \beta = -3\frac{Z_3}{Z_1^4} + 8\frac{Z_2^2}{Z_1^5}.$$

With these coefficients we may insert z, as given by (7.10) into (7.8), yielding

$$\begin{aligned} \frac{PV}{k_BT} = &\left(\frac{N}{Z_1} + \alpha N^2 + \beta N^3 + \dots\right) Z_1 + \left(\frac{N}{Z_1} + \alpha N^2 + \beta N^3 + \dots\right)^2 Z_2 \\ &+ \left(\frac{N}{Z_1} + \alpha N^2 + \beta N^3 + \dots\right)^3 Z_3 + \dots \\ =&N + N^2\left(-\frac{NZ_2}{Z_1^2} + \frac{Z_2}{Z_1^2}\right) + N^3\left(-\frac{3Z_3}{Z_1^3} + 8\frac{Z_2^2}{Z_1^4} - \frac{4Z_2^2}{Z_1^4} + \frac{Z_3}{Z_1^3}\right), \end{aligned}$$

i.e., we obtain the equation of state in the form:

$$P = nk_BT(1 + b(T)n + c(T)n^2 + \dots) \tag{7.11}$$

with

$$b(T) = -\frac{Z_2V}{Z_1^2}, \quad c(T) = -2\frac{Z_3V^2}{Z_1^3} + 4\frac{Z_2^2V^2}{Z_1^4}.$$

This is the virial expansion. $b(T)$ is called the second and $c(T)$ the third virial coefficient.

Let us discuss some of these coefficients. First, we have

$$Z_1 = Z(T, V, 1) = \frac{V}{\lambda_t^2},$$

where λ_t is the thermal de Broglie wavelength,

$$\lambda_t = \sqrt{\frac{h^2}{2m\pi k_B T}},$$

already introduced previously. The existence of a potential does not have any effect in this expression. Next, we have

$$\begin{aligned} Z(T, V, 2) =& \frac{1}{2h^6} \int d^6\mathbf{p}\, d^6\mathbf{q} \exp\left(-\beta\left[\frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} + V_2(\mathbf{q}_1 - \mathbf{q}_2)\right]\right) \\ =& \frac{1}{2}\lambda_t^{-6} \int d^3\mathbf{q}_1 d^3\mathbf{q}_2 e^{-\beta V_2(\mathbf{q}_1 - \mathbf{q}_2)} \\ =& \frac{1}{2}\lambda_t^{-6} V \int d^3\mathbf{q} e^{-\beta V_2(\mathbf{q})} \end{aligned}$$

and therefore

$$b(T) = -\frac{(Z(T, V, 2) - \frac{1}{2}Z^2(T, V, 1))V}{Z^2(T, V, 1)} = -\frac{1}{2}\int d^3\mathbf{q}\, f(\mathbf{q})$$

with

$$f(\mathbf{q}) = e^{-\beta V_2(\mathbf{q})} - 1.$$

For $c(T)$ one obtains in the same manner

$$c(T) = -\frac{1}{3V}\int d^3\mathbf{q}_1 d^3\mathbf{q}_2 d^3\mathbf{q}_3 f(\mathbf{q}_1 - \mathbf{q}_2) f(\mathbf{q}_1 - \mathbf{q}_3) f(\mathbf{q}_2 - \mathbf{q}_3).$$

Similarly one can express all higher virial coefficients in terms of the function $f(\mathbf{q})$. We will now calculate the virial coefficients for two potentials explicitly.

7.3.2. Hard core potential. We think of atoms as hard cores of radius $\sigma/2$, i.e., for $q \le \sigma$ we have $V_2(\mathbf{q}) = \infty$, $f(\mathbf{q}) = -1$. For $q > \sigma$ we take $\beta V_2(\mathbf{q}) = \beta V_2(q) \ll 1$ such that $f(\mathbf{q}) = -\beta V_2(q)$ is a good approximation for $f(\mathbf{q})$. Under these conditions we get

$$b(T) = -\frac{1}{2}\int d^3\mathbf{q}\, f(\mathbf{q}) = \frac{1}{2}\int_0^\sigma dq\, 4\pi q^2 + \frac{1}{2}\beta\int_\sigma^\infty dq\, 4\pi q^2 V_2(q) = 2\pi\frac{\sigma^3}{3} + \frac{2\pi}{k_B T}\int_\sigma^\infty dq\, q^2 V_2(q),$$

i.e.,

$$b(T) = b_0 - \frac{a}{k_B T}, \tag{7.12}$$

with

$$b_0 = 4\frac{4\pi}{3}\left(\frac{\sigma}{2}\right)^3$$

being four times the volume of one particle, and

$$a = -2\pi \int_{\sigma}^{\infty} dq\, q^2 V_2(q).$$

For an attractive potential ($V_2(q) < 0$ for $q \geq \sigma$) a is positive.

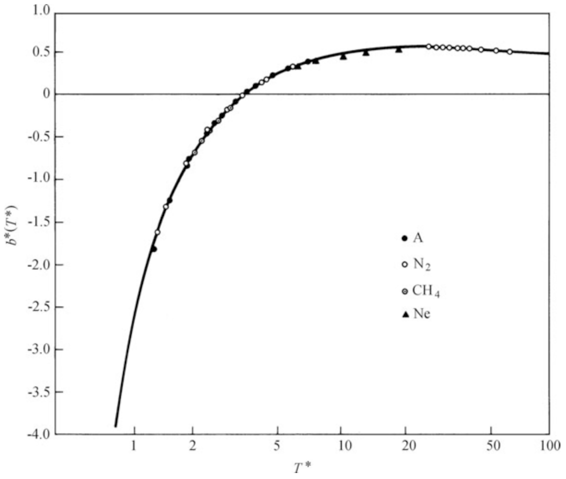
7.3.3. Lennard-Jones potential. A frequently employed model for the interaction between atoms is the Lennard-Jones potential

$$V_2(q) = 4\epsilon \left(\left(\frac{\sigma}{q} \right)^{12} - \left(\frac{\sigma}{q} \right)^{6} \right).$$

Setting $x \equiv \frac{q}{\sigma}$ and $T^* = k_B T/\epsilon$ we obtain for this potential

$$b(T) = -\frac{1}{2} \int d^3q \left(e^{-\beta V_2(\mathbf{q})} - 1 \right) = b_0 b^*(T^*). \tag{7.13}$$

Equations (7.12) and (7.13) describe approximately the experimental dependence of the second virial coefficient $b(T)$ on temperature, T: for decreasing temperature $b(T)$ becomes negative:



Only if we compare the results for a very large range of temperature, do we find that different potentials lead to different predictions for $b(T)$. Thus a discrimination between different potentials on the basis of a comparison between theoretical and experimental results is difficult.

In a similar way one can study $c(T)$ and one finds

$$c(T) = b_0^2 c^*(T^*),$$

where $c^*(T^*)$ is again a universal function (i.e., independent of the parameters of the Lennard-Jones potential).

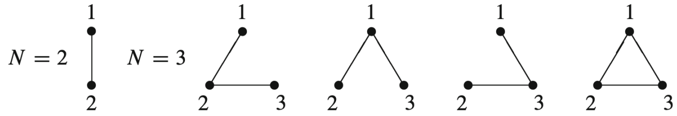
Remark 7.2. The higher virial coefficients are obtained systematically by the cluster expansion of Ursell and Mayer (Ursell 1927, Mayer 1941, see also [Römer and Filk 1994]). One writes

$$\begin{aligned} Z(T,V,N) =& \frac{1}{N!\lambda_t^{3N}} \int d^3\mathbf{q}_1 \dots d^3\mathbf{q}_N \exp\left(-\beta \sum_{i>j} V_2(\mathbf{q}_i - \mathbf{q}_j)\right) \\ =& \frac{1}{N!\lambda_t^{3N}} \int d^3\mathbf{q}_1 \dots d^3\mathbf{q}_N \prod_{i>j}(1+f_{ij}) \\ =& \frac{1}{N!\lambda_t^{3N}} \int d^3\mathbf{q}_1 \dots d^3\mathbf{q}_N \left(1 + \sum_{i>j} f_{ij} + \sum_{i>j,k>l} f_{ij} f_{kl} + \dots\right) \end{aligned}$$

with

$$f_{ij} = e^{-\beta V_2(\mathbf{q}_i - \mathbf{q}_j)} - 1.$$

Keeping control of the large number of contributions is greatly facilitated when they are represented graphically. $Z(T,V,N)$, for instance, leads to contributions which for $N=2$ and $N=3$ may be represented as follows:



Each circle represents a particle, each line stands for a factor f_{ij}. One can show that the contributions to the virial coefficients may also be represented by such objects; in fact the only graphs that occur are those where each pair of points can be connected by at least two independent, nonintersecting paths.

Remark 7.3. For $\beta \to 0$ all virial coefficients vanish, because $e^{-\beta V_2(\mathbf{q})} - 1 \to 0$ for $\beta \to 0$ (except in cases, where we assume that $V_2(q) = \infty$ somewhere). In this limit all fluids behave like ideal gases. It may happen that the second virial coefficient also vanishes at a certain finite temperature. In this case the equation of state corresponds, apart from higher order corrections, to that of an ideal gas. This temperature is also called θ-point.

Remark 7.4. The virial expansion is only useful when $n = N/V$ is sufficiently small that only a few virial coefficients are needed, since the determination of the higher coefficients becomes more and more difficult. One would thus like to know whether the equation of state obtained by taking into account only the first four to six virial coefficients also describes the liquid phase of a substance adequately. Essentially, liquids and gases differ only in their densities (whereas the solid state often shows crystalline structures). One might therefore expect that it is possible to determine an equation of state which is valid for fluids in general.

For the hard core gas, studies have shown how far one can get using the method of virial expansion. On the one hand, the virial expansion has been examined by taking into account the first five or six virial coefficients, and this expansion has then been extrapolated using a Padé approximation (Press et al. 2007). In a Padé approximation a polynomal series

$$f(x) = a_0 + a_1 x + \cdots + a_n x^n + O(x^{n+1})$$

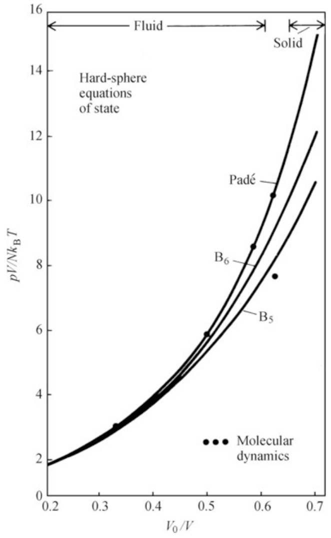
is replaced by a rational function

$$\overline{f}_{N,M}(x) = \frac{c_0 + c_1 x + \cdots + C_N x^N}{1 + d_1 x + \cdots + d_M x^M},$$

such that the expansion of this function at $x = 0$ coincides with $f(x)$ up to order x^{N+M} (see e.g. Bender and Orszag 1978; Press et al. 2007). For $N = M = 1$ one obtains, e.g.,

$$c_0 = a_0, \quad c_1 - c_0 d_1 = a_1, \quad -d_1 c_1 + d_1^2 c_0 = a_2.$$

On the other hand, some points of the equation of state have been determined by a molecular dynamics calculation. In molecular dynamics calculations (see, e.g., Rahman 1964; Verlet 1968) one solves the equations of motion for some hundred particles numerically and regards the macroscopic state variables as the time average determined from the corresponding microscopic quantities. In the Figure below the results of such an investigation are compared with those of a virial expansion including a Padé approximation. Basically we may conclude that the extrapolation to all virial coefficients by Padé approximation yields a qualitatively satisfactory equation of state. Quantitative agreement, however, is not to be expected.



Remark 7.5. In (7.6) we gave an equation of state for fluids which we now will write in the form

$$P = nk_BT\left(1 - \frac{n}{6k_BT}\int dq\, q^2 4\pi g_2(q)V'(q)\right).$$

Expanding $g_2(q)$ in powers of n,

$$g_2(q) = g_{20}(q) + ng_{21}(q) + O(n^2),$$

and comparing with (7.11) yields

$$b(T) = -\frac{1}{6k_BT}\int dq\, q^2 4\pi g_{20}(q)qV'(q).$$

This result then has to be compared with

$$b(T) = -\frac{1}{2}\int dq\, q^2 4\pi\left(e^{-\beta V_2(q)} - 1\right),$$

which by partial integration yields

$$\begin{aligned} b(T) =& -\frac{1}{2}\int_0^\infty dq 4\pi\left(\frac{d}{dq}\frac{q^3}{3}\right)\left(e^{-\beta V_2(q)} - 1\right) \\ =& \frac{1}{6}\int dq 4\pi q^2 q\left(-\beta V_2(q)\right)e^{-\beta V_2(q)} \\ =& -\frac{1}{6k_BT}\int dq\, q^2 4\pi V_2'(q)e^{-\beta V_2(q)}. \end{aligned}$$

So we obtain $g_{20}(q) = e^{-\beta V_2(q)}$. Thus, to first order in n, we can set $g_2(q) = e^{-\beta V_2(q)}$, which is consistent with $g_2(q) \equiv 1$ for ideal gases.

7.3.4. Integral Equations for the Radial Distribution Function. In the literature one can find various integrodifferential equations for the radial distribution function. The solutions of these equations reproduce the experimental results more or less satisfactory. We will briefly sketch the derivation of such integrodifferential equations, but otherwise refer to the literature (McQuarrie 1976; Balescu 1975).

We consider $\rho_1(\mathbf{r})$ from (7.1), i.e.,

$$\rho_1(\mathbf{r}) = \frac{1}{N!h^{3N}A}\int d^{3N}\mathbf{p}\int d^3\mathbf{q}_2 \dots d^3\mathbf{q}_N\; e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q})}\Big|_{\mathbf{q}_1=\mathbf{r}} \tag{7.14}$$

for the Hamiltonian function

$$\mathcal{H}(\mathbf{p},\mathbf{q}) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i>j} V_2(\mathbf{q}_i - \mathbf{q}_j) + \sum_{i=1}^N V_1(\mathbf{q}_i).$$

Since an external potential $V_1(\mathbf{q})$ is now also present, $\rho_1(\mathbf{r})$ is no longer independent of the position $\mathbf{r}$. Taking the derivative of $\rho_1(\mathbf{r})$ in (7.14) with respect to $\mathbf{r}$ we get

$$\begin{aligned}\nabla_{\mathbf{r}}\rho_1(\mathbf{r}) =& -\beta\nabla_{\mathbf{r}}V_1(\mathbf{r})\rho_1(\mathbf{r}) - \beta\frac{1}{h^{3N}N!Z}\int d^{3N}\mathbf{p}\int d^3\mathbf{q}_2 \\ & \times\int\int d^3\mathbf{q}_N\nabla_{\mathbf{r}}\sum_{j=2}^{N}V_2(\mathbf{r}-\mathbf{q}_j)\ e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q})}\Big|_{\mathbf{q}_1=\mathbf{r}} \\ =& -\beta\nabla_{\mathbf{r}}V_1(\mathbf{r})\rho_1(\mathbf{r}) - \beta(N-1)\int d^3\mathbf{q}_2\nabla_{\mathbf{r}}V_2(\mathbf{r}-\mathbf{q}2)\rho_2(\mathbf{r},\mathbf{q}_2).\end{aligned}$$

Using

$$N\rho_1(\mathbf{r}) = n_1(\mathbf{r})$$

and

$$N(N-1)\rho_2(\mathbf{r},\mathbf{r}') = n_2(\mathbf{r},\mathbf{r}') = n_1(\mathbf{r})n_1(\mathbf{r}')g_2(\mathbf{r},\mathbf{r}')$$

one obtains

$$\nabla_{\mathbf{r}}n_1(\mathbf{r}) = -\beta\nabla_{\mathbf{r}}V_1(\mathbf{r})n_1(\mathbf{r}) - \beta\int d^3\mathbf{q}_2\nabla_{\mathbf{r}}V_2(\mathbf{r}-\mathbf{q}_2)n_2(\mathbf{r},\mathbf{q}_2).$$

This equation for $n_1(\mathbf{r})$ is therefore not closed: on the right hand side there appears for the unknown quantity $n_2(\mathbf{r},\mathbf{q}_2)$. If one analogously derives a differential equation for this quantity, the next higher term moment $n_3(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ appears, etc. Hence, we never get a closed system of equations, but only an infinite hierarchy.

A closed system can obviously only be obtained if at some stage the moment of highest order is approximated by an expression containing only lower moments. Setting, e.g.,

$$n_2(\mathbf{r},\mathbf{r}') = n_1(\mathbf{r})n_1(\mathbf{r}'),$$

leads to the integrodifferential equation for $n_1(\mathbf{r})$:

$$\nabla_{\mathbf{r}}n_1(\mathbf{r}) = \left(-\beta\nabla_{\mathbf{r}}V_1(\mathbf{r}) - \beta\int d^3\mathbf{q}_2\nabla_{\mathbf{r}}V_2(\mathbf{r}-\mathbf{q}_2)n_1(\mathbf{q}_2)\right)n_1(\mathbf{r})$$

or

$$n_1(\mathbf{r}) = e^{-\beta\left(V_1(\mathbf{r})-\int d^3\mathbf{q}_2V(\mathbf{r}-\mathbf{q}_2)n_1(\mathbf{q}_2)\right)}.$$

A similar factorizing ansatz leading to an equation for $n_2(\mathbf{r},\mathbf{r}')$ is

$$n_3(\mathbf{r},\mathbf{r}',\mathbf{r}'') = \frac{n_2(\mathbf{r},\mathbf{r}')n_2(\mathbf{r}',\mathbf{r}'')n_2(\mathbf{r}'',\mathbf{r})}{n_1(\mathbf{r})n_1(\mathbf{r}')n_1(\mathbf{r}'')}.$$

Equations which may be derived by this or similar assumptions are, e.g.,

The Born-Green-Yvon (BGY) equation:

$$-k_BT\nabla_1\log g_2(\mathbf{r}_{12}) = \nabla_1V_2(\mathbf{r}_{12}) + n\int d^3\mathbf{r}_3\nabla_!V_2(\mathbf{r}_{13})g_2(\mathbf{r}_{13})g_2(\mathbf{r}_{23}),$$

The Percus-Yevick equation for $y(r) = e^{\beta V_2(r)} g_2(r)$:

$$y(\mathbf{r}_{12}) = 1 + n \int d^3\mathbf{r}_3 \left(e^{-\beta V_2(\mathbf{r}_{13})} - 1\right) y(\mathbf{r}_{13}) \left(e^{-\beta V_2(\mathbf{r}_{23})} y(\mathbf{r}_{23}) - 1\right),$$

The "hypernetted-chain equation" (HNC)

$$\log y(\mathbf{r}_{12}) = n \int d^3\mathbf{r}_3 h(\mathbf{r}_{23}) \left(h(\mathbf{r}_{13}) - \log g_2(\mathbf{r}_{13}) - V_2(\mathbf{r}_{13})/k_B T\right),$$

with $h(r) = g_2(r) - 1$. In the last two equations $g_2(r)$ represents the radial distribution function of a grand canonical system. From these equations one obtains to lowest order in n:

$$y \equiv 1, \qquad \text{etc.} \qquad g_2(r) = e^{-\beta V_2(r)}.$$

The form of the curve $g_2(r)$ as a function of the parameters n, T, calculated from the integral equations, may be compared with the molecular dynamics calculations for various potentials. Frequently one uses the hard core potential and the Lennard-Jones (12-6) potential.

It turns out that the Percus–Yevick equation yields a function $g_2(r)$ and an n-dependence of p/nk_BT which display the best agreement with the data from molecular dynamics (McQuarrie 1976; Balescu 1975; Barker and Henderson 1976).

7.4. Perturbation Theory

Along with many other approximation methods, the formalism of a perturbation expansion, known from classical mechanics, is also applicable in statistical mechanics.

For the potential we write

$$V(\mathbf{q}_1, \ldots, \mathbf{q}_N) = V^0(\mathbf{q}_1, \ldots, \mathbf{q}_N) + V^1(\mathbf{q}_1, \ldots, \mathbf{q}_N),$$

where $V^0(\mathbf{q}_1, \ldots, \mathbf{q}_N)$ is assumed to be a potential for which the partition function Z_N^0 is known. Let $\langle \cdot \rangle_0$ be the expectation value which is derived from the density

$$\rho_0(x) = \frac{1}{N! h^{3N} Z_N^0} \exp\left[-\beta(\mathcal{H}_{kin}(p,q) + V^0(\mathbf{q}_1, \ldots, \mathbf{q}_N))\right].$$

Then

$$\begin{aligned} Z_N &= \int d^{3N}\mathbf{p} \int d^{3N}\mathbf{q} \frac{1}{N! h^{3N}} e^{-\beta(\mathcal{H}_{kin}(p,q) + V^0(\mathbf{q}_1,\ldots,\mathbf{q}_N))} e^{-\beta V^1(\mathbf{q}_1,\ldots,\mathbf{q}_N)} \\ &= Z_N^0 \left\langle e^{-\beta V^1(\mathbf{q}_1,\ldots,\mathbf{q}_N)} \right\rangle_0 \\ &= Z_N^0 \left(1 - \beta \left\langle V^1 \right\rangle_0 + \frac{\beta^2}{2} \left\langle (V^1)^2 \right\rangle_0 + \ldots \right) \end{aligned}$$

where we have made a high-temperature expansion (i.e., an expansion in $\beta = 1/k_B T$) in the last line. Finally, we obtain

$$F = F_0 + F_1$$

where

$$F_0 = -k_B T \log Z_N^0(T,V,N)$$

and

$$\begin{aligned} F_1 =& -k_B T \log\left(1 - \beta \left\langle V^1 \right\rangle_0 + \frac{\beta^2}{2} \left\langle (V^1)^2 \right\rangle_0 + \dots\right) \\ =& \sum_{n=1}^{\infty} \frac{(-\beta)^{n-1}}{n!} \omega_n \\ \equiv& \left(\omega_1 - \frac{\omega_2}{2k_B T} + \dots\right) \end{aligned}$$

with

$$\begin{aligned} \omega_1 =& \left\langle V^1 \right\rangle_0 \\ \omega_2 =& \left\langle (V^1)^2 \right\rangle_0 - \left\langle V^1 \right\rangle_0^2 , \end{aligned}$$

etc.

From

$$V^1(\mathbf{q}_1, \dots, \mathbf{q}_N) = \sum_{i<j} \nu^1(\mathbf{q}_i - \mathbf{q}_j)$$

one finds

$$\omega_1 = \left\langle V^1 \right\rangle_0 = \frac{N(N-1)}{2} \left\langle \nu^1(\mathbf{q}_1 - \mathbf{q}_2) \right\rangle_0 = \frac{1}{2} n^2 V \int d^3\mathbf{q} \nu^1(\mathbf{q}) g_2^0(\mathbf{q}).$$

where $g_2^0(\mathbf{q})$ is the radial distribution function for $V^0(\mathbf{q}_1, \dots, \mathbf{q}_N)$.

In the calculation of $\left\langle (V^1)^2 \right\rangle_0$ expressions of the form

$$\langle \nu^1(\mathbf{q}_1 - \mathbf{q}_2) \nu^1(\mathbf{q}_3 - \mathbf{q}_4) \rangle_0$$

occur. They can only be written in a compact form like $\langle \nu^1(\mathbf{q}_1 - \mathbf{q}_2) \rangle_0$ if the corresponding four-particle distribution function $g_4(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4)$ is used. Such a four-particle distribution function, however, is difficult to calculate, thus revealing the limits of this method.

We now consider, as an example,

$$g_2^0(q) = \begin{cases} 0 & \text{for } q < \sigma \\ 1 & \text{for } q > \sigma. \end{cases}$$

Then

$$\omega_1 = \frac{1}{2} n^2 V \int_\sigma^\infty dq q^2 4\pi \nu^1(q) = -a \frac{N^2}{V}$$

with

$$a = -2\pi \int_\sigma^\infty dq q^2 \nu^1(q) \tag{7.15}$$

For an attractive potential ($\nu^1(q) < 0$ for $q \geq \sigma$) a is positive. This yields, to a first approximation,

$$F = F_0 - a\frac{N^2}{V},$$

and thus

$$P = -\frac{\partial F}{\partial V} = -\frac{\partial F_0}{\partial V} - a\frac{N^2}{V^2} = -\frac{\partial F_0}{\partial V} - \frac{a}{\nu^2}.$$

Instead of

$$P = -\frac{\partial F_0}{\partial V},$$

which is the equation of state for the potential $V = V^0$, taking into account the potential V^1, we now obtain the equation of state

$$\left(P + \frac{a}{\nu^2}\right) = -\frac{\partial F_0}{\partial V},$$

where a is determined from the potential $\nu^1(\mathbf{q})$ according to (7.15). For the attractive two-particle potential $\nu^1(\mathbf{q})$ one finds to first order in the perturbation expansion a decrease of pressure.

A suitable choice of $g_2^0(\mathbf{q})$ together with a good approximation for F_0 and inclusion of the contributions of higher orders in a high-temperature expansion lead to equations of state which are an improvement over methods where the radial distribution function is calculated from integral equations.

Chapter 8

Dynamics

Statistical mechanics offers a nuanced framework for correlating molecular-level behaviors with macroscopic thermodynamic properties. Central to this discourse is the dynamics domain, which scrutinizes how individual particle motions culminate in large-scale system behaviors. The interplay between the Langevin and Fokker-Planck equations, bridged by the Feynman-Kac formula, epitomizes this discourse.

The Langevin equation, a stochastic differential equation, models particle trajectories influenced by deterministic and random forces. It embodies microscopic dynamics, accounting for forces derived from potential energy and random thermal interactions reflective of the particle's surroundings.

In contrast, the Fokker-Planck equation transitions to a macroscopic vantage point. It delineates the evolution of probability densities, influenced by drift and diffusion processes, thereby linking individual particle dynamics with the collective behavior of particle ensembles.

The Feynman-Kac formula is pivotal in bridging these two perspectives. It translates the stochastic dynamics of the Langevin equation into a partial differential equation framework, akin to the Fokker-Planck equation. This translation facilitates the derivation of the Fokker-Planck equation from Langevin dynamics, cementing the theoretical foundation that connects microscopic particle trajectories with macroscopic probability distributions.

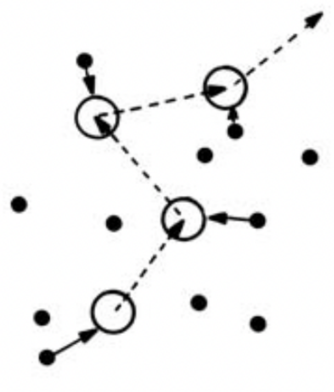
A significant implication of this connection is the emergence of the Boltzmann distribution in the Fokker-Planck equation's steady state. This distribution, fundamental in statistical mechanics, represents the distribution of particles across various energy states in thermal equilibrium. Deriving the Boltzmann distribution from foundational principles through the Langevin and Fokker-Planck equations underscores the deep-rooted relationship between particle behavior at the microscopic scale and the macroscopic attributes of systems in equilibrium.

This chapter discusses the ramifications of the Langevin and Fokker-Planck equations' interconnection. The ensuing discourse navigates from a detailed examination of particle dynamics to an expansive comprehension of statistical ensembles, thereby elucidating the trajectory from molecular interactions to thermodynamic equilibrium.

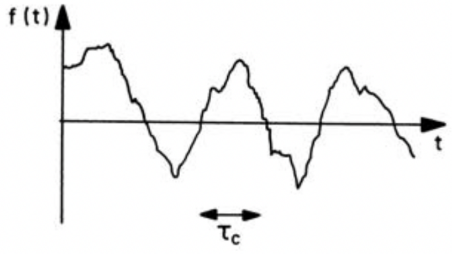
8.1. Langevin Equation

A variety of situations occur in Nature where one is not primarily interested in the complete dynamics of a many-body system, but rather in a subset of specific variables. The remaining variables, through their equations of motion, give rise to relatively rapidly varying stochastic forces and damping effects. Examples include the Brownian motion of a massive particle in a liquid, the equations of motion of conserved densities, and the dynamics of the order parameter in the vicinity of a critical point.

We begin our discussion with Brownian motion as a fundamental example of a stochastic process. Consider a heavy particle of mass m and velocity v moving in a liquid composed of lighter particles. This "Brownian particle" experiences random collisions with the molecules of the liquid:



These collisions result in an average frictional force on the massive particle and a stochastic force $f(t)$, which fluctuates around its average value:



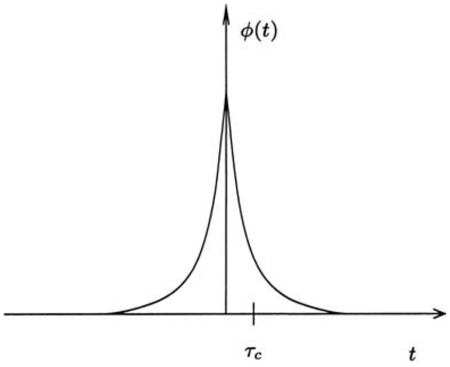
The first contribution to this force, denoted as $-\zeta mv$, is characterized by a coefficient of friction ζ. Under these physical conditions, the Newtonian equation of motion is modified to include these effects, leading to the formulation of the so-called Langevin equation:

$$m\dot{v} = -m\zeta v + f(t).$$

Such equations are referred to as stochastic equations of motion and the processes they describe as stochastic processes. The correlation time τ_c denotes the time during which the fluctuations of the stochastic force remain correlated. From this, we assume that the average force and its autocorrelation function have the following form at differing times

$$\langle f(t)\rangle = 0, \qquad \langle f(t)f(t')\rangle = \phi(t-t').$$

Here, $\phi(\tau)$ differs noticeably from zero only for some correlation time $\tau < \tau_c$:



Since we are interested in the motion of our Brownian particle over times of order t which are considerably longer than τ_c, we can approximate $\phi(\tau)$ by a delta function

$$\phi(\tau) = \lambda\delta(\tau).$$

The coefficient λ is a measure of the strength of the mean square deviation of the stochastic force. Since friction also increases proportionally to the strength of the collisions, there must be a connection between λ and the coefficient of friction ζ. In order to find this connection, we first solve the Langevin equation.

8.1.1. Solution to The Langevin Equation. In Section 9.1.1 we learn that the solution to a first order linear ODE with inhomogeneous term $q(t)$

$$\frac{dy}{dt} + p(t)y = q(t),$$

is

$$y(t) = \frac{1}{\mu(t)} \left(\int \mu(t) q(t) dt + C \right).$$

where $\mu(t) = \exp\left(\int p(t)dt\right)$ is an integrating factor. For the particular case of the Langevin equation $m\dot{v} = -m\zeta v + f(t)$ this procedure leads to the solution:

$$v(t) = v_0 e^{-\zeta t} + e^{-\zeta t} \int_0^t d\tau \, e^{\zeta t} f(\tau)/m.$$

Since $f(t)$ is a stochastic process (random variable parametrized by time), it will be different every time the particle is tracked, i.e. the function $\{f(t)\}_{t \in [0,T]}$ depends on $\omega \in \Omega$, the particular realization of the random experiment. From this we can compute various statistical moments. For example, the first moment is:

$$v(t) = v_0 e^{-\zeta t},$$

since $\langle f(t) \rangle = 0$. The second moment is

$$\begin{aligned}
\langle v(t)^2 \rangle =& v_0^2 e^{-2\zeta t} + e^{-2\zeta t} \int_0^t d\tau \int_0^t d\tau' \, e^{\zeta(\tau+\tau')} \underbrace{\langle f(\tau) f(\tau') \rangle}_{\lambda\delta(\tau-\tau')} m^{-2}, \\
=& v_0^2 e^{-2\zeta t} + e^{-2\zeta t} \lambda m^{-2} \int_0^t d\tau \, e^{2\zeta\tau}, \\
=& v_0^2 e^{-2\zeta t} + e^{-2\zeta t} \lambda m^{-2} \left[\frac{e^{2\zeta\tau}}{2\zeta} \right]_0^t, \\
=& v_0^2 e^{-2\zeta t} + \frac{\lambda}{2\zeta m^2} (1 - e^{-2\zeta t}) \overset{t \gg \zeta^{-1}}{\rightarrow} \frac{\lambda}{2\zeta m^2}
\end{aligned}$$

where the cross-terms vanish because of $\langle f(t) \rangle = 0$. For $t \gg \zeta^{-1}$ the contribution of the initial velocity v_0 vanishes, as the memory of the initial value is lost. ζ^{-1} plays the role of a relaxation or memory time.

We *require* that our particle attain *thermal equilibrium* after long times, $t \gg \zeta^{-1}$, i.e. that the average value of the kinetic energy obey the equipartition theorem

$$\frac{1}{2} m \langle v(t)^2 \rangle = \frac{1}{2} k_B T.$$

Substituting the result $\langle v(t)^2\rangle \to \frac{\lambda}{2\zeta m^2}$, we find the *Einstein relation*:

$$\lambda = 2\zeta m k_B T.$$

It is a type of *fluctuation-dissipation theorem.* It relates the fluctuation (λ, the amplitude of the stochastic force) to the dissipation (ζ, the friction coefficient). This relationship depends on temperature, as one would expect the fluctuations to be proportional to T.

We may also compute the velocity autocorrelation function (covariance function):

$$\langle v(t)v(t')\rangle = e^{-\zeta(t+t')}\int_0^t d\tau \int_0^{t'} d\tau' e^{\zeta(\tau+\tau')}\frac{\lambda}{m^2}\delta(\tau-\tau') + v_0^2 e^{-\zeta(t+t')}.$$

Since t and t' are interchangeable, we can assume w.l.o.g. that $t < t'$ and evaluate the two integrals in the order given, with the result $(e^{2\zeta\min(t,t')}-1)\frac{\lambda}{2\zeta m^2}$:

$$\langle v(t)v(t')\rangle = \left(v_0^2 - \frac{\lambda}{2\zeta m^2}\right)e^{-\zeta(t+t')} + \frac{\lambda}{2\zeta m^2}e^{-\zeta|t-t'|}.$$

For $t, t' \gg \zeta^{-1}$, the first term can be neglected since $e^{-\zeta(t+t')} \to 0$. To get the mean square displacement we integrate twice:

$$\begin{aligned}\langle x(t)^2\rangle = \int_0^t d\tau \int_0^t d\tau' \langle v(\tau)v(\tau')\rangle &= \int_0^t d\tau \int_0^t d\tau' \,\frac{\lambda}{2\zeta m^2}e^{-\zeta|\tau-\tau'|}\\ &= \frac{\lambda}{2\zeta m^2}2\int_0^t du(t-u)e^{-\zeta u} = \frac{\lambda}{\zeta^2 m^2}t,\end{aligned}$$

or $\langle x(t)^2\rangle = 2Dt$ with the diffusion constant $D = \frac{\lambda}{2\zeta^2 m^2} = \frac{k_B T}{\zeta m}$.

8.1.2. Langevin Equation in a Force Field. A generalization of the Langevin equation is obtained by adding an external force field:

$$m\dot{v} = -\zeta m v - \frac{\partial V(x)}{\partial x} + f(t). \tag{8.1}$$

There are special cases of interest, such as the limit of *strong damping* $m\zeta v \gg m\dot{v}$, which leads to

$$v = -\frac{1}{m\zeta}\frac{\partial V}{\partial x} + \frac{1}{m\zeta}f(t).$$

It can be shown that an equilibrium distribution for this stochastic process is

$$\propto \exp\left(-\left(\frac{p^2}{2m} + V(x)\right)/k_B T\right).$$

The Langevin equation therefore allows us to recover the Gibbs distribution $\frac{e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q})}}{Z}$ with a Hamiltonian $\mathcal{H}(\mathbf{p},\mathbf{q}) = \frac{p^2}{2m} + V(x)$ that is the sum of kinetic and potential energies.

8.1.3. Statistical Description of Particle Trajectories. The Langevin equation describes the random motion of a particle. Integration of the Langevin equation yields a single path $\{v(r)\}$. If the procedure is repeated many times, many paths are generated and we can compile statistics of the random process. We are interested, for example, in a statistical description that yields the probability distribution of particle velocities at some given time t.

We define the probability density for the random event that the Brownian particle has the velocity ξ at the time t:

$$p(\xi,t) = \langle \delta(\xi - v(t)) \rangle .$$

This means that $p(\xi,t)d\xi$ is the probability that the velocity lies within the interval $[\xi,\xi+d\xi]$. We now derive an equation of motion for $p(\xi,t)$:

$$\begin{aligned}
\frac{\partial}{\partial t} p(\xi,t) =& -\frac{\partial}{\partial \xi} \langle \delta(\xi - v(t)) \dot{v}(t) \rangle \\
=& -\frac{\partial}{\partial \xi} \left\langle \delta(\xi - v(t)) \left(-\zeta v(t) + \frac{1}{m} f(t) \right) \right\rangle \\
=& -\frac{\partial}{\partial \xi} \left\langle \delta(\xi - v(t)) \left(-\zeta \xi + \frac{1}{m} f(t) \right) \right\rangle \\
=& \frac{\partial}{\partial \xi} \left(\zeta p(\xi,t) \xi \right) - \frac{1}{m} \frac{\partial}{\partial \xi} \left\langle \delta(\xi - v(t)) f(t) \right\rangle ,
\end{aligned} \tag{8.2}$$

where the Langevin equation has been inserted in the second line. In the third line we have replaced $v(t)$ by its numerical value ξ, which is required because of the factor $\delta(\xi - v(t))$. In the last equality we have substituted the definition $p(\xi,t) \equiv \langle \delta(\xi - v(t)) \rangle$.

The probability density for the stochastic force is assumed to follow a Gaussian distribution:

$$\mathcal{P}[f(t)] = e^{-\int_{t_0}^{t_f} dt \frac{f(t)^2}{4\zeta m k_B T}} .$$

Computation of the averages $\langle \dots \rangle$ generally requires a functional integral. As an example, the last term:

$$\begin{aligned}
\langle \delta(\xi - v(t)) f(t) \rangle =& \int \mathcal{D}[f(t')] \delta(\xi - v(t)) f(t) e^{-\int \frac{f(t')^2 dt'}{4\zeta m k_B T}} \\
=& -2\zeta m k_B T \int \mathcal{D}[f(t')] \delta(\xi - v(t)) \frac{\delta}{\delta f(t)} e^{-\int \frac{f(t')^2 dt'}{4\zeta m k_B T}} \\
=& 2\zeta m k_B T \int \mathcal{D}[f(t')] e^{-\int \frac{f(t')^2 dt'}{4\zeta m k_B T}} \frac{\delta}{\delta f(t)} \delta(\xi - v(t)) \\
=& 2\zeta m k_B T \left\langle \frac{\delta}{\delta f(t)} \delta(\xi - v(t)) \right\rangle = -2\zeta m k_B T \frac{\partial}{\partial \xi} \left\langle \delta(\xi - v(t)) \frac{\delta v(t)}{\delta f(t)} \right\rangle .
\end{aligned} \tag{8.3}$$

where

$$\begin{aligned}
\mathcal{D}[r] \equiv& \lim_{\Delta\to 0}\prod_{i=0}^{N-1}\left(dr(t_i)\sqrt{\frac{\Delta}{4\Gamma k_B T\pi}}\right)\\
N =& \frac{t_f - t_i}{\Delta}, \qquad t_i = t_0 + i\Delta, \qquad i = 0,\dots,N-1\\
\int \mathcal{D}[r]\mathcal{P}[r(t)] \equiv& \lim_{\Delta\to 0}\prod_{i=0}^{N-1}\int\left(dr(t_i)\sqrt{\frac{\Delta}{4\Gamma k_B T\pi}}\right)e^{-\sum_i \Delta\frac{r(t_i)^2}{4\Gamma k_B T}} = 1\\
\langle r(t_i)r(t_j)\rangle =& \frac{4\Gamma k_B T}{2\Delta}\delta_{ij} = 2\Gamma k_B T\frac{\delta_{ij}}{\Delta} \to 2\Gamma k_B T\delta(t_i - t_j), \quad \langle r(t)\rangle = 0.
\end{aligned}$$

The infinite-dimensional path integral plays the role of the joint probability density of the stochastic process $\{f(t)\}_{t\in[0,T]}$. The use of a joint density is required because we are computing the average of a function of $v(t)$ whereas $v(t)$ is obtained by integrating $f(t)$, meaning that $v(t)$ is a function of all random variables $\{f(t)\}_{t\in[0,T]}$:

$$v(t) = v_0 e^{-\zeta t} + e^{-\zeta t}\int_0^t d\tau\frac{f(\tau)}{m}.$$

Indeed, averages such as $\langle\delta(\xi - v(t))\rangle$ must be computed using a path integral because it is a function of $v(t)$, which itself is a function of the entire path $\{f(t)\}_{t\in[0,T]}$. Using the fact that $\frac{\delta f(\tau)}{\delta f(t)} = \delta(\tau - t)$, we obtain

$$\frac{\delta v(\tau)}{\delta f(t)} = \int_0^t d\tau e^{-\zeta(t-\tau)}\frac{1}{m}\delta(t-\tau) = \frac{1}{2m}. \tag{8.4}$$

The factor $\frac{1}{2}$ results from the fact that the integration interval includes only half of the δ-function. Inserting (8.4) into (8.3) and (8.3) into (8.2), we obtain the equation of motion for the probability density, the Fokker-Planck equation:

$$\frac{\partial}{\partial t}p(v,t) = \zeta\frac{\partial}{\partial v}vp(x,t) + \zeta\frac{k_B T}{m}\frac{\partial^2}{\partial v^2}p(v,t).$$

Here, we have replaced the velocity ξ by v; it is not to be confused with the stochastic variable $v(t)$. This relation can also be written in the form of an equation of continuity

$$\frac{\partial}{\partial t}p(v,t) = -\zeta\frac{\partial}{\partial v}\left(-vp(x,t) - \frac{k_B T}{m}\frac{\partial}{\partial v}p(v,t)\right).$$

Remark 8.1. Thew following remarks can be made:

(i) The current density, the expression in large parentheses, is composed of a drift term and a diffusion current.

(ii) The current density vanishes if the probability density has the form $p(v,t) \propto e^{-\frac{mv^2}{2k_B T}}$. The Maxwell distribution is thus (at least one) equilibrium distribution. Here, the Einstein relation plays a decisive role. Conversely, we could have obtained the Einstein relation by requiring that the Maxwell distribution be a solution of the Fokker-Planck equation.

(iii) $p(v,t)$ becomes the Maxwell distribution in the course of time, and that the latter is therefore the only equilibrium distribution of the Fokker-Planck equation.

8.1.4. Statistics of Position and Velocity. For the Langevin equation (8.1) in a force field (see Section 8.1.2), which can also be written in the form

$$m\ddot{x} = -m\zeta\dot{x} - \frac{\partial V}{\partial x} + f(t),$$

Here, we must distinguish carefully between the quantities x and v and the stochastic variables $x(t)$ and $v(t)$. The meaning of the probability density $p(x,v,t)$ can be characterized as follows: $p(x,v,t)dxdv$ is the probability of finding the particle in the interval $[x, x+dx]$ with a velocity in $[v, v+dv]$. The equation of motion of $p(x,v,t)$, the generalized Fokker-Planck equation

$$\frac{\partial}{\partial t}p(x,v,t) + v\frac{\partial p}{\partial x} - \frac{1}{m}\left(\frac{\partial V(x)}{\partial x}\right)\frac{\partial p}{\partial v} = \zeta\left[\frac{\partial}{\partial v}vp + \frac{k_BT}{m}\frac{\partial^2 p}{\partial v^2}\right]$$

follows from a series of steps similar to the previous ones.

8.1.5. Solving the Fokker-Planck Equation. We now want to solve the Fokker-Planck equation for the free Brownian motion

$$\dot{p}(v) = \zeta\frac{\partial}{\partial v}\left(pv + \frac{k_BT}{m}\frac{\partial p}{\partial v}\right). \tag{8.5}$$

We expect that $p(v)$ will relax towards the Maxwell distribution, $e^{-\frac{mv^2}{2k_BT}}$ according to an exponential decay law $e^{-\zeta t}$. This makes it reasonable to introduce the variable $\rho v e^{\zeta t}$ in place of v. Then we have

$$p(v,t) = p(\rho e^{-\zeta t}, t) \equiv Y(\rho, t), \tag{8.6}$$

$$\frac{\partial p}{\partial v} = \frac{\partial Y}{\partial \rho}e^{\zeta t}, \quad \frac{\partial^2 p}{\partial v^2} = \frac{\partial^2 p}{\partial \rho^2}e^{2\zeta t}, \tag{8.7}$$

$$\frac{\partial p}{\partial t} = \frac{\partial Y}{\partial \rho}\frac{\partial \rho}{\partial t} + \frac{\partial Y}{\partial t} = \frac{\partial Y}{\partial \rho}\zeta\rho + \frac{\partial Y}{\partial t}. \tag{8.8}$$

Inserting this into Eq. (8.5) gives

$$\frac{\partial Y}{\partial t} = \zeta Y + \zeta\frac{k_BT}{m}\frac{\partial^2 Y}{\partial \rho^2}e^{2\zeta t}.$$

Thus suggests the substitution $Y = \chi e^{\zeta t}$. Due to $\frac{\partial Y}{\partial t} = \frac{\partial \chi}{\partial t}e^{\zeta t} + \zeta Y$, it follows that

$$\frac{\partial \chi}{\partial t} = \zeta\frac{k_BT}{m}\frac{\partial^2 \chi}{\partial \rho^2}e^{2\zeta t}.$$

Now we introduce a new time variable by means of $d\vartheta = e^{2\zeta t}dt$

$$\vartheta = \frac{1}{2\zeta}\left(e^{2\zeta t} - 1\right),$$

where $\vartheta(t=0)=0$. We then obtain the diffusion equation

$$\frac{\partial\chi}{\partial\vartheta}=\zeta\frac{k_BT}{m}\frac{\partial^2\chi}{\partial\rho^2}$$

with its solution

$$\chi(\rho\varphi)\frac{1}{\sqrt{4\pi q\varphi}}e^{-\frac{(\rho-\rho_0)^2}{4q\vartheta}}, \qquad q=\frac{\zeta k_BT}{m}.$$

By returning to the original variables v and t, we obtain

$$p(v,t)=\chi e^{\zeta t}=\sqrt{\frac{m}{2\pi k_BT(1-e^{-2\zeta t})}}e^{-\frac{m(v-v_0e^{-\zeta t})^2}{2k_BT(1-e^{-2\zeta t})}} \tag{8.9}$$

of the Fokker-Planck equation for a Brownian particle in the absence of external forces. Let us look at some properties of this solution.

In the limiting case $t\to 0$, we have

$$\lim_{t\to 0}p(v,t)=\delta(v-v_0). \tag{8.10}$$

In the limit of long times $t\to\infty$,

$$\lim_{t\to\infty}p(v,t)=e^{-mv^2/2k_BT}\sqrt{\frac{m}{2\pi k_BT}}.$$

Since $p(v,t)$ has the property (8.10) the density (8.9) we have also found the conditional probability density:

$$p(v,t|v_0,t_0)=p(v,t-t_0).$$

We recall that the conditional probability $p(v,t|v_0,t_0)$ gives the probability that at time t the value v occurs, under the condition that it was v_0 at the time t_0. The density $p(v,t|v_0,t_0)$ obeys the same Fokker-Planck equation as $p(v,t-t_0)$.

For an arbitrary integrable and normalized initial probability density $\rho(v_0)$ at time t_0

$$\int dv_0\,\rho(v_0)=1$$

we find with 8.9 the time dependence

$$\rho(v,t)=\int dv_0\,p(v,t-t_0)\rho(v_0).$$

Clearly, $\rho(v,t)$ fulfills the initial condition

$$\lim_{t\to t_0}\rho(v,t)=\rho(v_0),$$

while for long times

$$\lim_{t\to\infty}\rho(v,t)=e^{-\frac{mv^2}{2k_BT}}\sqrt{\frac{m}{2\pi k_BT}}\int dv_0\,\rho(v_0)=e^{-\frac{mv^2}{2k_BT}}\sqrt{\frac{m}{2\pi k_BT}} \tag{8.11}$$

the Maxwell distribution is obtained. Therefore, for the Fokker-Planck equation, we have proved that an arbitrary initial distribution relaxes towards the Maxwell distribution (8.11).

8.1.6. Smoluchowski Equation for the Overdamped Langevin Equation. The Langevin equation in an external force field

$$m\ddot{x} = -m\zeta\dot{x} - \frac{\partial V}{\partial x} + f(t), \tag{8.12}$$

in the overdamped case ($m\zeta\dot{x} \gg m\ddot{x}$) is

$$\dot{x} = \frac{1}{m\zeta}\left(-\Gamma\frac{\partial V}{\partial x} + f(t)\right) = -\Gamma\frac{\partial V}{\partial x} + r(t).$$

We can also define a probability density

$$p(\xi, t) = \langle \delta(\xi - x(t)) \rangle,$$

where $p(\xi, t)d\xi$ is the probability of finding the particle at time t at the position ξ in the interval $d\xi$. We now derive an equation of motion for $p(\xi, t)$, performing the operation ($F(x) \equiv -\frac{\partial V}{\partial x}$)

$$\begin{aligned}\frac{\partial}{\partial t}p(\xi, t) =& -\frac{\partial}{\partial \xi}\left\langle \delta(\xi - x(t))\dot{x}(t)\right\rangle \\ =& -\frac{\partial}{\partial \xi}\left\langle \delta(\xi - x(t))(\Gamma F(x) + r(t))\right\rangle \\ =& -\frac{\partial}{\partial \xi}(\Gamma p(\xi, t)F(\xi)) - \frac{\partial}{\partial \xi}\left\langle \delta(\xi - x(t))r(t)\right\rangle \end{aligned} \tag{8.13}$$

The overdamped Langevin equation (8.12) was inserted in the second line. For the last term, we find

$$\begin{aligned}\langle \delta(\xi - x(t))r(t)\rangle =& 2\Gamma k_B T\left\langle \frac{\delta}{\delta r(t)}\delta(\xi - x(t))\right\rangle \\ =& -2\Gamma k_B T\frac{\partial}{\partial \xi}\left\langle \delta(\xi - x(t))\frac{\delta x(t)}{\delta r(t)}\right\rangle = -\Gamma k_B T\frac{\partial}{\partial \xi}p(\xi, t).\end{aligned} \tag{8.14}$$

Here, we have integrated (8.12) from 0 to t

$$x(t) = x(0) + \int_0^t d\tau\,(\Gamma F(x(\tau)) + r(\tau)),$$

from which it follows that

$$\frac{\delta x(t)}{\partial x(t')} = \int_0^t \left(\frac{\partial \Gamma F(x(\tau))}{\partial x(\tau)}\frac{\delta x(\tau)}{\delta r(t')} + \delta(t' - \tau)\right)d\tau.$$

The derivative is $\frac{\delta x(\tau)}{\delta r(t')} = 0$ for $\tau < t'$ due to causality and is nonzero only for $\tau \geq t'$, with a finite value at $\tau = t'$. We thus obtain:

$$\frac{\delta x(t)}{\delta r(t')} = \int_0^t \frac{\partial \Gamma F(x(\tau))}{\partial x(\tau)}\frac{\delta x(\tau)}{\delta r(t')}d\tau + 1, \quad \text{for} \quad t' < t$$

and

$$\frac{\delta x(t)}{\delta r(t')} = \underbrace{\int_0^t \frac{\partial \Gamma F(x(\tau))}{\partial x(\tau)} \frac{\delta x(\tau)}{\delta r(t')}}_{0 \text{ for } t'=t} d\tau + \frac{1}{2} = \frac{1}{2}, \quad \text{for} \quad t' = t.$$

This demonstrates the last step in (8.14). From (8.14) and (8.13), we obtain the equation of motion for $p(\xi, t)$, the so called Smoluchowski equation

$$\frac{\partial}{\partial t} p(\xi, t) = -\frac{\partial}{\partial \xi} \left(\Gamma p(\xi, t) F(\xi)\right) + \Gamma k_B T \frac{\partial^2}{\partial \xi^2} p(\xi, t). \tag{8.15}$$

Remarks:

(i) One can cast the Smoluchowski equation (8.15) in the form of an equation of continuity

$$\frac{\partial}{\partial t} p(x, t) = -\frac{\partial}{\partial x} j(x, t),$$

with the current density

$$j(x, t) = -\Gamma \left(k_B T \frac{\partial}{\partial x} - F(x) \right) p(x, t).$$

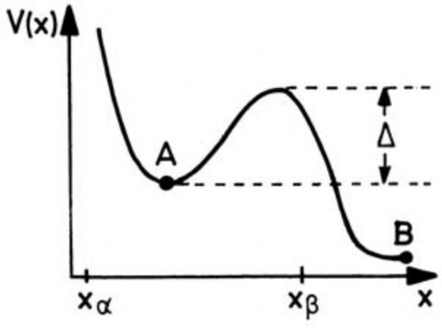
The current density $j(x, t)$ is composed of a diffusion term and a drift term, in that order.

(ii) Clearly,

$$p(x, t) \propto e^{-V(x)/k_B T}$$

is a stationary solution of the Smoluchowski equation. For this solution, $j(x, t)$ is zero.

8.1.7. Chemical Reactions. We now calculate the thermally activated transition over a barrier:



A thermally activated transition over a barrier from the minimum A into the minimum B.

An obvious physical application is the motion of an impurity atom in a solid from one local minimum of the lattice potential into another. Certain chemical reactions can also be described on this basis. Here, x refers to the reaction coordinate, which characterizes the state of the molecule. The vicinity of the point A can, for example, refer to an excited state of a molecule, while B signifies the dissociated molecule. The transition from A to B takes place via configurations which have higher energies and is made possible by the thermal energy supplied by the surrounding medium. We formulate the following calculation in the language of chemical reactions.

We require the reaction rate (also called the transition rate), i.e. the transition probability per unit time for the conversion of type A into type B. We assume that friction is so strong that we can employ the Smoluchowski equation

$$\dot{p} = -\frac{\partial}{\partial x} j(x).$$

Integrating from α to β:

$$\frac{d}{dt}\int_{x_\alpha}^{x_\beta} dv\, p(x,t) = -j(x_\beta) + j(x_\alpha), \tag{8.16}$$

where x_β lies between A and B. It then follows that $j(x_\beta)$ is the *transition rate* between the states (the chemical species) A and B.

To calculate $j(x_\beta)$, we assume that the barrier is sufficiently high so that the transition rate is small. Then in fact all the molecules will be in the region of the minimum A and will occupy states there according to the thermal distribution. The few molecules which have reached state B can be imagined to be filtered out. The strategy of our calculation is to find a stationary solution $p(x)$ which has the properties

$$p(x) = \frac{1}{Z} e^{-V(x)/k_B T} \qquad \text{in the vicinity of } A \tag{8.17}$$

$$p(x) = 0 \qquad \text{in the vicinity of } B \tag{8.18}$$

From the requirement of stationarity, it follows that

$$0 = \Gamma \frac{\partial}{\partial x}\left(k_B T \frac{\partial}{\partial x} + \frac{\partial V}{\partial x}\right) p(x),$$

from which we find by integrating once

$$\Gamma\left(k_B T \frac{\partial}{\partial x} + \frac{\partial V}{\partial x}\right) p(x) = -j_0. \tag{8.19}$$

The integration constant j_0 plays the role of the current density which, owing to the fact that (8.16) is source-free between A and B, is independent of x. This integration constant can be determined from the boundary conditions given above. We make use of the following Ansatz for $p(x)$:

$$p(x) = e^{-V/k_B T}\hat{p} \tag{8.20}$$

in equation 8.19

$$\frac{\partial}{\partial x}\hat{p} = -\frac{j_0}{k_B T \Gamma} e^{V(x)/k_B T}.$$

Integrating this equation from A to x

$$\hat{p}(x) = const. - \frac{j_0}{k_B T\Gamma}\int_A^x dx\, e^{V(x)/k_B T}. \tag{8.21}$$

The boundary condition at A, that there p follows the thermal equilibrium distribution requires

$$const. = \frac{1}{\int_A dx\, e^{-V/k_B T}}.$$

Here, $\int_A$ means that the integral is evaluated in the vicinity of A. If the barrier is sufficiently high, contributes from regions more distant from the minimum are negligible[1]. The boundary condition at B requires

$$0 = e^{-V_B/k_B T}\left(const. - \frac{j_0}{k_B T\Gamma}\int_A^B dx\, e^{V(x)/k_B T}\right).$$

so that

$$j_0 = \frac{k_B T\Gamma\left(\int_A dx\, e^{-V(x)/k_B T}\right)^{-1}}{\int_A^B dx\, e^{V(x)/k_B T}}. \tag{8.22}$$

For $V(x)$ in the vicinity of A, we set $V_A(x) \approx \frac{1}{2}(2\pi\nu)^2 x^2$, and, without loss of generality, take the zero point of the energy scale at the point A. We then find

$$\int_A dx\, e^{-V_A/k_B T} = \int_{-\infty}^{\infty} dx\, e^{-\frac{1}{2}(2\pi\nu)^2 x^2/k_B T} = \frac{\sqrt{k_B T}}{\sqrt{2\pi}\nu}.$$

Here, the integration was extended beyond the neighborhood of A out to $[-\infty, \infty]$, which is permissible owing to the rapid decrease of the integrand. The main contribution to the integral in the denominator of (8.22) comes from the vicinity of the barrier, where we set $V(x) \approx \Delta - (2\pi\nu')^2 x^2/2$. Here Δ is the height of the barrier and ν'^2 characterizes the barrier's curvature.

$$\int_A^B dx\, e^{V/k_B T} \approx e^{\Delta/k_B T}\int_{-\infty}^{\infty} dx\, e^{-\frac{(2\pi\nu')^2 x^2}{2k_B T}} = e^{\frac{\Delta}{k_B T}}\frac{\sqrt{k_B T}}{\sqrt{2\pi}\nu'}.$$

This yields all together for the current density of the *transition rate*

$$j_0 = 2\pi\nu\nu'\Gamma e^{-\Delta/k_B T}.$$

We point out some important aspects of the thermally activated transition rate: the decisive factor in this result is the Arrhenius dependence $e^{-\Delta/k_B T}$, where Δ denotes the barrier height, i.e. the activation energy. We can rewrite the prefactor by making the replacements $(2\pi\nu)^2 = m\omega^2$, $(2\pi\nu')^2 = m\omega'^2$ and $\Gamma = \frac{1}{m\zeta}$:

$$j_0 = \frac{\omega\omega'}{2\pi\zeta}e^{-\Delta/k_B T}.$$

---

[1] Inserting (8.21) with (8.22) into (8.20) , one obtains from the first term in the vicinity of point A just the equilibrium distribution, while the second term is negligible due to $\int_A^x dx\, e^{V/k_B T}/\int_A^B dx\, e^{V/k_B T} \ll 1$.

If we assume that $\omega' \approx \omega$, then the prefactor is proportional to the square of the vibration frequency characterized by the potential well.

Remark 8.2. ω is the frequency (attempt frequency) with which the particle arrives at the right side of the potential well, from where it has the possibility (with however a small probability $\sim e^{-\Delta/k_BT}$ of overcoming the barrier.

8.1.8. The Eigenvalue Problem. In order to bring the Smoluchowski equation (8.15) ($V' \equiv \partial V/\partial x \equiv -F$)

$$\frac{\partial p}{\partial t} = \Gamma \frac{\partial}{\partial x}\left(k_BT\frac{\partial}{\partial x} + V'\right)p$$

into a form which contains only the second derivative with respect to x, we apply the Ansatz

$$p(x,t) = e^{-V(x)/2k_BT}\rho(x,t), \tag{8.23}$$

obtaining

$$\frac{\partial \rho}{\partial t} = k_BT\Gamma\left(\frac{\partial^2}{\partial x^2} + \frac{V''}{2k_BT} - \frac{V'^2}{4(k_BT)^2}\right)\rho \tag{8.24}$$

This is a Schrödinger equation with an imaginary time

$$i\hbar\frac{\partial \rho}{\partial(-i\hbar 2k_BT\Gamma(t)} = \left(-\frac{1}{2}\frac{\partial^2}{\partial x^2}\right)$$

with the potential

$$V^0(x) = \frac{1}{2}\left[\frac{V'^2}{4(k_BT)^2} - \frac{V''}{2k_BT}\right]. \tag{8.25}$$

Following the separation of the variables

$$\rho(x,t) = e^{-2k_BT\Gamma E_n t}\varphi_n(x) \tag{8.26}$$

we obtain from Eq. (8.24) the eigenvalue equation

$$\frac{1}{2}\varphi_n'' = (-E_n + V^0(x))\varphi_n. \tag{8.27}$$

Formally, equation (8.27) is identical with a time-independent Schrödinger equation. In (8.26) and (8.27), we have numbered the eigenfunctions and eigenvalues which follow from (8.27) with the index n. The ground state of (8.27) is given by

$$\varphi_0 = \mathcal{N}e^{-\frac{V}{2k_BT}}, \qquad E_0 = 0, \tag{8.28}$$

where $\mathcal{N}$ is a normalization factor. Inserting in (8.23), we find for $p(x,t)$ the equilibrium distribution

$$p(x,t) = \mathcal{N}e^{-V(x)/k_BT}.$$

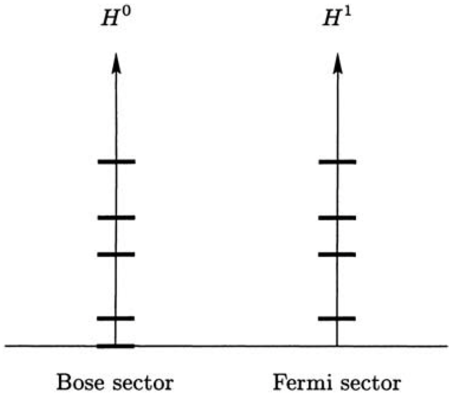
From (8.25), we can immediately see the connection with supersymmetric quantum mechanics. The supersymmetric partner to V^0 has the potential

$$V^1 = \frac{1}{2}\left[\frac{V'^2}{4(k_BT)^2} + \frac{V"}{2k_BT}\right]$$

The excitation spectra of the two Hamiltonians

$$H^{0,1} = -\frac{1}{2}\frac{d^2}{dx^2} + V^{0,1}(x)$$

are related in the manner shown below:



Excitation spectra of the two Hamiltonians H^0 and H^1.

One can advantageously make use of this connection if the problem with H^1 is simpler to solve than that with H^0.

8.1.9. Relaxation towards Equilibrium. We can now solve the initial value problem for the Smoluchowski equation in general. Starting with an arbitrarily normalized initial distribution $p(x)$, we can calculate $\rho(x)$ and expand in the eigenfunctions of (8.27)

$$\rho(x) = e^{V(x)/2k_BT}p(x) = \sum_n c_n\varphi_n(x),$$

with the expansion coefficients

$$c_n = \int dx\, \varphi_n^*(x)e^{V(x)/2k_BT}p(x).$$

From (8.26), we find the time dependence

$$\rho(x,t) = \sum_n e^{-2k_BT\Gamma E_n t}c_n\varphi_n(x),$$

from which, with (8.3.39),

$$p(x,t) = e^{-V(x)/k_BT} \sum_{n=0}^{\infty} c_n e^{-2k_BT\Gamma E_n t} \varphi_n(x) \tag{8.29}$$

follows. The normalized ground state has the form

$$\varphi_0 = \frac{e^{-V(x)/2k_BT}}{\sqrt{\int dx\, e^{-V(x)/k_BT}}}.$$

Therefore, the expansion coefficient c_0 is given by

$$c_0 = \int dx\, \varphi_0^* e^{V(x)/k_BT} p(x) = \frac{\int dx\, p(x)}{\sqrt{\int dx\, e^{-V(x)/k_BT}}} = \frac{1}{\sqrt{\int dx\, e^{-V(x)/k_BT}}}.$$

This allows us to cast (8.29) in the form

$$p(x,t) = \frac{e^{-V(x)/k_BT}}{\int dx\, e^{-V(x)/k_BT}} + e^{-V(x)/2k_BT} \sum_{n=1}^{\infty} c_n e^{-2k_BT\Gamma E_n t} \varphi_n(x).$$

With this, the initial-value problem for the Smoluchowski equation is solved in general. Since $E_n > 0$ for $n \geq 1$, it follows from this expansion that

$$\lim_{t\to\infty} p(x,t) = \frac{e^{-V(x)/k_BT}}{\int dx\, e^{-V(x)/k_BT}}, \tag{8.30}$$

which means that, starting from an arbitrary initial distribution, $p(x,t)$ develops at long times towards the equilibrium distribution (8.28) or (8.30).

8.2. Thermodynamics Connection via the Feynman-Kac Theorem

Remark 8.3. In this section we will denote expectation values as $\mathbb{E}[X]$ instead of $\langle X \rangle$, because the mathematical literature on stochastic processes uses $\mathbb{E}[X]$.

Let us recast the Langevin equation for a particle of mass m, located at position $\mathbf{x}$, moving at velocity $\mathbf{v}$ and subjected to an external, deterministic force $\mathbf{f}$ in the following form

$$m d\mathbf{v} = \underbrace{[\mathbf{f}(\mathbf{x}) - \gamma m \mathbf{v}]}_{\sum \text{Forces}} dt + \underbrace{\Gamma d\mathbf{W}_t}_{\text{random force}}$$

where $\gamma m \mathbf{v}$ is the drag force and Γ is the strength of random fluctuations. The noise term $\Gamma d\mathbf{W}_t$, which is Brownian motion (see Section 8.2.2), models the complicated interactions with the solvent.

8.2.1. Random Walk.

In this section, we present the Brownian motion as the limit of a random walk. Consider a sequence of random displacements. The position of a particle at any given time is the sum of a all steps taken up to that point. We consider the 1D case for simplicity. Starting at $S_0 = 0$, each displacement X_i can be of magnitude $+\sigma$ or $-\sigma$

with equal probabilities $\frac{1}{2}$. After n such steps, the net displacement is

$$S_n = X_1 + \cdots + X_n.$$

Since $\mathbb{E}X_i = 0$, we have $\mathbb{E}S_n = 0$. However,

$$var(X_i) = \mathbb{E}X_i^2 - (\mathbb{E}X_i)^2 = \sigma^2.$$

Since the X_i are statistically independent,

$$\mathbb{E}(S_n^2) = \sum_{i=1}^{n} var(X_i) = n\sigma^2.$$

Since the total duration of the walk is

$$t = n\Delta t,$$

this is equivalent to

$$\mathbb{E}S_n^2 = (\sigma^2/\Delta t)t.$$

This is the signature property of Brownian motion: the mean square displacement is proportional to t. The quantity $(\sigma^2/\Delta t)$ divided by 2 is called the *diffusion constant.*

Observe that by the central limit theorem (CLT), the probability law of this random walk converges to a Gaussian, regardless of the distribution of each individual step:

$$S_n = X_1 + X_2 + \cdots + X_n \sim \mathcal{N}(0, n\sigma^2) \qquad \text{as} \qquad n \to \infty.$$

8.2.2. Brownian Motion. A stochastic process is a random variable that depends on time. It may be denoted as $X(\omega, t)$ or $X_t(\omega)$, or simply X_t or $X(t)$ if the ω notation is dropped. We shall write simply X_t. A stochastic process $\{X_t\}$ is described by a joint probability: for *any* choice of times $t_1, t_2, \ldots, t_n$ and intervals B_1, B_2, $\ldots$, B_n, the value of the function

$$\mathbb{P}(X_{t_1} \in B_1, X_{t_2} \in B_2, \ldots, X_{t_n} \in B_n)$$

must be specified. A graphical representation of this probability is shown in Fig. 8.1, where the sets $B_1, \ldots, B_5$ are shown in blue as vertical bars. This value of P is the probability that a sample path ω passes through the vertical bars (or "gates") $B_1, \ldots, B_5$.

A set of the form

$$C_{t_1,\ldots,t_n}(B_1, \ldots, B_n) = \{\omega : X_{t_1}(\omega) \in B_1, X_{t_2}(\omega) \in B_2, \ldots, X_{t_n}(\omega) \in B_n\}$$

is an event called *cylinder set.*

The (standard) Brownian motion or *Wiener process* is a process $\{W_t\}$ with continuous paths which starts at 0, and has independent increments $W_{t+s} - W_s$ $(t > 0)$ whose distribution is Gaussian with mean 0 and variance t. In other words,

$$\mathbb{P}(W_{s+t} - W_s \in B) = \int_B \frac{e^{-x^2/2t}}{\sqrt{2\pi t}} dx.$$

Figure 8.1. A sample path ω of a random process is shown for the Dow Jones Industrial Average. The joint probability $\mathbb{P}(X_{t_1} \in B_1, \dots, X_{t_n} \in B_5)$ is graphically represented in blue by the cylinder sets $B_1, \dots B_5$.

This can be seen by subdividing the time axis as $0 = t_0 < t_1 < t_2 < \cdots < t_n = t$, each interval having width t/n, and telescoping W_t:

$$W_t = (W_{t_1} - W_{t_0}) + (W_{t_2} - W_{t_1}) + \cdots + (W_{t_n} - W_{t_{n-1}}).$$

From the above definition, each of these increments are independent, with mean 0 and variance t/n. By the CLT, W_t should be Gaussian with mean 0 and variance t, i.e. $W_t \sim \mathcal{N}(0, t)$. Also, the increments are independent and Gaussian: $W_{t_i - t_{i-1}} \sim \mathcal{N}(0, t_i - t_{i-1})$ for all $i = 1, \dots, n$.

A consequence of this definition is that the joint distribution of random variables $W_{t_1}, \dots, W_{t_n}$ at any n time points $0 \le t_1 < t_2 < \cdots < t_n \le 1$ is Gaussian with mean 0 and covariance

$$cov(W_{t_i}, W_{t_j}) = \mathbb{E}\left\{W_{t_i} W_{t_j}\right\} = \mathbb{E}\left\{W_{t_i}\left[W_{t_i} + (W_{t_j} - W_{t_i})\right]\right\} = t_i,$$

for $t_i < t_j$. For any s and t

$$\mathbb{E}\left\{W_s W_t\right\} = s \wedge t \equiv \min(s, t).$$

The joint probability density is therefore,

$$p_{t_1,\dots,t_n}(x_1, \dots, x_n) = \prod_{i=1}^{n} \frac{1}{\sqrt{2\pi(t_i - t_{i-1})}} \cdot \exp\left\{-\sum_{i=1}^{n} \frac{(x_i - x_{i-1})^2}{2(t_i - t_{i-1})}\right\}$$

Three possible sample paths of Brownian motion are shown in Figure 8.2.

The reader can verify that the following processes for $t > 0$ are also Wiener processes (i.e. that the covariance $cov(\hat{W}_s, \hat{W}_t) = s \wedge t$):

a) $\hat{W}_t = \{-W_t\}$

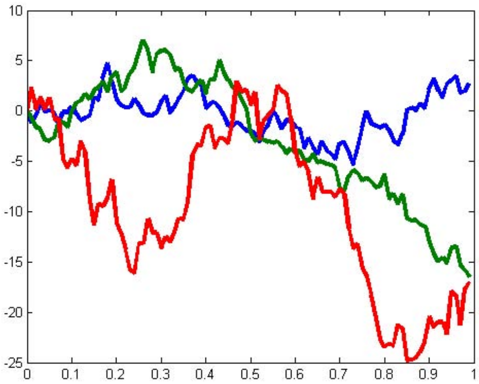


Figure 8.2. The curves in red, blue and green represent plots of the functions $X(\cdot,\omega):t\to X(t,\omega)$ for three different values of ω (or equivalently, for three different realizations of the random process).

b) $\hat{W}_t=\{\frac{1}{\sqrt{c}}W_{ct}\}$ for some constant $c>0$

c) $\hat{W}_t=\{tW_{1/t}\}$

For an interpretation of the joint density, we refer to Fig. 8.1, which illustrates the probability

$$\mathbb{P}(W_{t_1}\in B_1,W_{t_2}\in B_2,\ldots,W_{t_n}\in B_n)$$

of a Brownian path ω to fall within the intervals $B_1,\ldots,B_n$. Writing the intervals B_i as $[a_i,b_i]$, we see that this probability is equal to:

$$\mathbb{P}(W_{t_1}\in B_1,\ldots,W_{t_n}\in B_n)=\int_{a_1}^{b_1}\cdots\int_{a_n}^{b_n}p_{t_1,\ldots,t_n}(x_1,\ldots,x_n)dx_1\ldots dx_n.$$

This joint probability applies to any choice of times and vertical sets. It can be used to compute expectation values for any functional of Brownian motion.

8.2.3. Itô's Lemma. We now proceed to develop methods that will allow us to manipulate stochastic equations. We start by determining the differential dY_t for $Y_t=V(X_t,t)$ (V is assumed to be sufficiently differentiable). X_t is the solution of

$$dX_t=\mu(X_t,t)dt+\sigma(X_t,t)dW_t \tag{8.31}$$

where dW_t is the increment of the Brownian motion $dW_t=W_{t+dt}-W_t$. Here we will be using the order relation

$$[dW_t]^2=dt$$

which holds in the mean squared sense (i.e. its mean equals dt and its variance vanishes):

$$\mathbb{E}[dW_t]^2 = \mathbb{E}\left[W_{t+dt} - W_t\right]^2 = dt,$$

$$var[dW_t]^2 = \mathbb{E}[dW_t]^4 - \left[\mathbb{E}dW_t^2\right]^2 = 3dt^2 - (dt)^2 = 2dt^2 \to 0.$$

where we have used the fourth moment of a Gaussian $\mathcal{N}(0,\sigma^2)$, namely $3\sigma^4$. By application of Taylor's theorem,

$$dV(X_t,t) = V_x(X_t,t)dX_t + V_t(X_t,t)dt + \tfrac{1}{2}V_{xx}(X_t,t)[dX_t]^2 + V_{xt}(X_t,t)dX_t dt + \tfrac{1}{2}V_{tt}(X_t,t)(dt)^2 + \ldots$$

Substituting dX_t from Eq.(8.31) and invoking $[dW_t]^2 = dt$ we get:

$$dV(X_t,t) = \left[V_x(X_t,t)\mu(X_t,t) + V_t(X_t,t) + \tfrac{1}{2}V_{xx}(X_t,t)\sigma^2(X_t,t)\right]dt + V_x(X_t,t)\sigma(X_t,t)dW_t.$$

8.2.4. Itô's Integral. If we write the differential formula,

$$dX_t = \mu(X_t,t)dt + \sigma(X_t,t)dW_t$$

in integral form:

$$X_t - X_0 = \int_0^T \mu(X_t,t)dt + \int_0^T \sigma(X_t,t)dW_t,$$

it is important to properly define the integral $\int_0^T \sigma(X_t,t)dW_t$ with respect to Brownian motion. The ordinary Riemann-Stieltjes integral does not work here because dW_t fluctuates so much (almost all of its paths are nowhere differentiable!), on any length scale, that it would diverge immediately.

Given a partition of the time axis $0 = t_0 < t_1 < t_2 < \cdots < t_n = T$, Kyosi Itô has defined the integral as the limit:

$$\int_0^T \sigma(X_t,t)dW_t = \lim_{n\to\infty}\sum_{i=0}^{n-1}\sigma(X_{t_i},t_i)\left[W_{t_{i+1}} - W_{t_i}\right].$$

where the limit is taken so that the mesh of the partition gets progressively finer.

The important thing to notice is the term $\sigma(X_{t_i},t_i)\left[W_{t_{i+1}} - W_{t_i}\right]$ which is a product of the increment $W_{t_{i+1}} - W_{t_i}$ times the function $\sigma(X_{t_i},t_i)$ evaluated at time t_i (i.e. at the beginning of the time interval $[t_i, t_{i+1}]$). By definition of the Brownian motion, the increment $W_{t_{i+1}} - W_{t_i}$ is statistically independent from the past. Therefore its expectation value is zero,

$$\mathbb{E}\left(\sigma(X_{t_i},t_i)\left[W_{t_{i+1}} - W_{t_i}\right]\right) = \mathbb{E}\left[\sigma(X_{t_i},t_i)\right]\cdot\mathbb{E}\left[W_{t_{i+1}} - W_{t_i}\right] = 0.$$

Therefore, the expectation value of the entire Itô integral is zero:

$$\mathbb{E}\left[\int_0^T \sigma(X_t,t)dW_t\right] = 0.$$

8.2.5. Theorem of Feynman and Kac. Consider the initial value problem

$$\frac{\partial}{\partial t}u(x,t) + Lu(x,t) = \varphi(x), \qquad u(x,T) = \phi(x) \tag{8.32}$$

$$L = \frac{1}{2}\sigma^2(x,t)\frac{\partial^2}{\partial x^2} + \mu(x,t)\frac{\partial}{\partial x} + c(x,t)$$

and for every $(x,t) \in \mathbb{R} \times [0,T]$ consider the stochastic differential equation

$$dX_s = \mu(X_s,s)ds + \sigma(X_s,s)dW_s \qquad \text{on } [t,T] \tag{8.33}$$

with initial value $X_t = x$, the solution $u(x,t)$ of the initial value problem is given by

$$u(x,t) = \mathbb{E}\left[\phi(X_T)\exp\left(\int_t^T c(X_s,s)ds\right)\right] - \mathbb{E}\left[\int_t^T \varphi(X_r)\exp\left(\int_t^r c(X_s,s)ds\right)dr\right].$$

To prove this statement, we apply Itô's formula to the function

$$u(X_s,s)\exp\left(\int_t^s c(X_r,r)dr\right).$$

First of all, we recall Itô's formula for a function $V(X_s,s)$ and stochastic differential

$$dX_s = \mu(X_s,s)ds + \sigma(X_s,s)dW_s$$

as being[2]

$$dV(X_s,s) = \left[V_s(X_s,s) + V_x(X_s,s)\mu(X_s,s) + \frac{1}{2}V_{xx}(X_s,s)\sigma^2(X_s,s)\right]ds + V_x(X_s,s)\sigma(X_s,s)dW_s.$$

Carrying out this operation, integrating from t to T and taking $\mathbb{E}$,

$$\begin{aligned}\mathbb{E}\left[\phi(X_T)\exp\left(\int_t^T c(X_s,s)ds\right)\right] - u(x,t) =& \mathbb{E}\left[\int_t^T [(\partial_r + L)u(X_r,r)]\exp\left(\int_t^r c(X_s,s)ds\right)dr\right] \\ =& \mathbb{E}\left[\int_t^T \varphi(X_r)\exp\left(\int_t^r c(X_s,s)ds\right)dr\right].\end{aligned}$$

We have made use of the fact that the expectation value of the Itô integral vanishes:

$$\mathbb{E}\left[\int_t^T V_x(X_r,r)\sigma(X_r,r)dW_r\right] = \mathbb{E}\left[\int_t^T \frac{\partial u}{\partial x}(X_r,r)\exp\left(\int_t^r c(X_s,s)ds\right)\sigma(X_r,r)dW_r\right] = 0.$$

The Feynman-Kac theorem is a turning point in mathematical physics, elegantly connecting the realms of stochastic differential equations (SDEs, e.g., Eq. 8.33) and partial differential equations (PDEs, Eq. 8.32). This theorem allows us to interpret each SDE in terms of an associated probability density, $u(x,t)$, as introduced in this section. While the SDE characterizes individual trajectories of particles undergoing Brownian motion, the associated PDE, derived through the Feynman-Kac formulation, offers a more comprehensive physical description. In many physical and financial models, the detailed trajectories of individual particles or entities are less critical than the statistical properties of the system as a whole. Here, $u(x,t)$ signifies the probability of locating the particle within a specific spatial region at a given time.

The Feynman-Kac theorem's true power lies in its ability to translate the stochastic behavior of systems into the language of PDEs, enabling the use of well-established analytical

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[2] Here V_s means $\partial V/\partial s$, $V_{xx} = \partial^2 V/\partial_x^2$, etc.

and numerical methods for PDEs to solve problems initially formulated in stochastic terms. This translation is particularly valuable in scenarios where direct analytical solutions of SDEs are challenging or intractable. Furthermore, in the context of quantum mechanics and statistical physics, the Feynman-Kac theorem is a basis of the path integral formulation, providing deep insights into the evolution of quantum systems. In fields like finance, it plays a crucial role in option pricing models, where the evolution of prices can be modeled by SDEs, and risk assessments require understanding the probability distributions of future outcomes. The concept of a probability density as a "weight" factor under the integral in the computation of macroscopic averages, such as expectation values, further emphasizes the theorem's utility in a wide range of scientific inquiries, from fundamental physics to applied financial analysis.

There are also compelling reasons why an SDE framework might be preferred in specific contexts. One primary advantage of SDEs lies in their ability to capture the detailed dynamics of systems at a microscopic level. This aspect is particularly crucial in fields like molecular dynamics (MD) simulations, where the intricacies of particle interactions, governed by intermolecular potentials, are fundamental. In contrast to PDEs, which often rely on effective-medium coefficients representing averaged properties, SDEs can explicitly model the stochastic nature of particle collisions and interactions. This fine-grained modeling is essential in scenarios where details of individual paths and interactions significantly influence the system's behavior, such as in the study of complex fluids or biomolecular systems.

Furthermore, the path integral formulation in quantum mechanics, often solved numerically, aligns more closely with SDE methods than PDEs. This alignment is because path integrals encompass a sum over all possible paths, akin to examining a multitude of stochastic trajectories, each weighted by its quantum mechanical probability. The SDE approach thus offers a more natural and direct framework for implementing these numerical techniques, providing insights into the probabilistic nature of quantum systems. Consequently, the SDE methodology is not just an alternative to PDEs but a complementary approach that excels in situations where the details of randomness, individual trajectories, and microscopic interactions are pivotal to understanding the phenomena under study.

8.2.6. Parallel between Feynman-Kac and Green's Method. The Feynman-Kac theorem and the Green's function method both offer profound insights into solving differential equations, yet they do so from different perspectives. Understanding the connection between these approaches may enhance one's grasp of the underlying physics and mathematics. The Feynman-Kac theorem addresses the solution to certain PDEs using the language of stochastic processes. Consider a linear inhomogeneous PDE and its associated initial value problem:

$$\frac{\partial}{\partial t}u(x,t) + Lu(x,t) = \varphi(x), \qquad u(x,T) = \phi(x),$$

where L is a differential operator. The solution $u(x,t)$ according to the Feynman-Kac theorem is given by an expectation value over a stochastic process X_s:

$$u(x,t) = \mathbb{E}\left[\phi(X_T)\exp\left(\int_t^T c(X_s,s)ds\right)\right] - \mathbb{E}\left[\int_t^T \varphi(X_r)\exp\left(\int_t^r c(X_s,s)ds\right)dr\right].$$

To the differential operator L in the PDE corresponds an Ito SDE that describes the evolution of the stochastic process X_s:

$$dX_s = \mu(X_s,s)ds + \sigma(X_s,s)dW_s,$$

where $\mu(X_s,s)$ and $\sigma(X_s,s)$ are the drift and diffusion coefficients, respectively, and dW_s represents the increment of a Wiener process (or Brownian motion). The solution to this SDE, X_s, starting from an initial condition $X_t = x$ at time t, is a stochastic process that captures the dynamics encoded in the differential operator L.

The Feynman-Kac solution to the PDE can now be understood in terms of this stochastic process. The solution $u(x,t)$ to the PDE is expressed as an expectation value over the realizations of X_s, as shown above in the explicit expression for $u(x,t)$.

On the other hand, the Green's function method, employs a Green's function, denoted as $G(x,t;\xi,\tau)$, to describe the response of the system at point x and time t due to an impulse applied at point ξ and time τ. The solution of the inhomogeneous PDE can be written as:

$$u(x,t) = \int_{\text{domain}} G(x,t;\xi,\tau)\varphi(\xi)d\xi + \int_{\text{initial}} G(x,t;\xi,T)\phi(\xi)d\xi.$$

The first integral represents the effect of the inhomogeneous term $\varphi(x)$ propagated through the Green's function, analogous to the second expectation term in the Feynman-Kac solution. The second integral represents the influence of the initial condition $\phi(x)$ at time T, similar to the first expectation term in the Feynman-Kac formula.

While the Feynman-Kac theorem uses stochastic processes and expectation values to describe the solution, the Green's function method relies on the deterministic propagation of effects (both from the initial conditions and inhomogeneous terms) through the Green's function. Both approaches, though seemingly different, converge on the same solution, illustrating the deep interconnections between stochastic processes and traditional PDE methods. This duality enriches our understanding of physical systems, whether we analyze them through the lens of probability or deterministic equations.

8.2.7. Theorem of Feynman and Kac Recast As Initial Value Problem. The usual (textbook) formulation of the Feynman-Kac problem is given in terms of a final value problem, as we did. However, we can also easily recast it as an initial value problem:

$$\frac{\partial}{\partial t}u(x,t) + Lu(x,t) = \varphi(x), \qquad u(x,0) = \phi(x)$$

where $L = \frac{1}{2}\sigma^2(x,t)\frac{\partial^2}{\partial x^2} + \mu(x,t)\frac{\partial}{\partial x} + c(x,t)$ is the differential operator.

For every $(x,t) \in \mathbb{R} \times [0,T]$, consider the stochastic differential equation

$$dX_s = \mu(X_s,s)ds + \sigma(X_s,s)dW_s \qquad \text{on } [0,t]$$

with initial value $X_0 = x$. The solution $u(x,t)$ of the initial value problem is given by

$$u(x,t) = \mathbb{E}\left[\phi(X_0)\exp\left(\int_0^t c(X_s,s)ds\right)\right] + \mathbb{E}\left[\int_0^t \varphi(X_r)\exp\left(\int_0^r c(X_s,s)ds\right)dr\right].$$

8.2.8. Langevin Equation. Let us return to the Langevin equation[3]

$$dX_t = \underbrace{a(t)X_t}_{\mu}\, dt + \sigma(X_t,t)\cdot dW_t.$$

Consider the process $V(X_t,t) = e^{-\int_0^t a(s)ds}X_t$ and apply Itô's formula

$$dV = \left[V_x\mu + V_t + \tfrac{1}{2}V_{xx}\sigma^2\right]dt + V_x\sigma dW_t,$$

to get

$$\begin{aligned} d\left(e^{-\int_0^t a(s)ds}X_t\right) &= \left[\underbrace{e^{-\int_0^t a(s)ds}a(t)X_t}_{V_x\mu}\underbrace{-a(t)e^{-\int_0^t a(s)ds}X_t}_{V_t}\right]dt + \underbrace{e^{-\int_0^t a(s)ds}\sigma(X_t,t)}_{V_x\sigma}dW_t \\ &= e^{-\int_0^t a(s)ds}\sigma(X_t,t)dW_t. \end{aligned}$$

Integrating both sides we obtain

$$e^{-\int_0^t a(s)ds}X_t - X_0 = \int_0^t e^{-\int_0^r a(s)ds}\sigma(X_r,r)dW_r,$$

and finally

$$X_t = X_0 e^{\int_0^t a(s)ds} + e^{\int_0^t a(s)ds}\cdot\int_0^t e^{-\int_0^r a(s)ds}\sigma(X_r,r)dW_r. \tag{8.34}$$

8.2.9. Solution via Feynman-Kac theorem. It is interesting to see that we may also solve the Schrödinger equation in imaginary time – a diffusion equation – using the Feynman-Kac theorem. First, we may write down a probabilistic solution to the PDE

$$-\partial_t\psi(x,t) = [-D\nabla^2 + V_{eff}]\psi(x,t)$$

subjected to the initial condition[4]

$$\psi(x,T) = \delta(x - x_A)$$

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[3] This equation is reminiscent of a linear ODE but with an inhomogeneous term σdW_t. Recall that such an equation is solved with the use of an integrating factor $\exp[-\int_0^t a(s)ds]$. When dealing with SDEs, we must use Itô's formula to write down total differentials.

[4] Note: this is a "final condition" rather than an initial condition, according to how we have derived the Feynman-Kac (FK) theorem. However, the FK theorem can be derived with T as the initial condition. It is equivalent to reversing the order of the times $t \leftrightarrow T$ and adding a sign change in the exponent and under the square root coefficient to account for the sign change of the time steps $(t_i - t_{i-1})$.

by setting up an Itô diffusion [with parameters: $\mu = 0$, $\frac{1}{2}\sigma^2 = -D$, $c(x,t) = V_{eff}(x,t)$] which can be immediately integrated:

$$dX_s = \sqrt{-2D}dW_s, \qquad X_s = x + i\sqrt{2D}(W_s - W_t)$$

The probability law[5] for X_s is therefore $X_s \sim \mathcal{N}(x, -2D(s-t))$. The solution to the PDE is given by:

$$\psi(x,t) = \mathbb{E}\left[\delta(X_T - x_A)e^{\int_t^T V_{eff}(X_s,s)ds}\right]$$

Inserting the probability density corresponding to the Weiner measure

$$p_{t_1,\ldots,t_n}(x_1,\ldots,x_n) = \prod_{i=1}^{n} \frac{1}{\sqrt{2\pi(t_i - t_{i-1})}} \cdot e^{-\sum_{i=1}^{n} \frac{(x_i - x_{i-1})^2}{2(t_i - t_{i-1})}}$$

(but using the initial point x_A and scaling the variance by $-2D$) we may rewrite this expectation value as

$$\psi(x,t) = \lim_{\substack{n\to\infty \\ \Delta t \to 0}} \int \prod_i dx_i \frac{1}{\sqrt{(-2D)2\pi(t_i - t_{i-1})}} \delta(x - (x_A - x_n)) e^{\sum_{i=1}^{n} \frac{(x_i - x_{i-1})^2}{4D(t_i - t_{i-1})}} e^{\int_t^T V_{eff}(X_s,s)ds}$$

Taking the limit $\Delta t = \max_i |t_i - t_{i-1}| \to 0$ allows us to replace the finite differences by derivatives. This expression gives the conditional probability density for the particle initially at (x_A, T) and ending at (x,t).

However, the initial time occurs after the final time ($T > t$), due to the way we have constructed the Feynman-Kac solution. To reverse the order of $t \leftrightarrow T$ so the initial time precedes the final time, we flip the sign of all time steps dt and $(t_i - t_{i-1})$. The result is:

$$\psi(x,t) = \int_{x(0)=x_A} \mathcal{D}[x(\tau)] e^{-\int_T^t \left[\frac{1}{4D}(\frac{dx}{dt})^2 + V_{eff}(x(t),t)\right]dt}$$

where:

$$\int_{x(0)=x_A} \mathcal{D}[x(\tau)] = \lim_{n\to\infty} \int \prod_i dx_i \frac{1}{\sqrt{(-2D)2\pi(t_i - t_{i-1})}} \delta(x - (x_A - x_n)).$$

This can be written as [with $(t_i - t_{i-1}) > 0$]:

$$p(x_B, t_B | x_A, t_A) = \lim_{n\to\infty} \int \prod_i dx_i \frac{1}{\sqrt{4\pi D(t_i - t_{i-1})}} e^{-\int_{t_A}^{t_B} \left[\frac{1}{4D}(\frac{dx}{dt})^2 + V_{eff}(x(t),t)\right]dt}. \tag{8.35}$$

$$= \int_{x(t_A)=x_A} \mathcal{D}[x(\tau)] e^{-\int_{t_A}^{t_B} \left[\frac{1}{4D}(\frac{dx}{dt})^2 + V_{eff}(x(t),t)\right]dt}. \tag{8.36}$$

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[5] There is no need to worry about the apparently negative variance of the distribution. This is because we have not yet settled the sign of $s - t$, which we will do later.

Review of Math Concepts

9.1. Differential Equations

9.1.1. First-Order Linear ODE with Inhomogeneous Term. Consider a first-order linear ordinary differential equation (ODE) of the form

$$\frac{dy}{dt} + p(t)y = q(t),$$

where $p(t)$ and $q(t)$ are given functions of t, and $y = y(t)$ is the unknown function we seek to determine. The term $q(t)$ makes the equation inhomogeneous.

The key to solving this type of ODE is to find an integrating factor that will allow us to rewrite the equation in an integrable form. The integrating factor, $\mu(t)$, is obtained from the corresponding homogeneous equation (i.e., setting $q(t) = 0$). The integrating factor is defined as

$$\mu(t) = \exp\left(\int p(t)dt\right).$$

Multiplying both sides of the original ODE by $\mu(t)$, we get

$$\mu(t)\frac{dy}{dt} + \mu(t)p(t)y = \mu(t)q(t).$$

Notice that the left-hand side of this equation is the derivative of $\mu(t)y$. Therefore, the equation can be rewritten as

$$\frac{d}{dt}[\mu(t)y] = \mu(t)q(t).$$

To solve for $y(t)$, we integrate both sides of the equation with respect to t:

$$\int \frac{d}{dt}[\mu(t)y]dt = \int \mu(t)q(t)dt.$$

This yields

$$\mu(t)y = \int \mu(t)q(t)dt + C,$$

where C is the constant of integration, which is determined by the initial condition. Solving for $y(t)$, we find

$$y(t) = \frac{1}{\mu(t)}\left(\int \mu(t)q(t)dt + C\right). \tag{9.1}$$

The solution can be expressed as a sum of two terms: one corresponding to the solution of the homogeneous equation (initial condition term) and the other to the inhomogeneous part (convolution term). The first term, involving C, represents the effect of the initial conditions, while the second term represents the contribution from the inhomogeneous term $q(t)$.

9.1.2. Green's Function Method. Suppose that we have a linear differential operator $\hat{L}$ defined on $[a, b]$ acting on a function $y(x)$ and yielding $f(x)$:

$$\hat{L}[y(x)] = f(x).$$

The Langevin equation has this form, with $\hat{L} = m(\frac{d}{dt} + \zeta)$. The Green's function $G(x, \xi)$ is defined to be a kind of inverse to the differential operator:

$$\hat{L}[G(x, \xi)] = \delta(x - \xi),$$

with the additional "causality" requirement that $G(x, \xi) = 0$ for $x < \xi$. Thus, $G(x, \xi)$, when viewed as a function of x is defined over the interval $[a, b] - \{\xi\}$. Using the sifting property of the Dirac delta function and substituting the definition of the Green's function:

$$\hat{L}[y(x)] = f(x) = \int_a^b f(\xi)\delta(x - \xi)d\xi = \int_a^b f(\xi)\hat{L}[G(x, \xi)]d\xi = \hat{L}\int_a^b f(\xi)G(x, \xi)d\xi.$$

The limits of integration are required since $\hat{L}$ is only defined on $[a, b]$. Without this restriction, the last step would not be allowed. Application of the inverse $\hat{L}$ from the left leads to the particular solution to the inhomogeneous equation:

$$y_{inh}(x) = \int_a^b f(\xi)G(x, \xi)d\xi.$$

Because the operator $\hat{L}$ is linear, we can always add two solutions together, and obtain a new solution to the ODE. In particular, we can add $y_{hom}(x)$, the solution to the homogeneous equation $\hat{L}[y(x)] = 0$

$$y(x) = y_{hom}(x) + y_{inh}(x),$$

and the result $y(x)$ is still a solution to the inhomogeneous equation.

Let us return to the Langevin equation to demonstrate this method. The independent variable here is t. Let's take the time origin at $t = 0$ to keep the notation compact. We can always shift the origin as needed. The obtain the "retarded Green's function" we must solve

$$\frac{dG}{dt} + \zeta G = \delta(t),$$

under conditions where $g = 0$ for $t < 0$. Here, $G(t)$ is the Green's function, ζ is a constant coefficient, and $\delta(t)$ is the Dirac delta function, we consider the response in two time regions: $t < 0$ and $t > 0$.

For $t < 0$: The equation simplifies to the homogeneous differential equation:

$$\frac{dG}{dt} + \zeta G = 0.$$

Solving this yields:

$$G(t) = A \exp(-\zeta t),$$

where A is an integration constant. However, $A = 0$ for $t < 0$ as the Green's function should be zero before the impulse. *This is not a result from mathematics; it is a physical argument about causality: the cause (impulse from the delta-function) must come before the effect.*

For $t > 0$: After the impulse at $t = 0$, the equation again becomes:

$$\frac{dG}{dt} + \zeta g = 0.$$

Solving this, we get:

$$G(t) = B \exp(-\zeta t),$$

where B is a constant. To find B, we use the property of the Dirac delta function at $t = 0$. Integrating the original differential equation across an infinitesimally small interval around $t = 0$ gives:

$$\int_{-\epsilon}^{\epsilon} \left(\frac{dG}{dt} + \zeta g \right) dt = \int_{-\epsilon}^{\epsilon} \delta(t) dt.$$

This yields $G(\epsilon) - G(-\epsilon) = 1$. Since $G(-\epsilon) = 0$, we find $G(\epsilon) = 1$, indicating that $B = 1$.

Therefore, for $t > 0$, $G(t) = \exp(-\zeta t)$.

Combining these results, the full solution for the Green's function is:

$$G(t) = \Theta(t) \exp(-\zeta t),$$

where $\Theta(t)$ is the Heaviside step function, which is 0 for $t < 0$ and 1 for $t \geq 0$.

In the case of the Langevin equation the ODE is of the form:

$$\frac{dy}{dt} + p(t) y = q(t),$$

with an initial condition $y(t_0) = y_0$. Here, $p(t)$ and $q(t)$ are known functions, and $y(t)$ is the unknown function we seek. The operator $\hat{L}$ is assumed to be defined on the interval $[t_0, t]$.

Once the Green's function $G(t,t')$ is known, the solution to the original inhomogeneous ODE can be expressed as:

$$y(t) = y_{\text{hom}}(t) + y_{\text{inh}}(t),$$

where $y_{\text{hom}}(t)$ is the solution to the homogeneous equation (i.e., with $q(t) = 0$), and $y_{\text{inhom}}(t)$ is the particular solution due to the inhomogeneous term. The two components of the solution are:

1. **Homogeneous Solution**: The homogeneous solution, $y_{\text{hom}}(t)$, can be obtained using the initial condition:

$$y_{hom}(t) = y_0 G(t, t_0).$$

2. **Inhomogeneous Solution (Convolution Term)**: The inhomogeneous solution is obtained via the convolution of the Green's function with the inhomogeneous term $q(t)$:

$$y_{inh}(t) = \int_{t_0}^{t} G(t,t')q(t')dt'.$$

Combining these components, the solution to the inhomogeneous ODE is:

$$y(t) = y_0 G(t,t_0) + \int_{t_0}^{t} G(t,t')q(t')dt'. \tag{9.2}$$

This solution comprises the initial condition influenced by the Green's function and the cumulative effect of the inhomogeneous term over the interval from t_0 to t, as expressed by the convolution integral.

For the Langevin equation, the solution is therefore:

$$\begin{aligned} y(t) =& v_0 e^{-\zeta(t-t_0)}\Theta(t-t_0) + \int_{t_0}^{t} \Theta(t-t')e^{-\zeta(t-t')}f(t')dt' \\ =& v_0 e^{-\zeta(t-t_0)} + \int_{t_0}^{t} e^{-\zeta(t-t')}f(t')dt' \\ =& v_0 e^{-\zeta(t-t_0)} + \int_{t_0}^{t} e^{-\zeta(t-t_0+t_0-t')}f(t')dt' \\ =& v_0 e^{-\zeta(t-t_0)} + e^{-\zeta(t-t_0)} \int_{t_0}^{t} e^{\zeta(t'-t_0)}f(t')dt' \end{aligned}$$

where we have expressed the solution in several equivalent forms. Alternatively, we can absorb the factor $e^{\zeta t_0}$ into the constant v_0, renaming it $\tilde{v}_0$. (In the second term, t_0 was artificially introduced for demonstration purposes and hence can be dropped.). We recover a form that is identical to the integrating factor method (see Eq. 9.1):

$$y(t) = \tilde{v}_0 e^{-\zeta t} + e^{-\zeta t}\int_{t_0}^{t} e^{\zeta t'}f(t')dt' = \frac{1}{e^{\zeta t}}\left(C + \int^{t} e^{\zeta t'}f(t')dt'\right).$$

The indefinite integral is used in the last step, as the lower limit of integration (t_0) is absorbed in the integration constant C. Similarly for the integration factor $e^{\zeta t}$, where any integration constant can be absorbed in C (whereas in the second term, such integration constants from the integration factor cancel out with the factor $e^{\zeta t'}$ in the integrand.).

9.1.3. In the Dirac Bra-Ket Notation. We may also employ the elegant notation of Dirac bra kets to derive the same result. We start with the ODE $\hat{L}_x[u] = f(x)$, where $\hat{L}_x$ is a linear differential operator. In abstract Dirac notation this can be formally written as $\hat{L}\,|u\rangle = |f\rangle$. If $\hat{L}$ has an inverse $\hat{L}^{-1} \equiv \hat{G}$, the solution can be formally written as $|u\rangle = \hat{L}^{-1}\,|f\rangle = \hat{G}\,|f\rangle$. Multiplying this by $\langle x|$ and inserting the resolution of the identity $1 = \int dy\,|y\rangle\,w(y)\,\langle y|$ between $\hat{G}$ and $|f\rangle$ gives:

$$u(x) = \int dy\, G(x,y)w(y)f(y), \tag{9.3}$$

where the integration is over the range of definition of the functions involved. Once we know $G(x,y)$, this equation gives the solution $u(x)$ in an integral form. How do we find $G(x,y)$?

Sandwiching both sides of $\hat{L}\hat{G} = 1$ between $\langle x|$ and $|y\rangle$ and using

$$1 = \int dx'\ |x'\rangle\, w(x')\, \langle x'|$$

between $\hat{L}$ and $\hat{G}$ yields

$$\int dx'\, L(x,x')w(x')G(x',y) = \langle x|y\rangle = \frac{\delta(x-y)}{w(x)}$$

In particular, if $\hat{L}$ is a local differential operator, then $L(x,x') = [\delta(x-x')/w(x)]\hat{L}_x$, and we obtain

$$\hat{L}_x G(x,y) = \frac{\delta(x-y)}{w(x)} \quad \text{or} \quad \hat{L}_x G(x,y) = \delta(x-y), \tag{9.4}$$

where the second equation makes the frequently used assumption that $w(x) = 1$. $G(x,y)$ is called the Green's function for the differential operator $\hat{L}_x$. $\hat{L}_x$ might not be defined for all functions on $\mathbb{R}$.

Moreover, a complete specification of $\hat{L}_x$ requires some initial (or boundary) conditions. Therefore, we expect $G(x,y)$ to depend on such initial conditions as well. We note that when $\hat{L}_x$ is applied to (9.3), we get

$$\hat{L}_x u(x) = \int dy\, \left[\hat{L}_x G(x,y)\right] w(y)f(y) = \int dy\, \frac{\delta(x-y)}{w(x)} w(y)f(y) = f(x),$$

indicating that $u(x)$ is indeed a solution of the original ODE. Equation (9.4) involving the generalized function $\delta(x-y)$ is meaningful only in the same context. Thus, we treat $G(x,y)$ not as an ordinary function but as a distribution. Finally, (9.3) is assumed to hold for an arbitrary (well-behaved) function f.

9.2. The Derivative as a Linear Map

Let $U \subset \mathbb{R}^n$ be an open set and $f : U \to \mathbb{R}^m$ a function. The derivative of f at a point $\mathbf{a} \in U$ is defined as a linear transformation $L : \mathbb{R}^n \to \mathbb{R}^m$ that satisfies the following condition:

$$f(\mathbf{a} + \mathbf{h}) = f(\mathbf{a}) + L(\mathbf{h}) + o(\|\mathbf{h}\|) \text{ as } \mathbf{h} \to \mathbf{0}$$

In this definition: - $\mathbf{h}$ is a small perturbation or change in the input. - $L(\mathbf{h})$, which is the derivative of f at $\mathbf{a}$, denoted as $Df(\mathbf{a})$ or $f'(\mathbf{a})$, represents the best linear approximation to the change in f due to $\mathbf{h}$. - $o(\|\mathbf{h}\|)$ is a term that becomes negligible faster than $\|\mathbf{h}\|$ as $\mathbf{h} \to \mathbf{0}$. This term captures the error of the linear approximation and ensures that the approximation becomes increasingly accurate as $\mathbf{h}$ becomes smaller.

The derivative L is typically represented by the Jacobian matrix in the case of functions between Euclidean spaces.

Example 1: Linear Function
Consider $f : \mathbb{R}^n \to \mathbb{R}^m$ defined by $f(\mathbf{x}) = A\mathbf{x}$, where A is an $m \times n$ matrix. To find the derivative at any point $\mathbf{x}_0 \in \mathbb{R}^n$:

$$f(\mathbf{x}_0 + \mathbf{h}) - f(\mathbf{x}_0) = A(\mathbf{x}_0 + \mathbf{h}) - A\mathbf{x}_0 = A\mathbf{h}$$

Since $A\mathbf{h}$ is linear in $\mathbf{h}$ and there are no higher-order terms, the derivative $Df(\mathbf{x}_0)$ is the matrix A itself.

Example 2: Scalar Field
Consider the scalar field $f : \mathbb{R}^2 \to \mathbb{R}$ given by $f(x, y) = x^2 + y^2$. The derivative at a point (x_0, y_0) is defined as the linear map $Df(x_0, y_0)(h, k)$ that satisfies:

$$f(x_0 + h, y_0 + k) - f(x_0, y_0) = Df(x_0, y_0)(h, k) + o(\|(h, k)\|)$$

Expanding $f(x_0 + h, y_0 + k)$:

$$\begin{aligned} f(x_0 + h, y_0 + k) &= (x_0 + h)^2 + (y_0 + k)^2 \\ &= x_0^2 + 2x_0h + h^2 + y_0^2 + 2y_0k + k^2 \end{aligned}$$

Subtracting $f(x_0, y_0)$ and rearranging:

$$2x_0h + h^2 + 2y_0k + k^2 = Df(x_0, y_0)(h, k) + o(\|(h, k)\|)$$

The derivative $Df(x_0, y_0)(h, k)$ must be the linear part of the expression, which is $2x_0h + 2y_0k$. The remaining terms $h^2 + k^2$ are higher-order and are represented by the little-o notation $o(\|(h, k)\|)$ as they become negligible compared to $\|(h, k)\|$ when $(h, k) \to (0, 0)$.

Therefore, the derivative at (x_0, y_0) is given by the linear map:

$$Df(x_0, y_0)(h, k) = 2x_0h + 2y_0k$$

This result corresponds to the gradient of f at (x_0, y_0) and is the best linear approximation of the change in f at (x_0, y_0) due to an infinitesimal change in the direction (h, k).

Example 3: Nonlinear Mapping
Consider $f : \mathbb{R}^2 \to \mathbb{R}^2$ defined by $f(x, y) = (x^2, e^y)$. The derivative at a point (x_0, y_0) is found as:

$$\begin{aligned} f(x_0 + h, y_0 + k) - f(x_0, y_0) &= ((x_0 + h)^2, e^{y_0+k}) - (x_0^2, e^{y_0}) \\ &= (2x_0h + h^2, e^{y_0}e^k - e^{y_0}) \end{aligned}$$

Identifying the linear terms gives the Jacobian matrix:

$$Df(x_0, y_0) = \begin{pmatrix} 2x_0 & 0 \\ 0 & e^{y_0} \end{pmatrix}$$

The higher-order term h^2 and the term $e^{y_0}(e^k - 1)$ which is little-o of k for small k, are ignored in the derivative.

Example 4: Trigonometric Function
Consider the function $f : \mathbb{R}^2 \to \mathbb{R}^2$ defined by $f(x, y) = (\sin(x), \cos(y))$. To find the derivative at a point (x_0, y_0), we use the Taylor expansion of sin and cos around x_0 and y_0 respectively.

The Taylor expansion of sin and cos gives:

$$\sin(x_0 + h) = \sin(x_0) + \cos(x_0)h + o(h)$$
$$\cos(y_0 + k) = \cos(y_0) - \sin(y_0)k + o(k)$$

Substituting these into $f(x_0 + h, y_0 + k)$ and subtracting $f(x_0, y_0)$, we have:

$$\begin{aligned} f(x_0 + h, y_0 + k) - f(x_0, y_0) &= (\sin(x_0 + h), \cos(y_0 + k)) - (\sin(x_0), \cos(y_0)) \\ &= (\cos(x_0)h + o(h), -\sin(y_0)k + o(k)) \end{aligned}$$

The linear terms in this expression are $\cos(x_0)h$ and $-\sin(y_0)k$. Therefore, the derivative at (x_0, y_0) is given by the Jacobian matrix:

$$Df(x_0, y_0) = \begin{pmatrix} \cos(x_0) & 0 \\ 0 & -\sin(y_0) \end{pmatrix}$$

This matrix represents the best linear approximation of f at (x_0, y_0), and the higher-order terms $o(h)$ and $o(k)$ become negligible as $(h, k) \to (0, 0)$.

Example 5: Composition of Functions
Let $g : \mathbb{R}^n \to \mathbb{R}^m$ and $h : \mathbb{R}^m \to \mathbb{R}^p$ be differentiable functions. We aim to find the derivative of the composition $h \circ g$ at a point $\mathbf{x}_0 \in \mathbb{R}^n$.

The composition $h \circ g$ at $\mathbf{x}_0$ is given by:

$$(h \circ g)(\mathbf{x}_0 + \mathbf{h}) - (h \circ g)(\mathbf{x}_0) = h(g(\mathbf{x}_0 + \mathbf{h})) - h(g(\mathbf{x}_0))$$

Using the differentiability of g and h, we can expand:

$$g(\mathbf{x}_0 + \mathbf{h}) = g(\mathbf{x}_0) + Dg(\mathbf{x}_0)(\mathbf{h}) + o(\|\mathbf{h}\|)$$
$$h(\mathbf{y}_0 + \mathbf{k}) = h(\mathbf{y}_0) + Dh(\mathbf{y}_0)(\mathbf{k}) + o(\|\mathbf{k}\|)$$

where $\mathbf{y}_0 = g(\mathbf{x}_0)$ and $\mathbf{k} = Dg(\mathbf{x}_0)(\mathbf{h})$.

Substituting these expansions into the composition, we get:

$$h(g(\mathbf{x}_0 + \mathbf{h})) - h(g(\mathbf{x}_0)) = Dh(g(\mathbf{x}_0)) \cdot Dg(\mathbf{x}_0)(\mathbf{h}) + o(\|\mathbf{h}\|)$$

Therefore, the derivative of the composition $h \circ g$ at $\mathbf{x}_0$ is given by the matrix product of the derivatives of h and g:

$$D(h \circ g)(\mathbf{x}_0) = Dh(g(\mathbf{x}_0)) \cdot Dg(\mathbf{x}_0)$$

This represents the linear transformation that approximates $h \circ g$ near $\mathbf{x}_0$.

The derivative in multivariable calculus, defined as a linear map, extends the concept of the derivative in single-variable calculus and provides a powerful tool for analysis in higher dimensions.

9.3. Matrix Derivative

The derivative of a matrix function $f : \mathbb{R}^{m\times n} \to \mathbb{R}^{p\times q}$ at a matrix $X \in \mathbb{R}^{m\times n}$ can be understood both formally and practically.

Formal Definition: The formal definition of the derivative is given by the limit:

$$\lim_{\|H\|\to 0} \frac{\|f(X+H) - f(X) - Df(X)(H)\|}{\|H\|} = 0$$

where: - H is a matrix representing a small perturbation in $\mathbb{R}^{m\times n}$. - $Df(X)$ is the derivative of f at X, a linear map from $\mathbb{R}^{m\times n}$ to $\mathbb{R}^{p\times q}$. - The norm $\|\cdot\|$ is a suitable matrix norm.

Practical Definition (Little-oh Notation): Practically, the derivative is often used in the form:

$$f(X+H) = f(X) + Df(X)(H) + o(\|H\|) \text{ as } \|H\| \to 0$$

where: - $o(\|H\|)$ represents a matrix function whose norm becomes negligible faster than $\|H\|$ as $\|H\| \to 0$. - This notation emphasizes the linear approximation $Df(X)(H)$ and the error term $o(\|H\|)$, which diminishes relative to $\|H\|$.

The practical definition using little-oh notation is particularly useful in applications and computations, as it directly relates the change in f due to a small perturbation H to the linear approximation provided by the derivative $Df(X)$.

9.3.1. Derivative of $\log(X)$ is X^{-1}.

Let us show that for a matrix function $f(X) = \log(X)$, where X is an invertible square matrix, the derivative $Df(X)$ is the linear map X^{-1}. To find $D\log(X)$, we consider the first-order Taylor expansion of $\log(X+H)$ around X:

$$\log(X+H) \approx \log(X) + X^{-1}H.$$

Substitute into the limit definition:

$$\lim_{\|H\|\to 0} \frac{\|f(X+H) - f(X) - Df(X)(H)\|}{\|H\|} = \lim_{\|H\|\to 0} \frac{\|\log(X+H) - \log(X) - X^{-1}H\|}{\|H\|}$$

Using the Taylor expansion, the expression within the limit becomes 0. Hence the limit is 0. Thus, the derivative of $\log(X)$ with respect to X is X^{-1}. The linear map is $Df(X)(H) = D\log(X)(H) = X^{-1}H$.

9.3.2. Example: density matrix $\log(\hat{\rho} + \delta\hat{\rho})$. The result we just derived can be directly applied to the density matrix. Consider $\hat{\rho}$ as the expansion point and $\delta\hat{\rho}$ as a small perturbation. The expansion at $\hat{\rho}$ is:

$$\log(\hat{\rho} + \delta\hat{\rho}) = \log(\hat{\rho}) + \frac{d}{dX}\log(X)\bigg|_{X=\hat{\rho}} \cdot \delta\hat{\rho} + o(\|\delta\hat{\rho}\|).$$

The derivative of $\log(X)$ with respect to X is X^{-1}, hence the expansion becomes:

$$\log(\hat{\rho} + \delta\hat{\rho}) \approx \log(\hat{\rho}) + \hat{\rho}^{-1} \cdot \delta\hat{\rho}.$$

The approximation implies that the change in $\log(\hat{\rho})$ due to the small variation $\delta\hat{\rho}$ is approximately proportional to the variation itself, scaled by $\hat{\rho}^{-1}$.

9.3.3. Derivative of $\mathrm{Tr}[\rho]$ with Respect to ρ. The derivative of $\mathrm{Tr}(\rho)$ with respect to ρ is the identity matrix I. This is shown by considering a small perturbation $\delta\rho$ and observing that:

$$\mathrm{Tr}(\rho + \delta\rho) = \mathrm{Tr}(\rho) + \mathrm{Tr}(\delta\rho) = \mathrm{Tr}(\rho) + \mathrm{Tr}(I\delta\rho)$$

Hence, the derivative is I.

To see that this is indeed the case we consider the function $f(\rho) = \mathrm{Tr}(\rho)$, where ρ is a matrix, and explain why the derivative of f with respect to ρ is the identity matrix I, using the definition of the derivative in little-oh notation. The derivative of a matrix function f at a point X is a linear transformation $Df(X)$ that satisfies:

$$f(X + H) = f(X) + Df(X)(H) + o(\|H\|)$$

where H is a small perturbation, and $o(\|H\|)$ represents a term that becomes negligible faster than $\|H\|$ as $H \to 0$. Now for the derivative of $\mathrm{Tr}(\rho)$, we consider a small perturbation $\delta\rho$ to ρ. We evaluate $f(\rho + \delta\rho)$:

$$f(\rho + \delta\rho) = \mathrm{Tr}(\rho + \delta\rho).$$

The trace function is linear, so we expand:

$$\mathrm{Tr}(\rho + \delta\rho) = \mathrm{Tr}(\rho) + \mathrm{Tr}(\delta\rho)$$

To satisfy the derivative definition:

$$f(\rho) + Df(\rho)(\delta\rho) + o(\|\delta\rho\|) = \mathrm{Tr}(\rho) + \mathrm{Tr}(\delta\rho).$$

It follows that $Df(\rho)(\delta\rho) = \mathrm{Tr}(I\delta\rho) = \mathrm{Tr}(\delta\rho)$. The identity matrix I is the only matrix that, when applied to $\delta\rho$ in the trace function, yields $\mathrm{Tr}(\delta\rho)$ itself:

$$\mathrm{Tr}(I\delta\rho) = \mathrm{Tr}(\delta\rho)$$

Therefore, we interpret $Df(\rho)(\delta\rho)$ as an inner product, $\langle Df(\rho), \delta\rho\rangle$, that involves multiplying $Df(\rho)$ and $\delta\rho$ followed by the trace operation. Within this context, the derivative of $\mathrm{Tr}(\rho)$ with respect to ρ is the identity matrix I, confirming that $Df(\rho) = I$. This is consistent with the linear transformation that relates $\delta\rho$ to $\mathrm{Tr}(\delta\rho)$ in the best possible way.

The derivative of $\mathrm{Tr}(\rho)$ with respect to the matrix ρ can also be computed as a Jacobian matrix, which is a matrix of partial derivatives. Let ρ be an $n \times n$ matrix with entries ρ_{ij}. The trace of ρ is given by:

$$\mathrm{Tr}(\rho) = \sum_{i=1}^{n} \rho_{ii}.$$

The Jacobian matrix is constructed by taking the partial derivatives of $\mathrm{Tr}(\rho)$ with respect to each element ρ_{ij} of ρ:

$$\frac{\partial \mathrm{Tr}(\rho)}{\partial \rho_{ij}} = \frac{\partial}{\partial \rho_{ij}} \left(\sum_{k=1}^{n} \rho_{kk} \right)$$

This partial derivative is 1 when $i = j$ (for diagonal elements) and 0 otherwise (for off-diagonal elements). Therefore, the Jacobian matrix of $\mathrm{Tr}(\rho)$ with respect to ρ is the identity matrix I. This proves that the derivative of $\mathrm{Tr}(\rho)$ with respect to ρ is indeed I.

9.3.4. Derivative as a One-Form. We have just encountered a difficulty in defining the derivative because our function involved taking the trace. Let's provide an alternative definition of derivative as a one-form, extending the notion of differentiation to abstract vector spaces. Consider a vector space V over a field $\mathbb{F}$ and a function $f : V \to \mathbb{F}$. The derivative of f at a point $x \in V$, denoted $Df(x)$, is a one-form if it is a linear functional on V. This means $Df(x) : V \to \mathbb{F}$ satisfies for any $u, v \in V$ and $a, b \in \mathbb{F}$: 1) Linearity:

$$Df(x)(au + bv) = aDf(x)(u) + bDf(x)(v)$$

2) The action of $Df(x)$ on $h \in V$ is defined as:

$$Df(x)(h) = \lim_{t\to 0} \frac{f(x + th) - f(x)}{t}$$

representing the directional derivative of f at x in the direction h. The function f is differentiable at x if such a linear functional $Df(x)$ exists, approximating f near x as:

$$f(x + h) = f(x) + Df(x)(h) + o(\|h\|)$$

where $o(\|h\|)$ becomes negligible faster than $\|h\|$ as $h \to 0$ in V.

9.3.4.1. *Derivative of Tr(ρ) with Respect to ρ.* Consider the function $f(\rho) = \mathrm{Tr}(\rho)$ where ρ is a density operator (matrix). The derivative of f at ρ, $Df(\rho)$, acts on a perturbation h in the matrix space. According to the definition:

$$Df(\rho)(h) = \lim_{t\to 0} \frac{f(\rho + th) - f(\rho)}{t}$$

For $f(\rho) = \mathrm{Tr}(\rho)$:

$$f(\rho + th) = \mathrm{Tr}(\rho + th)$$

Using the linearity of the trace:

$$\mathrm{Tr}(\rho + th) = \mathrm{Tr}(\rho) + t\mathrm{Tr}(h)$$

The limit yields:

$$Df(\rho)(h) = \lim_{t\to 0} \frac{\mathrm{Tr}(\rho) + t\mathrm{Tr}(h) - \mathrm{Tr}(\rho)}{t} = \mathrm{Tr}(h)$$

The derivative of $\mathrm{Tr}(\rho)$ with respect to ρ, when acting on a perturbation h, is given by $\mathrm{Tr}(h)$. This result confirms that $Df(\rho)$ acts as the identity operator on h in the context of matrix trace.

9.3.5. Derivative of Tr$[\rho \log \rho]$ with Respect to ρ. For the function $\mathrm{Tr}(\rho \log \rho)$, the derivative with respect to ρ is $\log(\rho) + I$. Applying a perturbation $\delta\rho$ and using the first-order expansion of the logarithm, we have:

$$\mathrm{Tr}((\rho+\delta\rho)\log(\rho+\delta\rho)) \approx \mathrm{Tr}(\rho\log\rho)+\mathrm{Tr}(\delta\rho\log\rho)+\mathrm{Tr}(\delta\rho) = \mathrm{Tr}(\rho\log\rho)+\mathrm{Tr}((\log\rho+I)\delta\rho).$$

Therefore, the derivative is $\log(\rho) + I$.

The derivative of $f(\rho) = \mathrm{Tr}(\rho \log \rho)$ with respect to the matrix ρ is computed as follows: Consider the function:

$$f(\rho) = \sum_{i,j=1}^{n} \rho_{ij} (\log \rho)_{ji}$$

The partial derivative of $f(\rho)$ with respect to each element ρ_{ij} of ρ is:

$$\begin{aligned}
\frac{\partial f(\rho)}{\partial \rho_{mn}} &= \sum_{i,j=1}^{n} \delta_{im}\delta_{jn}(\log\rho)_{ji} + \rho_{ij}\frac{\partial(\log\rho)_{ji}}{\partial\rho_{mn}} \\
&= (\log\rho)_{nm} + \sum_{i,j=1}^{n} \rho_{ij}(\rho^{-1}\frac{\partial\rho}{\partial\rho_{mn}})_{ji} \\
&= (\log\rho)_{nm} + \sum_{i=1}^{n} (\rho\rho^{-1}\frac{\partial\rho}{\partial\rho_{mn}})_{ii} \\
&= (\log\rho)_{nm} + \delta_{mn}
\end{aligned}$$

since $\partial\mathrm{Tr}[\rho]/\partial\rho_{mn} = \delta_{mn}$. The Jacobian matrix is thus:

$$J = (\log\rho) + I$$

where I is the identity matrix. This matrix has $(\log\rho)_{ii} + 1$ on the diagonal and $(\log\rho)_{ji}$ on the off-diagonal elements, corresponding to the matrix $(\log\rho) + I$. The Jacobian matrix of $\mathrm{Tr}(\rho\log\rho)$, computed as a matrix of partial derivatives, is $(\log\rho) + I$.

9.3.6. Differentiation with Respect to Matrices. Matrix differentiation is an extension of classical differentiation to matrices. It is used to find how a matrix-dependent function changes with variations in the matrix.

Definition 9.1. Consider a matrix A with elements A_{ij}. The derivative of a function $f(A)$ with respect to A is defined as a matrix B where $B_{ij} = \frac{\partial f}{\partial A_{ij}}$.

Remark 9.2. To find B_{ij}, we consider the change in f when A_{ij} is varied, keeping other elements constant. In quantum mechanics, the density matrix $\hat{\rho}$ is a key example. To differentiate a function $F(\hat{\rho})$ with respect to $\hat{\rho}$, we compute the partial derivative with respect to each element ρ_{ij}. Consider the von Neumann entropy $S = -k_B \text{Tr}(\hat{\rho} \log \hat{\rho})$. Differentiating this with respect to $\hat{\rho}$ involves calculating how the trace changes with slight changes in $\hat{\rho}$. The result is $-k_B(\log \hat{\rho} + I)$.

9.3.6.1. *Limiting Procedure.* The derivative of a matrix-valued function using a limiting procedure is defined using norms. Let $F : \mathbb{R}^{m \times n} \to \mathbb{R}$ be a function, and A an $m \times n$ matrix. The derivative $DF(A)$ of F at A is a linear map satisfying:

$$\lim_{\|H\| \to 0} \frac{\|F(A+H) - F(A) - DF(A)(H)\|}{\|H\|} = 0$$

where H is a matrix of the same size as A, and $\|H\|$ is the norm of H. $DF(A)$ is the best linear approximation of F at A. The norm $\|H\|$ is typically the Frobenius norm, defined as $\|A\|_F = \sqrt{\sum_{i,j} A_{ij}^2}$. If such a linear map $DF(A)$ exists, then F is differentiable at A.

9.3.6.2. *Example (Derivative of a Matrix-Valued Function).* We calculate the derivative of $F(A) = \text{Tr}(AB)$ with respect to the matrix A using the limiting procedure. Consider a function $F(A) = \text{Tr}(AB)$, where A and B are matrices of the same size. The derivative $DF(A)$ is found via:

$$\lim_{\|H\| \to 0} \frac{\|\text{Tr}((A+H)B) - \text{Tr}(AB) - DF(A)(H)\|}{\|H\|} = 0.$$

Expanding $\text{Tr}((A+H)B)$:

$$\text{Tr}((A+H)B) = \text{Tr}(AB) + \text{Tr}(HB)$$

Thus, the limit becomes:

$$\frac{\|\text{Tr}(HB) - DF(A)(H)\|}{\|H\|}.$$

The linear map $DF(A)$ satisfying the limit is:

$$DF(A)(H) = \text{Tr}(HB).$$

The derivative of $F(A) = \text{Tr}(AB)$ with respect to A is the linear map $DF(A)(H) = \text{Tr}(HB)$.

9.3.6.3. *Detailed Examples of Matrix Differentiation.*

Example 1: Derivative of $F(A) = A^2$. With a function $F(A) = A^2$, we find $DF(A)(H)$ such that:

$$\lim_{\|H\|\to 0} \frac{\|(A+H)^2 - A^2 - DF(A)(H)\|}{\|H\|} = 0.$$

Expanding the square:

$$(A+H)^2 = A^2 + AH + HA + H^2$$

Leads to $DF(A)(H) = AH + HA$. In quantum mechanics $AH + HA$ is the anticommutator $\{A, H\}$ of A and H. The derivative $DF(A)$ is therefore the anticommutation superoperator $\{A, \cdot\}$.

Example 2: Derivative of $F(A) = A^{-1}$ (Matrix Inverse). Given a function: $F(A) = A^{-1}$, our task is to find $DF(A)(H)$ such that:

$$\lim_{\|H\|\to 0} \frac{\|(A+H)^{-1} - A^{-1} - DF(A)(H)\|}{\|H\|} = 0.$$

This is done by invoking the approximation:

$$(A+H)^{-1} \approx A^{-1} - A^{-1}HA^{-1} + O(H^2).$$

From which we can read off the result:

$$DF(A)(H) = -A^{-1}HA^{-1}.$$

Note: the approximation for $(A+H)^{-1}$ in the context of the derivative of $F(A) = A^{-1}$ is justified using the Neumann series. The Neumann series expression for a matrix inverse is:

$$(I - M)^{-1} = I + M + M^2 + \cdots$$

To obtain an expression for $(A+H)^{-1}$, we factor out A^{-1}:

$$(A+H)^{-1} = (I + A^{-1}H)^{-1}A^{-1}.$$

Applying the Neumann series for small H:

$$(I + A^{-1}H)^{-1} \approx I - A^{-1}H.$$

Substituting into the expression for $(A+H)^{-1}$:

$$(A+H)^{-1} \approx A^{-1} - A^{-1}HA^{-1}.$$

The derivative is then:

$$DF(A)(H) = -A^{-1}HA^{-1}.$$

Example 3: Derivative of $F(A) = \mathrm{Tr}(e^A)$ (Matrix Exponential). For the function $F(A) = \mathrm{Tr}(e^A)$, we find $DF(A)(H)$ such that:

$$\lim_{\|H\|\to 0} \frac{\|\mathrm{Tr}(e^{A+H}) - \mathrm{Tr}(e^A) - DF(A)(H)\|}{\|H\|} = 0.$$

This is accomplished by invoking the approximation $e^{A+H} \approx e^A + e^AH + O(H^2)$. The result is $DF(A)(H) = \mathrm{Tr}(He^A)$.

Note: the approximation $e^{A+H} \approx e^A + e^A H + O(H^2)$ is justified using the Baker-Campbell-Hausdorff formula, or the the Zassenhaus formula. The latter provides a rigorous expansion of e^{A+H} for the derivative of $F(A) = \mathrm{Tr}(e^A)$:

$$e^{A+H} = e^A e^H e^{-\frac{1}{2}[A,H]} \dots$$

For small H, the expansion simplifies to $e^{A+H} \approx e^A(I + H)$. Thus, $e^{A+H} \approx e^A + e^A H$. (This approximation can also be justified by the Suzuki-Trotter formula.) The derivative $DF(A)(H)$ is then $DF(A)(H) = \mathrm{Tr}(He^A)$.

Example 4: Derivative of $F(A) = \log(\det(A))$ (Log Determinant). Starting from the function $F(A) = \log(\det(A))$, we find $DF(A)(H)$ such that:

$$\lim_{\|H\|\to 0} \frac{\| \log(\det(A+H)) - \log(\det(A)) - DF(A)(H)\|}{\|H\|} = 0.$$

We do this by invoking the approximation:

$$\log(\det(A+H)) \approx \log(\det(A)) + \mathrm{Tr}(A^{-1}H),$$

which leads to the final result:

$$DF(A)(H) = \mathrm{Tr}(A^{-1}H).$$

The log determinant approximation of $F(A) = \log(\det(A))$ we invoked is based on a first-order Taylor expansion. We consider the determinant as product of eigenvalues:

$$\det(A) = \prod_i \lambda_i$$

Taking the log

$$\log(\det(A)) = \sum_i \log(\lambda_i)$$

For a small perturbation H, the eigenvalues change to $\lambda_i + \delta\lambda_i$:

$$\log(\det(A+H)) = \sum_i \log(\lambda_i + \delta\lambda_i)$$

Next, we perform a first-order Taylor expansion:

$$\log(\lambda_i + \delta\lambda_i) = \log \lambda_i (1 + \delta\lambda_i/\lambda_i) = \log \lambda_i + \log(1 + \delta\lambda_i/\lambda_i) \approx \log(\lambda_i) + \frac{\delta\lambda_i}{\lambda_i}$$

Next we sum over eigenvalues:

$$\log(\det(A+H)) \approx \sum_i \log(\lambda_i) + \sum_i \frac{\delta\lambda_i}{\lambda_i}.$$

The trace representation is:

$$\sum_i \frac{\delta\lambda_i}{\lambda_i} \approx \mathrm{Tr}(A^{-1}H).$$

Finally,

$$\log(\det(A+H)) \approx \log(\det(A)) + \mathrm{Tr}(A^{-1}H).$$

Note: the step $\sum_i \frac{\delta\lambda_i}{\lambda_i} \approx \mathrm{Tr}(A^{-1}H)$ follows from the approximation for the change in eigenvalues due to a perturbation. This is based on first-order perturbation theory. Starting from the eigenvalue problem where, for $Au_i = \lambda_i u_i$, u_i is the eigenvector, and λ_i is the eigenvalue of a Hermitian matrix A. Adding a small perturbation H to A results in a new matrix $A + H$. The perturbed eigenvalues and eigenvectors are $\lambda_i' = \lambda_i + \delta\lambda_i$ and $u_i' = u_i + \delta u_i$. We then have the perturbed eigenvalue equation:

$$(A + H)(u_i + \delta u_i) \approx (\lambda_i + \delta\lambda_i)(u_i + \delta u_i).$$

Invoking $Au_i = \lambda_i u_i$ leaves us with

$$A\delta u_i + H(u_i + \delta u_i) \approx \lambda_i \delta u_i + \delta\lambda_i(u_i + \delta u_i).$$

We want to solve for $\delta\lambda_i$. To lowest order in u_i, we find $Hu_i \approx \delta\lambda_i u_i$. Projecting onto u_i leads to $\langle u_i, Hu_i\rangle \approx \delta\lambda_i \langle u_i, u_i\rangle$. Solving for $\delta\lambda_i$ gives $\delta\lambda_i \approx \frac{\langle u_i, Hu_i\rangle}{\langle u_i, u_i\rangle}$.

Example 5: Derivative of $F(A) = \|A\|_F^2$ (Frobenius Norm Squared). When $F(A) = \|A\|_F^2$, finding $DF(A)(H)$ such that:

$$\lim_{\|H\|\to 0} \frac{\|\|A + H\|_F^2 - \|A\|_F^2 - DF(A)(H)\|}{\|H\|} = 0.$$

This follows from direct application of the definition of the Frobenius norm:

$$\|A+H\|_F^2 = \mathrm{Tr}[(A+H)^*(A+H)] = \mathrm{Tr}[A^*A+A^*H+H^*A+H^*H] = \|A\|_F^2+2\mathrm{Tr}(A^TH)+\|H\|_F^2$$

which leads to

$$DF(A)(H) = 2\mathrm{Tr}(A^TH).$$

Example 6: Maximizing Entropy to Find the Canonical Density Matrix. In quantum statistical mechanics, the canonical density matrix is derived by maximizing the von Neumann entropy subject to normalization and energy constraints.

The von Neumann Entropy is: $S = -k_B \mathrm{Tr}(\hat\rho \log \hat\rho)$. The constraints are: 1) Normalization: $\mathrm{Tr}(\hat\rho) = 1$. 2) Average Energy: $\mathrm{Tr}(\hat\rho \hat H) = \langle E\rangle$. Introduce Lagrange multipliers α and β:

$$\mathcal{L}(\hat\rho) = -k_B \mathrm{Tr}(\hat\rho \log \hat\rho) - \alpha(\mathrm{Tr}(\hat\rho) - 1) - \beta(\mathrm{Tr}(\hat\rho \hat H) - \langle E\rangle)$$

Let $\delta\hat\rho$ be a small variation in $\hat\rho$. We expand each term in $\mathcal{L}(\hat\rho + \delta\hat\rho)$: The entropy term is:

$$-k_B \mathrm{Tr}((\hat\rho + \delta\hat\rho)\log(\hat\rho + \delta\hat\rho))$$

Using the series expansion for the logarithm:

$$\log(\hat\rho + \delta\hat\rho) \approx \log(\hat\rho) + \hat\rho^{-1}\delta\hat\rho$$

The expanded entropy term becomes:

$$-k_B \mathrm{Tr}\left((\hat\rho + \delta\hat\rho)(\log(\hat\rho) + \hat\rho^{-1}\delta\hat\rho)\right)$$

Simplifying, we have:

$$-k_B \mathrm{Tr}(\hat\rho \log \hat\rho) - k_B \mathrm{Tr}(\delta\hat\rho \log \hat\rho) - k_B \mathrm{Tr}(\hat\rho\hat\rho^{-1}\delta\hat\rho) - k_B \mathrm{Tr}(\delta\hat\rho\hat\rho^{-1}\delta\hat\rho)$$

The normalization term is:

$$-\alpha(\mathrm{Tr}(\hat{\rho}+\delta\hat{\rho})-1).$$

Expanding the trace:

$$-\alpha(\mathrm{Tr}(\hat{\rho})+\mathrm{Tr}(\delta\hat{\rho})-1).$$

Invoking the energy constraint:

$$-\beta(\mathrm{Tr}((\hat{\rho}+\delta\hat{\rho})\hat{H})-\langle E\rangle).$$

Expanding the trace term:

$$-\beta(\mathrm{Tr}(\hat{\rho}\hat{H})+\mathrm{Tr}(\delta\hat{\rho}\hat{H})-\langle E\rangle).$$

Combining these terms, we get:

$$\begin{aligned}\mathcal{L}(\hat{\rho}+\delta\hat{\rho}) &= -k_B\mathrm{Tr}(\hat{\rho}\log\hat{\rho})-k_B\mathrm{Tr}(\delta\hat{\rho}\log\hat{\rho})-k_B\mathrm{Tr}(\delta\hat{\rho})-k_B\mathrm{Tr}(\delta\hat{\rho}\hat{\rho}^{-1}\delta\hat{\rho})\\ &\quad -\alpha(\mathrm{Tr}(\hat{\rho})+\mathrm{Tr}(\delta\hat{\rho})-1)-\beta(\mathrm{Tr}(\hat{\rho}\hat{H})+\mathrm{Tr}(\delta\hat{\rho}\hat{H})-\langle E\rangle)\end{aligned}$$

The linear map $D\mathcal{L}(\hat{\rho})$ applied to $\delta\hat{\rho}$ is:

$$D\mathcal{L}(\hat{\rho})(\delta\hat{\rho})=\mathrm{Tr}\left(\left(-k_B(\log\hat{\rho}+I)-\alpha I-\beta\hat{H}\right)\delta\hat{\rho}\right).$$

The condition for $\mathcal{L}$ to be stationary under the variation $\delta\hat{\rho}$ is:

$$\lim_{\|\delta\hat{\rho}\|\to 0}\frac{\|\mathcal{L}(\hat{\rho}+\delta\hat{\rho})-\mathcal{L}(\hat{\rho})-D\mathcal{L}(\hat{\rho})(\delta\hat{\rho})\|}{\|\delta\hat{\rho}\|}=0$$

Example 7: Grand Canonical Density Operator. In quantum statistical mechanics, the grand canonical ensemble is used to describe systems in thermal equilibrium with a reservoir of energy and particles. The grand canonical density operator $\hat{\rho}$ is determined by maximizing the entropy subject to certain constraints. The entropy in quantum mechanics is given by the von Neumann entropy:

$$S=-k_B\mathrm{Tr}(\hat{\rho}\log\hat{\rho})$$

where k_B is the Boltzmann constant. The constraints are:

1. Normalization: $\mathrm{Tr}(\hat{\rho})=1$.
2. Fixed average energy: $\langle\hat{H}\rangle=\mathrm{Tr}(\hat{\rho}\hat{H})$, where $\hat{H}$ is the Hamiltonian.
3. Fixed average number of particles: $\langle\hat{N}\rangle=\mathrm{Tr}(\hat{\rho}\hat{N})$, where $\hat{N}$ is the particle number operator.

The Lagrange function $\mathcal{L}$ incorporating these constraints with Lagrange multipliers α, β, and γ is:

$$\mathcal{L}(\hat{\rho})=-k_B\mathrm{Tr}(\hat{\rho}\log\hat{\rho})-\alpha(\mathrm{Tr}(\hat{\rho})-1)-\beta(\mathrm{Tr}(\hat{\rho}\hat{H})-\langle\hat{H}\rangle)-\gamma(\mathrm{Tr}(\hat{\rho}\hat{N})-\langle\hat{N}\rangle).$$

To find the extremum of $\mathcal{L}$, we compute the derivative of $\mathcal{L}$ with respect to the matrix $\hat{\rho}$ and set it to zero:

$$\frac{\partial\mathcal{L}}{\partial\hat{\rho}}=0.$$

See Section 9.3.5 for the derivative of $\mathrm{Tr}(\hat{\rho}\log\hat{\rho})$ and similar trace expressions. Expanding this, we get:

$$-k_B(\log\hat{\rho}+I)-\alpha I-\beta\hat{H}-\gamma\hat{N}=0$$

we rearrange and divide by $-k_B$:

$$\log\hat{\rho}+I=-\frac{\alpha}{k_B}I-\frac{\beta}{k_B}\hat{H}-\frac{\gamma}{k_B}\hat{N}.$$

Exponentiating both sides gives:

$$\hat{\rho}\cdot e\cdot I=\exp\left(-\frac{\alpha}{k_B}I-\frac{\beta}{k_B}\hat{H}-\frac{\gamma}{k_B}\hat{N}\right).$$

Introducing the normalization condition with partition function Z:

$$\hat{\rho}=\frac{1}{Z}\exp\left(-\frac{\alpha}{k_B}I-\frac{\beta}{k_B}\hat{H}-\frac{\gamma}{k_B}\hat{N}\right)$$

The negative signs in the exponential are absorbed into the Lagrange multipliers for conventional representation:

$$\hat{\rho}=\frac{1}{Z}\exp\left(\frac{\alpha}{k_B}I+\frac{\beta}{k_B}\hat{H}+\frac{\gamma}{k_B}\hat{N}\right).$$

This representation ensures the correct handling of negative signs and maintains the physical requirement of normalization.

The Lagrange multipliers α, β, and γ are determined by substituting $\hat{\rho}$ back into the constraints. Typically, β is associated with the inverse temperature $\frac{1}{k_BT}$ and γ with the chemical potential μ. Thus, the grand canonical density operator in quantum statistical mechanics is derived by maximizing the entropy under constraints of normalization, fixed average energy, and fixed average number of particles.

9.3.7. The Fréchet Derivative. The Fréchet derivative is an extension of the classical derivative concept, tailored for operators between Banach spaces. Named after Maurice Fréchet, it plays a vital role in functional analysis and is essential for understanding systems within infinite-dimensional spaces. In simple terms, the derivative in single-variable calculus represents the slope of the tangent to a function's graph at a point, indicating how the function value changes with a small change in input. The Fréchet derivative expands this idea to functions with functions as inputs or outputs, essential for dealing with changes in the shape or behavior of function outputs in response to perturbations.

Definition 9.3 (Fréchet derivative)**.** Given Banach spaces X and Y, a function $F : X \to Y$ is said to be Fréchet differentiable at a point $x \in X$ if there exists a bounded linear operator $A : X \to Y$ such that:

$$\lim_{h\to 0}\frac{\|F(x+h)-F(x)-Ah\|_Y}{\|h\|_X}=0.$$

Here h is a small perturbation in x, and Ah represents the linear approximation of the change in F at x. The operator A is the Fréchet derivative of F at x, denoted as $F'(x)$.

Consider F as a physical system where x represents a set of conditions. The Fréchet derivative, $F'(x)$, then describes the system's response to infinitesimal variations in these conditions.

Examples in Physics. 1. **Quantum Mechanics:** Operators in quantum mechanics symbolize physical observables. The Fréchet derivative aids in understanding how these observables change under transformations.

2. **Field Theory:** In classical field theory, fields are functions over space-time. The Fréchet derivative is instrumental in analyzing field responses to perturbations, crucial for comprehending aspects like wave propagation and interactions.

9.3.7.1. *Worked Examples of Fréchet Derivative Computations.*

Example 1: Linear Map. Consider a linear map $L : \mathbb{R}^n \to \mathbb{R}^m$ defined by a matrix A. The Fréchet derivative of L at any point is the map itself.

Computation:

Given $L(x) = Ax$, we need to find a linear map A' such that:

$$\lim_{h\to 0} \frac{\|L(x+h) - L(x) - A'h\|}{\|h\|} = 0.$$

Since L is linear, $L(x+h) - L(x) = Ah$. Thus, we choose $A' = A$. The limit becomes:

$$\lim_{h\to 0} \frac{\|Ah - Ah\|}{\|h\|} = \lim_{h\to 0} \frac{\|0\|}{\|h\|} = 0.$$

Hence, the Fréchet derivative of L at any point is A.

Example 2: Nonlinear Map. Consider the nonlinear function $F : \mathbb{R}^2 \to \mathbb{R}^2$ defined by $F(x, y) = (x^2, e^y)$.

Computation:

The Fréchet derivative of F at a point (x_0, y_0) is a linear map A such that:

$$\lim_{(h,k)\to(0,0)} \frac{\|F(x_0+h, y_0+k) - F(x_0, y_0) - A(h,k)\|}{\|(h,k)\|} = 0.$$

Expanding F, we have:

$$F(x_0+h, y_0+k) - F(x_0, y_0) = (x_0^2 + 2x_0h + h^2 - x_0^2, e^{y_0+k} - e^{y_0}).$$

We propose $A(h, k) = (2x_0h, e^{y_0}k)$. Then,

$$\lim_{(h,k)\to(0,0)} \frac{\|(h^2, e^{y_0+k} - e^{y_0} - e^{y_0}k)\|}{\|(h,k)\|} = 0.$$

Since the terms h^2 and $e^{y_0+k} - e^{y_0} - e^{y_0}k$ are of higher order compared to $\|h\|$ and $\|k\|$, the limit goes to zero. Therefore, the Fréchet derivative of F at (x_0, y_0) is given by the Jacobian matrix:

$$F'(x_0, y_0) = \begin{pmatrix} 2x_0 & 0 \\ 0 & e^{y_0} \end{pmatrix}.$$

Example 3: Quadratic Function. Consider a quadratic function $Q : \mathbb{R} \to \mathbb{R}$ defined by $Q(x) = x^2$.

Computation:

The Fréchet derivative of Q at a point x_0 is a linear map A such that:

$$\lim_{h \to 0} \frac{|Q(x_0 + h) - Q(x_0) - A(h)|}{|h|} = 0.$$

Expanding Q, we have $Q(x_0 + h) - Q(x_0) = x_0^2 + 2x_0h + h^2 - x_0^2 = 2x_0h + h^2$. We propose $A(h) = 2x_0h$. Then,

$$\lim_{h \to 0} \frac{|2x_0h + h^2 - 2x_0h|}{|h|} = \lim_{h \to 0} \frac{|h^2|}{|h|} = \lim_{h \to 0} |h| = 0.$$

Thus, the Fréchet derivative of Q at x_0 is the function $2x_0$.

Example 4: Exponential Function. Consider the exponential function $E : \mathbb{R} \to \mathbb{R}$ defined by $E(x) = e^x$.

Computation:

The Fréchet derivative of E at a point x_0 is a linear map A such that:

$$\lim_{h \to 0} \frac{|E(x_0 + h) - E(x_0) - A(h)|}{|h|} = 0.$$

Since $E(x_0 + h) = e^{x_0}e^h$, the expression becomes $e^{x_0}e^h - e^{x_0}$. We propose $A(h) = e^{x_0}h$. Then,

$$\lim_{h \to 0} \frac{|e^{x_0}e^h - e^{x_0} - e^{x_0}h|}{|h|} = e^{x_0} \lim_{h \to 0} \frac{|e^h - 1 - h|}{|h|} = 0.$$

As $h \to 0$, $e^h - 1 - h$ is of higher order than h, making the limit zero. Hence, the Fréchet derivative of E at x_0 is e^{x_0}.

Example 5: Polynomial Function. Consider a polynomial function $P : \mathbb{R} \to \mathbb{R}$ defined by $P(x) = a_0 + a_1x + a_2x^2 + \ldots + a_nx^n$.

Computation:

The Fréchet derivative of P at a point x_0 is a linear map A such that:

$$\lim_{h \to 0} \frac{|P(x_0 + h) - P(x_0) - A(h)|}{|h|} = 0.$$

Expanding P and using the binomial theorem, we get $P(x_0 + h) = \sum_{k=0}^{n} a_k(x_0 + h)^k$.

We propose $A(h) = \sum_{k=1}^{n} ka_kx_0^{k-1}h$. Then,

$$\lim_{h \to 0} \frac{|\sum_{k=0}^{n} a_k(x_0 + h)^k - P(x_0) - \sum_{k=1}^{n} ka_kx_0^{k-1}h|}{|h|} = 0.$$

The terms of higher order in h become negligible, and the limit goes to zero. Therefore, the Fréchet derivative of P at x_0 is the polynomial $\sum_{k=1}^{n} ka_kx_0^{k-1}$.

Example 6: Sine Function. Consider the sine function $S : \mathbb{R} \to \mathbb{R}$ defined by $S(x) = \sin(x)$.

Computation:

The Fréchet derivative of S at a point x_0 is a linear map A such that:

$$\lim_{h \to 0} \frac{|\sin(x_0 + h) - \sin(x_0) - A(h)|}{|h|} = 0.$$

Using the sum formula for sine, $\sin(x_0 + h) = \sin(x_0)\cos(h) + \cos(x_0)\sin(h)$. We propose $A(h) = \cos(x_0)h$. Then,

$$\lim_{h \to 0} \frac{|\sin(x_0)\cos(h) + \cos(x_0)\sin(h) - \sin(x_0) - \cos(x_0)h|}{|h|} = 0.$$

As $h \to 0$, the terms involving higher powers of h become negligible. Hence, the Fréchet derivative of S at x_0 is $\cos(x_0)$.

Example 7: Functional Derivative in Field Theory. Consider a functional S in field theory, defined over a field $\phi(x)$ as $S[\phi] = \int f(\phi(x), \nabla\phi(x), x)\, dx$, where f is a function of the field ϕ, its gradient $\nabla\phi$, and position x.

Computation:

The Fréchet derivative, or functional derivative, of S with respect to ϕ at ϕ_0, denoted $\frac{\delta S}{\delta \phi}$, is defined such that for a small variation $\epsilon\eta(x)$ in ϕ, where η is a test function and ϵ is a small parameter, we have:

$$\frac{\delta S}{\delta \phi(x)} = \lim_{\epsilon \to 0} \frac{S[\phi_0 + \epsilon\eta] - S[\phi_0]}{\epsilon}.$$

Expanding and simplifying the functional using the fundamental lemma of calculus of variations, we obtain:

$$\frac{\delta S}{\delta \phi(x)} = \frac{\partial f}{\partial \phi} - \nabla \cdot \left(\frac{\partial f}{\partial \nabla \phi} \right).$$

Example 8: Functional Derivative in Quantum Mechanics. Consider a functional in quantum mechanics, $F[\psi] = \int |\nabla\psi(x)|^2\, dx$, where $\psi(x)$ is a wave function.

Computation:

The Fréchet derivative of F with respect to ψ at ψ_0, denoted $\frac{\delta F}{\delta \psi}$, is defined similarly:

$$\frac{\delta F}{\delta \psi(x)} = \lim_{\epsilon \to 0} \frac{F[\psi_0 + \epsilon\eta] - F[\psi_0]}{\epsilon}.$$

Expanding F and simplifying, we find:

$$\frac{\delta F}{\delta \psi(x)} = -\nabla^2\psi(x).$$

This represents the second spatial derivative of the wave function, indicating how the kinetic energy part of the quantum Hamiltonian operator varies with respect to changes in the wave function.

Example 9: Functional in Elasticity Theory. Consider a functional J in elasticity theory representing the total potential energy of an elastic body, defined as $J[u] = \int_\Omega \left(\frac{1}{2} A\nabla u \cdot \nabla u - fu\right) dx$, where $u(x)$ is the displacement field, A is a positive-definite matrix representing material properties, f is a body force, and Ω is the region occupied by the body.

Computation:

The Fréchet derivative of J with respect to u at u_0, denoted $\frac{\delta J}{\delta u}$, is defined as:

$$\frac{\delta J}{\delta u(x)} = \lim_{\epsilon \to 0} \frac{J[u_0 + \epsilon v] - J[u_0]}{\epsilon}.$$

For a variation $\epsilon v(x)$ in u, where v is a test function, expanding J and applying the limit, we obtain:

$$\frac{\delta J}{\delta u(x)} = -A\nabla^2 u(x) - f(x).$$

This represents the Euler-Lagrange equation in elasticity theory, connecting the material response to external forces.

Example 10: Operator in Heat Equation. Consider an operator K associated with the heat equation, defined as $K[\theta] = \int_0^T \int_\Omega \left(\frac{\partial \theta}{\partial t} - \alpha \nabla^2 \theta\right)^2 dx\, dt$, where $\theta(x, t)$ is the temperature distribution, α is the thermal diffusivity, T is the time interval, and Ω is the spatial domain.

Computation:

The Fréchet derivative of K with respect to θ at θ_0, denoted $\frac{\delta K}{\delta \theta}$, is defined as:

$$\frac{\delta K}{\delta \theta(x, t)} = \lim_{\epsilon \to 0} \frac{K[\theta_0 + \epsilon \phi] - K[\theta_0]}{\epsilon}.$$

For a small perturbation $\epsilon \phi(x, t)$ in θ, where ϕ is a test function, expanding K and taking the limit, we find:

$$\frac{\delta K}{\delta \theta(x, t)} = 2\left(\frac{\partial \theta}{\partial t} - \alpha \nabla^2 \theta\right).$$

This derivative indicates how the integral of the squared residual in the heat equation changes with respect to small variations in temperature distribution.

Example 11: Fréchet Derivative in Optimal Control Theory. Consider an optimal control problem where the objective is to minimize a cost functional $J[u, y] = \int_0^T L(y(t), u(t), t)\, dt$ subject to a differential equation $\dot{y}(t) = f(y(t), u(t), t)$ with initial condition $y(0) = y_0$. Here, $y(t)$ is the state variable, $u(t)$ is the control variable, and L is a given Lagrangian.

Computation:

To find the Fréchet derivative of J with respect to u, we consider variations $\delta u(t)$ in the control variable. The corresponding variation in the state variable is denoted $\delta y(t)$.

The Fréchet derivative $\frac{\delta J}{\delta u}$ is defined as:

$$\frac{\delta J}{\delta u(t)} = \lim_{\epsilon \to 0} \frac{J[u + \epsilon \delta u, y + \epsilon \delta y] - J[u, y]}{\epsilon}.$$

Applying the chain rule and using the Euler-Lagrange equation, we obtain an expression involving partial derivatives of L and f, which leads to the necessary conditions for optimal control, known as the Pontryagin's Maximum Principle.

Example 12: Fréchet Derivative in Nonlinear Schrödinger Equation. Consider the nonlinear Schrödinger equation given by $i\frac{\partial\psi}{\partial t} + \Delta\psi + |\psi|^2\psi = 0$ in a domain Ω with appropriate boundary conditions. We define a functional $F[\psi] = \int_\Omega \left(|\nabla\psi|^2 - \frac{1}{2}|\psi|^4\right) dx$, where ψ is a complex-valued function.

Computation:

The Fréchet derivative of F with respect to ψ gives the variational formulation of the nonlinear Schrödinger equation. For a variation $\epsilon\phi$ in ψ, where ϕ is a test function, we compute:

$$\frac{\delta F}{\delta\psi} = \lim_{\epsilon\to 0} \frac{F[\psi + \epsilon\phi] - F[\psi]}{\epsilon}.$$

Expanding this and applying the limit, we obtain the weak form of the nonlinear Schrödinger equation, which is essential in understanding soliton solutions and stability analysis in nonlinear wave mechanics.

9.3.8. Green's Functions for Linear Inhomogeneous ODEs. Suppose we have a linear differential operator $\hat{L}$ operating on a function space. Define the Green's function as the solution to:

$$\hat{L}[G(x,\xi)] = \delta(x-\xi)$$

Then,

$$\hat{L}[y(x)] = f(x) = \int f(\xi)\underbrace{\delta(x-\xi)}_{\hat{L}[G(x,\xi)]}d\xi = \hat{L}[\int f(\xi)G(x,\xi)d\xi].$$

Thus, we have proved that $\hat{L}[y(x)] = \hat{L}[\int f(\xi)G(x,\xi)d\xi]$. If we can find an inverse of the operator $\hat{L}$, i.e. $\hat{L}^{-1}\hat{L} = \mathbf{1}$, then this implies that

$$y(x) = \int f(\xi)G(x,\xi)d\xi.$$

9.4. Matrix Logarithmic Property

The matrix logarithmic property is

$$\log(AB) = \log(A) + \log(B),$$

where A and B are matrices of suitable dimensions. This obviously does not hold in most situations. However, under certain restrictions on A and B, the result can hold.

9.4.1. Case 1: Commuting Matrices.

Theorem 9.4. *The relationship* $\log(AB) = \log(A) + \log(B)$ *holds under the conditions:*

(1) $AB = BA$ *(Commutativity).*

(2) There exists a unitary matrix U such that $A = UD_AU^\dagger$ and $B = UD_BU^\dagger$, where D_A and D_B are diagonal matrices (Simultaneous Diagonalizability).

Proof. Given $A = UD_AU^\dagger$ and $B = UD_BU^\dagger$, we can write the product AB as:

$$AB = UD_AU^\dagger UD_BU^\dagger = UD_AD_BU^\dagger$$

The logarithm of a diagonal matrix is a diagonal matrix of the logarithms of its entries. Hence, for D_A and D_B:

$$\log(D_A) = \mathrm{diag}(\log(\lambda_{A,1}), \log(\lambda_{A,2}), \ldots)$$
$$\log(D_B) = \mathrm{diag}(\log(\lambda_{B,1}), \log(\lambda_{B,2}), \ldots)$$

where $\lambda_{A,i}$ and $\lambda_{B,i}$ are the eigenvalues of A and B, respectively. Since D_A and D_B are diagonal and commute, D_AD_B is also diagonal. The logarithm of D_AD_B is:

$$\log(D_AD_B) = \mathrm{diag}(\log(\lambda_{A,1}\lambda_{B,1}), \log(\lambda_{A,2}\lambda_{B,2}), \ldots)$$

Using the logarithmic property for real numbers:

$$\log(\lambda_{A,i}\lambda_{B,i}) = \log(\lambda_{A,i}) + \log(\lambda_{B,i})$$

Thus:

$$\log(D_AD_B) = \log(D_A) + \log(D_B)$$

Finally, applying the unitary transformation U, we have:

$$\begin{aligned}\log(AB) = \log(UD_AD_BU^\dagger) &= U\log(D_AD_B)U^\dagger \\ = U(\log(D_A) + \log(D_B))U^\dagger &= \log(UD_AU^\dagger) + \log(UD_BU^\dagger) \\ &= \log(A) + \log(B)\end{aligned}$$

Thus, under the assumptions of commutativity and simultaneous diagonalizability, $\log(AB) = \log(A) + \log(B)$ for matrices A and B. ☐

9.4.2. Case 2: Small B.

Theorem 9.5. *The relationship* $\log(AB) \approx \log(A) + \log(B)$ *holds under the conditions:*

- *A is an invertible matrix.*
- *B is a matrix close to the identity, i.e., $\|B - I\|$ is sufficiently small.*

Proof. If a matrix B is close to I, then $\log(B) \approx \log(I+(B-I)) \approx B-I$. Now, considering AB as the product of A and a matrix close to I, we can use the linear approximation to write:

$$\begin{aligned}\log(AB) &= \log(A(I + (B - I))) = \log(A + A(B - I))) \\ &= \log(A) + \underbrace{D\log(A)}_{A^{-1}} \cdot A(B - I) + o(\|A(B - I)\|) \approx \log(A) + B - I\end{aligned}$$

Comparing this with the expansion of $\log(B)$, we have:

$$\log(AB) \approx \log(A) + \log(B)$$

Thus, for B close to I, the matrix logarithmic property $\log(AB) \approx \log(A) + \log(B)$ holds.

□

9.5. Volume of a Sphere in n Dimensions

Let $\Omega_n(R)$ be the volume of the n-dimensional sphere of radius R:

$$\Omega_n(R) = \int_{|\vec{x}|\leq R} \mathrm{d}^n x.$$

By analogy with the 3D case, $V(R) = \frac{4}{3}\pi R^3$, it is reasonable to assume that in n dimensions we will get $\Omega_n(R) = C_n R^n$. In that case, the surface $S_n(R)$ of the n-dimensional sphere will be given by

$$S_n(R) = \frac{\mathrm{d}\Omega_n(R)}{\mathrm{d}R} = nC_n R^{n-1}.$$

The constant C_n can be evaluated starting from the identity

$$\begin{aligned}\pi^{n/2} &= \int_{-\infty}^{\infty} \mathrm{d}x_1 \cdots \int_{-\infty}^{\infty} \mathrm{d}x_n \exp[-(x_1^2 + \cdots + x_n^2)] \\ &= \int_0^{\infty} \mathrm{d}R\, S_n(R) \exp(-R^2) = nC_n \int_0^{\infty} \mathrm{d}R\, R^{n-1} \exp(-R^2).\end{aligned}$$

We recall the integral representation of Euler's gamma function $\Gamma(z)$, for $\Re(z) > 0$

$$\Gamma(z) = \int_0^{\infty} t^{z-1} e^{-t}\, \mathrm{d}t.$$

Setting $t = R^2$, $\mathrm{d}t = \mathrm{d}(R^2) = 2R\mathrm{d}R$, so that $\mathrm{d}R = \frac{\mathrm{d}t}{2R} = \frac{\mathrm{d}t}{2\sqrt{t}}$, we find

$$\int_0^{\infty} R^{n-1} \exp(-R^2)\, \mathrm{d}R = \int_0^{\infty} t^{(n-1)/2} e^{-t} \frac{\mathrm{d}t}{2\sqrt{t}} = \frac{1}{2}\int_0^{\infty} t^{n/2-1} e^{-t}\, \mathrm{d}t = \frac{1}{2}\Gamma(n/2)$$

and then, eventually:

$$C_n = \frac{2\pi^{n/2}}{n\Gamma(n/2)}$$

which leads to

$$\boxed{\Omega_n(R) = \frac{2\pi^{n/2}}{n\Gamma(n/2)} R^n.}$$

9.6. The Dirac Delta Function

The Dirac delta function, denoted as $\delta(x)$, is a fundamental concept in mathematics and engineering, particularly in the fields of signal processing and physics. It is not a function in the traditional sense, but rather a distribution or generalized function that encapsulates an idealized point mass or point charge.

Properties of the Dirac Delta Function. The one dimensional Dirac delta function, denoted by $\delta(x)$, is a distribution with the following defining property, known as the sifting property:

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)\,dx = f(a),$$

where $f(x)$ is a test function that is continuous at $x = a$.

In multiple dimensions, for $\mathbf{x} \in \mathbb{R}^n$ and $\mathbf{a} \in \mathbb{R}^n$, the Dirac delta is defined similarly by:

$$\int_{\mathbb{R}^n} f(\mathbf{x})\delta(\mathbf{x}-\mathbf{a})\,d\mathbf{x} = f(\mathbf{a})$$

Sifting Property. For any continuous function $f(x)$ and a real number a:

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)\,dx = f(a).$$

Proof:

$$\begin{aligned}\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} f(x)\frac{1}{\epsilon\pi}\frac{\sin^2(\frac{x-a}{\epsilon})}{(x-a)^2}\,dx &= \lim_{\epsilon\to 0}\int_{a-\epsilon}^{a+\epsilon} f(x)\frac{1}{\epsilon\pi}\frac{\sin^2(\frac{x-a}{\epsilon})}{(x-a)^2}\,dx \\ &= \lim_{\epsilon\to 0} f(a)\int_{a-\epsilon}^{a+\epsilon}\frac{1}{\epsilon\pi}\frac{\sin^2(\frac{x-a}{\epsilon})}{(x-a)^2}\,dx = f(a).\end{aligned}$$

Scaling Property. For a non-zero scalar α:

$$\delta(\alpha x) = \frac{1}{|\alpha|}\delta(x).$$

Proof:

$$\begin{aligned}\int_{-\infty}^{\infty} f(x)\delta(\alpha x)\,dx &= \int_{-\infty}^{\infty} f\left(\frac{u}{\alpha}\right)\delta(u)\frac{1}{|\alpha|}\,du \\ &= \frac{1}{|\alpha|}f(0) = \frac{1}{|\alpha|}\int_{-\infty}^{\infty} f(x)\delta(x)\,dx.\end{aligned}$$

Representations.

Representations. Although the Dirac delta cannot be represented as a function in the traditional sense, it can be approximated by functions that concentrate a unit mass at a point. Two common representations are:

Integral Representation as a Fourier Integral: The Dirac delta can also be represented as the Fourier transform of the constant function $f(k) = 1$. This integral representation is given by:

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}\,dk$$

This integral diverges for any finite value of x, but in the distributional sense, it converges to the Dirac delta function.

Infinite Sum Representation:

$$\delta(x) = \lim_{N\to\infty} \sum_{n=-N}^{N} e^{2\pi i n x}$$

Limit of a sequence of Gaussians:

$$\delta(x) = \lim_{\epsilon\to 0} \frac{1}{\epsilon\sqrt{\pi}} e^{-x^2/\epsilon^2}.$$

Proof:

$$\begin{aligned}\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} f(x)\frac{1}{\epsilon\sqrt{\pi}}e^{-x^2/\epsilon^2}\,dx &= \lim_{\epsilon\to 0}\int_{-\infty}^{\infty} f(0)\frac{1}{\epsilon\sqrt{\pi}}e^{-x^2/\epsilon^2}\,dx \\ &= f(0)\lim_{\epsilon\to 0}\frac{1}{\epsilon\sqrt{\pi}}\int_{-\infty}^{\infty} e^{-x^2/\epsilon^2}\,dx = f(0).\end{aligned}$$

Lorentzian Representation:

$$\delta(x) = \lim_{\epsilon\to 0} \frac{1}{\pi}\frac{\epsilon}{x^2+\epsilon^2}$$

Derivative of the Heaviside Function. The Dirac delta function is the derivative of the Heaviside step function $H(x)$:

$$\delta(x) = \frac{dH(x)}{dx}.$$

The Heaviside step function, denoted as $H(x)$, is defined as:

$$H(x) = \begin{cases} 0 & \text{if } x < 0, \\ \frac{1}{2} & \text{if } x = 0, \\ 1 & \text{if } x > 0. \end{cases}$$

Proof:

$$\int_{-\infty}^{\infty} f(x)\frac{dH(x)}{dx}\,dx = \int_{-\infty}^{\infty} f(x)\,dH(x) = f(0).$$

where the last step follows from the Stieltjes integral.

Scaling Property: Consider the integral:

$$\int_{-\infty}^{\infty} f(x)\delta(ax)\,dx$$

By substituting $u = ax$, we have $dx = \frac{du}{a}$, and the integral becomes:

$$\int_{-\infty}^{\infty} f\left(\frac{u}{a}\right)\delta(u)\frac{du}{a} = \frac{1}{|a|}f(0)$$

which implies that $\delta(ax) = \frac{1}{|a|}\delta(x)$.

Composition with a Function. For a smooth function $g(x)$ with a simple zero at x_0, i.e., $g(x_0) = 0$ and $g'(x_0) \neq 0$, the composition of the delta function with $g(x)$ is:

$$\delta(g(x)) = \frac{\delta(x - x_0)}{|g'(x_0)|}$$

Derivatives. The n-th derivative of the delta function is defined via its action on a test function $f(x)$:

$$\int_{-\infty}^{\infty} f(x)\delta^{(n)}(x-a)\,dx = (-1)^n f^{(n)}(a)$$

9.7. Solving Systems of 2 Equations and 2 Unknowns

To solve for N unknowns in N equations we can use the matrix inverse. The formula for the inverse of a 2×2 matrix is:

$$\boxed{\begin{pmatrix} a & b \\ c & d \end{pmatrix}^{-1} = \frac{1}{ad - bc}\begin{pmatrix} d & -b \\ -c & a \end{pmatrix}.}$$

The cross product $ad - bc$ is the determinant of the 2×2 matrix. Students unfamiliar with matrix inverses should check that the inverse of this 2×2 matrix $A = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$, denoted A^{-1}, satisfies the following conditions: $AA^{-1} = I$ and $A^{-1}A = I$. Here, I is the 2×2 identity matrix, $I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$.

Suppose that we need to solve:

$$\begin{aligned} An + B\sum x_i &= \sum y_i \\ A\sum x_i + B\sum x_i^2 &= \sum x_i y_i. \end{aligned}$$

This is done by rewriting it in matrix form:

$$\begin{pmatrix} n & \sum x_i \\ \sum x_i & \sum x_i^2 \end{pmatrix}\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} \sum y_i \\ \sum x_i y_i \end{pmatrix}.$$

Multiplying both sides on the left by the inverse of $\begin{pmatrix} n & \sum x_i \\ \sum x_i & \sum x_i^2 \end{pmatrix}$, we solve for A, B:

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} n & \sum x_i \\ \sum x_i & \sum x_i^2 \end{pmatrix}^{-1}\begin{pmatrix} \sum y_i \\ \sum x_i y_i \end{pmatrix}. \tag{9.5}$$

Here, the inverse of that matrix is:

$$\begin{pmatrix} n & \sum x_i \\ \sum x_i & \sum x_i^2 \end{pmatrix}^{-1} = \frac{1}{\Delta}\begin{pmatrix} \sum x_i^2 & -\sum x_i \\ -\sum x_i & n \end{pmatrix}. \tag{9.6}$$

Substitution of (9.6) into (9.5) gives the final result:

$$\boxed{\begin{pmatrix} A \\ B \end{pmatrix} = \frac{1}{\Delta}\begin{pmatrix} \sum x_i^2 \sum y_i - \sum x_i \sum x_i y_i \\ n \sum x_i y_i - \sum x_i \sum y_i \end{pmatrix}, \quad \Delta = n \sum x_i^2 - (\sum x_i)^2.}$$

9.8. Changing Variables Under the Integral Sign

We often need to change variables under the integral sign to express the probabilistic integral in terms of *known* probability densities. At the same time, we should use a convenient coordinate system where the integrals can be computed.

Suppose that we want to integrate $f(u,v)$ over a region R. Under the inverse of the transformation $u = u(x,y)$, $v = v(x,y)$ the region R becomes S and the double integral becomes

$$\boxed{\iint_R f(u,v)\,\mathrm{d}u\,\mathrm{d}v = \iint_S f(u(x,y),v(x,y)) \left| \frac{\partial(u,v)}{\partial(x,y)} \right| \mathrm{d}x\,\mathrm{d}y,}$$

where $\frac{\partial(u,v)}{\partial(x,y)}$ is the Jacobian determinant:

$$\frac{\partial(u,v)}{\partial(x,y)} \equiv \begin{Vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{Vmatrix} = \frac{\partial u}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial u}{\partial y}\frac{\partial v}{\partial x}.$$

If we look at the area elements, we see that the Jacobian plays the role of a scaling factor indicating by how much the area element is scaled in the new coordinates:

$$\mathrm{d}u\,\mathrm{d}v = \left| \frac{\partial(u,v)}{\partial(x,y)} \right| \mathrm{d}x\,\mathrm{d}y.$$

This idea extends to multi-dimensional integrals, where the Jacobian represents the scaling of the volume element, etc. To simplify the notation we may use the shorthand notation $\partial_x u = \frac{\partial u}{\partial x}$, etc. for partial derivatives.

For those who don't remember the change-of-variables formula, there is another method which does not require you to remember anything except for the rules of alternating forms. $\mathrm{d}u$ and $\mathrm{d}v$ are differential 1-forms (covector fields). The product $\mathrm{d}u\mathrm{d}v$ should instead be viewed as a "wedge product" $\mathrm{d}u \wedge \mathrm{d}v$, which is a 2-form. A 2-form $\mathrm{d}u \wedge \mathrm{d}v$ is an oriented area element spanned by the covectors $\mathrm{d}u$ and $\mathrm{d}v$. In the left hand side we replace $dudv$ by the wedge product $\mathrm{d}u \wedge \mathrm{d}v$

$$\iint_R f(u,v)\,\mathrm{d}u\,\mathrm{d}v = \iint_R f(u,v)\,\mathrm{d}u \wedge \mathrm{d}v$$

Then, viewing u and v as functions of x and y, we expand $\mathrm{d}u$ and $\mathrm{d}v$ as total differentials:

$$\mathrm{d}u(x,y) = (\partial_x u)\mathrm{d}x + (\partial_y u)\mathrm{d}y$$

and

$$\mathrm{d}v(x,y) = (\partial_x v)\mathrm{d}x + (\partial_y v)\mathrm{d}y.$$

Then we form the wedge product of $\mathrm{d}u$ and $\mathrm{d}v$:

$$\mathrm{d}u \wedge \mathrm{d}v = [(\partial_x u)\mathrm{d}x + (\partial_y u)\mathrm{d}y] \wedge [(\partial_x v)\mathrm{d}x + (\partial_y v)\mathrm{d}y]\,,$$

When distributing the product, we apply the rules of the alternating algebra: since $\mathrm{d}x \wedge \mathrm{d}y$ is an oriented area element spanned by the covectors $\mathrm{d}x$ and $\mathrm{d}y$, we have that $\mathrm{d}x \wedge \mathrm{d}y = -\mathrm{d}y \wedge \mathrm{d}x$ (sign flipped because we have an "oriented area element" and this amounts to changing from the left hand rule to the right hand rule in a cross product), $\mathrm{d}x \wedge \mathrm{d}x = 0$ and $\mathrm{d}y \wedge \mathrm{d}y = 0$ (zero because the area spanned by two collinear vectors is zero). We are left with:

$$\mathrm{d}u \wedge \mathrm{d}v = (\partial_x u)(\partial_y v)\mathrm{d}x \wedge \mathrm{d}y + (\partial_y u)(\partial_x v)\mathrm{d}y \wedge \mathrm{d}x = (\partial_x u\,\partial_y v - \partial_y u\,\partial_x v)\mathrm{d}x \wedge \mathrm{d}y.$$

You will recognize the coefficient of $\mathrm{d}x \wedge \mathrm{d}y$ on the right hand side as the Jacobian determinant $\frac{\partial(u,v)}{\partial(x,y)}$. Thus, the alternating algebra of differential forms took care of calculating the determinant for us. This works in any number of dimensions.

Let us work out an example. Suppose that we have an integral

$$\iint_R f(x,y)\,\mathrm{d}x\,\mathrm{d}y$$

and want to change from Cartesian to polar coordinates, i.e.

$$x = r\cos\theta, \qquad y = r\sin\theta.$$

The total differentials are:

$$\mathrm{d}x(r,\theta) = \partial_r x\,\mathrm{d}r + \partial_\theta x\,\mathrm{d}\theta = \cos\theta\,\mathrm{d}r - r\sin\theta\,\mathrm{d}\theta$$
$$\mathrm{d}y(r,\theta) = \partial_r y\,\mathrm{d}r + \partial_\theta y\,\mathrm{d}\theta = \sin\theta\,\mathrm{d}r + r\cos\theta\,\mathrm{d}\theta.$$

Forming the wedge product $\mathrm{d}x \wedge \mathrm{d}y$:

$$\mathrm{d}x \wedge \mathrm{d}y = [\cos\theta\,\mathrm{d}r - r\sin\theta\,\mathrm{d}\theta] \wedge [\sin\theta\,\mathrm{d}r + r\cos\theta\,\mathrm{d}\theta]\,.$$

Applying the rules $\mathrm{d}\theta \wedge \mathrm{d}\theta = 0$, $\mathrm{d}r \wedge \mathrm{d}r = 0$ and $\mathrm{d}r \wedge \mathrm{d}\theta = -\mathrm{d}\theta \wedge \mathrm{d}r$, we are left with:

$$\mathrm{d}x \wedge \mathrm{d}y = r\cos^2\theta\,\mathrm{d}r \wedge \mathrm{d}\theta - r\sin^2\theta\,\mathrm{d}\theta \wedge \mathrm{d}r = r\,\mathrm{d}r \wedge \mathrm{d}\theta,$$

which is the familiar area element in polar coordinates.

Now let us return to the example of the previous section where we had the integral $\iint p_U(u)p_V(v)\mathrm{d}u\mathrm{d}v$, where $v = z$ and $u = zy$. Writing $\mathrm{d}u\mathrm{d}v$ as a wedge product $\mathrm{d}u \wedge \mathrm{d}v$, expanding the total differentials: $\mathrm{d}u(y,z) = z\mathrm{d}y + y\mathrm{d}z$ and $\mathrm{d}v(y,z) = \mathrm{d}z$ yields $\mathrm{d}u \wedge \mathrm{d}v = z\mathrm{d}y \wedge \mathrm{d}z$, where z is the Jacobian determinant that was sought and $\mathrm{d}y \wedge \mathrm{d}z$ are the new integration variables. The alternating algebra of differential forms automatically computes the determinant for us.

9.9. Leibniz Formula

The Leibniz formula for differentiation of integrals (the Leibniz integral rule) is:

$$\frac{\mathrm{d}}{\mathrm{d}y}\left(\int_{a(y)}^{b(y)} f(x,y)\,\mathrm{d}x\right) = \underbrace{\int_{a(y)}^{b(y)} \frac{\partial}{\partial y} f(x,y)\,\mathrm{d}x}_{1} + \underbrace{f\big(b(y),y\big)\cdot b'(y)}_{2} - \underbrace{f\big(a(y),y\big)\cdot a'(y)}_{3}$$

which consists of the sum of three terms: in the first one the differentiation is carried out inside the integral; the remaining two terms are surface (boundary) terms. This formula will help you compute PDFs from CDFs.

Let's look at an example of obtaining the PDF from the CDF $\mathbb{P}(Y < y)$ when $X \sim \mathcal{N}(\mu, \sigma^2)$ and $Y = e^X$, by differentiating with respect to y. Since the y dependence occurs only in the upper limit of the integral, only the second term in the Leibniz formula is non-zero:

$$p_Y(y) \equiv \frac{\mathrm{d}\mathbb{P}(Y<y)}{\mathrm{d}y} = \frac{\mathrm{d}}{\mathrm{d}y}\int_{-\infty}^{\log y} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2}\mathrm{d}x = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(\log y-\mu)^2/2\sigma^2}\cdot\frac{1}{y}.$$

This particular PDF is also known as the log-normal distribution.

9.10. Infinitesimals

It is important to know how to work with infinitesimals. Let us take the link between CDF and PDF as an example. Denoting the CDF as $\mathbb{P}(X < x) = F(x)$, let us Taylor expand $F(x+\epsilon)$ about the point x (here $\epsilon > 0$ is a small quantity):

$$F(x+\epsilon) = F(x) + \epsilon \cdot F'(x) + o(|\epsilon|) \tag{9.7}$$

where $F'(x) = \mathrm{d}F(x)/\mathrm{d}x$ and $o(|\epsilon|)$ denotes higher order terms (in this case ϵ^2 and higher powers of ϵ) which decay to 0 faster than ϵ in the limit $\epsilon \to 0$:

$$\lim_{\epsilon\to 0}\frac{o(|\epsilon|)}{|\epsilon|} = 0,$$

so that taking the limit $\epsilon \to 0$ in Eq. (9.7) leads to $F(x+\epsilon) = F(x) + \epsilon\mathrm{d}F(x)/\mathrm{d}x$. Taking $\epsilon = \mathrm{d}x$ (infinitesimal) this can be rewritten as:

$$F(x+\mathrm{d}x) - F(x) = \cancel{F(x)} + \mathrm{d}x\cdot F'(x) + o(|\mathrm{d}x|) - \cancel{F(x)} = \mathrm{d}F(x) + o(|\mathrm{d}x|),$$

since $F'(x) = \mathrm{d}F(x)/\mathrm{d}x$. Thus, as $\mathrm{d}x \to 0$ (without being equal to 0) the term $o(|\mathrm{d}x|)$ vanishes and we have that

$$\boxed{F(x+\mathrm{d}x) - F(x) = \mathrm{d}F(x).} \tag{9.8}$$

(This is only true if $\mathrm{d}x$ is an infinitesimal. In that case, $\mathrm{d}F$ is the total differential of F.)

Denote the CDF as $F(x) \equiv \mathbb{P}(X < x)$ and recall the interpretation of the PDF. Given a random variable X its PDF $p_X(x)$ times $\mathrm{d}x$ gives the probability that X will lie in the interval $(x, x+\mathrm{d}x)$:

$$\boxed{p_X(x)\mathrm{d}x = \mathbb{P}(x \le X \le x+\mathrm{d}x) = \mathbb{P}(X \le x+\mathrm{d}x) - \mathbb{P}(X \le x) = \mathrm{d}\mathbb{P}(X \le x),}$$

where $\mathrm{d}F(x) = F(x+\mathrm{d}x) - F(x)$ was used in the last step. In the second equality we have made use of the definition of the "probability function" $\mathbb{P}(\cdot)$ as an integral of the PDF, i.e.

$$\begin{aligned}\mathbb{P}(a \le X \le b) = \int_a^b p_X(x)\mathrm{d}x = \int_{-\infty}^b p_X(x)\mathrm{d}x - \int_{-\infty}^a p_X(x)\mathrm{d}x \\ = \mathbb{P}(X \le b) - \mathbb{P}(X \le a)\end{aligned}$$

hence $\mathbb{P}(x \le X \le x+\mathrm{d}x) = \mathbb{P}(X \le x+\mathrm{d}x) - \mathbb{P}(X \le x)$. Another way to look at the quantity $\mathbb{P}(x \le X \le x+\mathrm{d}x)$ is the integral of the PDF from x to $x+\mathrm{d}x$

$$\mathbb{P}(x \le X \le x+\mathrm{d}x) = \int_x^{x+\mathrm{d}x} p_X(x')\mathrm{d}x' = p_X(x)\mathrm{d}x.$$

The last equality follows because the integral is a Riemann sum containing only 1 term. It contains only 1 term because the interval $[x, x+\mathrm{d}x]$ where the integral is carried out is infinitesimally small.

So integrating from a to b we get the probability that X takes values between a and b:

$$\begin{aligned}\int_a^b p_X(x')\mathrm{d}x' = \int_a^b \mathbb{P}(x \le X \le x+\mathrm{d}x) &= \int_a^b [\mathbb{P}(X \le x+\mathrm{d}x) - \mathbb{P}(X \le x)] \\ &= \int_a^b \mathrm{d}\mathbb{P}(X \le x) = \mathbb{P}(X \le b) - \mathbb{P}(X \le a) \\ &= \mathbb{P}(a \le X \le b).\end{aligned}$$

If the interval (a, b) is chosen to be $(-\infty, x)$ we get the CDF:[1]

$$\int_{-\infty}^x p_X(x')\mathrm{d}x' = \mathbb{P}(-\infty \le X \le x) = \mathbb{P}(X \le x).$$

Differentiating with respect to x yields a method for obtaining the PDF from the CDF:

$$\boxed{\frac{\mathrm{d}\mathbb{P}(X \le x)}{\mathrm{d}x} = p_X(x).} \tag{9.9}$$

So now you know how to go from PDF to CDF or from CDF to PDF. The two concepts are related to each other by an integral or a derivative. If you are asked to obtain the probability distribution of a rv you can derive either the PDF or the CDF. In general, obtaining the CDF is easier because fewer steps are needed and the interpretation of the CDF in terms of probability is also simpler.

---

[1] Notice that we wrote $\mathbb{P}(X \le x)$ instead of $\mathbb{P}(-\infty \le X \le x)$ because the statement that $X \ge -\infty$ is always true and therefore, unnecessary or redundant.

9.11. Taylor's Theorem in Several Variables

Because nonlinear optimization methods make extensive use of partial derivatives, here we review partial derivatives and the Taylor's theorem in multiple variables. We will show how to compute the partial derivatives of $1/r$, where $r = |\mathbf{r}|$ and $\mathbf{r}$ has components $\mathbf{r} = (x, y, z)$. r is its Euclidean length:

$$|\mathbf{r}| \equiv r \equiv \sqrt{x^2 + y^2 + z^2}.$$

9.11.1. Einstein summation convention. To simplify the notation one may use the Einstein summation convention. Whenever two indices are repeated in the same term, a summation is implied. For example, in the dot product of $\mathbf{u} = (u_x, u_y, u_z)$ and $\mathbf{v} = (v_x, v_y, v_z)$ we have:

$$\mathbf{u} \cdot \mathbf{v} = u_\alpha v_\alpha \equiv \sum_{i=1}^{3} u_i v_i = u_x v_x + u_y v_y + u_z v_z.$$

It is simpler to write $u_\alpha v_\alpha$ than the entire summation.

9.11.2. Multivariate Taylor expansion. In 1D the Taylor expansion of $f(x+h)$ at x is:

$$f(x+h) = f(x) + f'(x)h + \frac{1}{2}f''(x)h^2 + \frac{1}{3!}f^{(3)}(x)h^3 + \dots$$

In n-D, a scalar-valued function $f(\mathbf{x})$, where $\mathbf{x} \in \mathbb{R}^n$, is expanded as:

$$f(\mathbf{x}+\mathbf{h}) = f(\mathbf{x}) + \sum_{i=1}^{n} \frac{\partial f(\mathbf{x})}{\partial x_i} h_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{\partial^2 f(\mathbf{x})}{\partial x_i \partial x_j} h_i h_j + \frac{1}{3!} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \frac{\partial^3 f(\mathbf{x})}{\partial x_i \partial x_j \partial x_k} h_i h_j h_k + \dots$$

9.11.3. Abbreviation for Partial Derivatives. We will often use the shorthand notation to abbreviate the notation for partial differentiation:

$$\partial_\alpha \equiv \frac{\partial}{\partial x_\alpha}$$

In this notation, and using the summation convention, the multivariate Taylor expansion looks particularly neat:

$$\boxed{f(\mathbf{x}+\mathbf{h}) = f(\mathbf{x}) + h_i \partial_i f(\mathbf{x}) + \frac{1}{2} h_i h_j \partial_i \partial_j f(\mathbf{x}) + \frac{1}{3!} h_i h_j h_k \partial_i \partial_j \partial_k f(\mathbf{x}) \dots}$$

(summation convention). The vectors $\mathbf{h}$ have been moved to the left-hand-side of all derivative operators to avoid any possible confusion about which quantity is differentiated.

9.11.4. Example: Derivative of $1/r$. The first order partial derivative of

$$\frac{1}{r} \equiv \frac{1}{|\mathbf{r}|} = \frac{1}{\sqrt{x^2+y^2+z^2}}$$

with respect to x is:

$$\frac{\partial}{\partial x}\left(\frac{1}{r}\right) \equiv \partial_x\left(\frac{1}{r}\right) = -\frac{1}{2}\frac{(2x)}{(x^2+y^2+z^2)^{3/2}} = -\frac{x}{r^3}.$$

Similar expressions are found for differentiation with respect to y or z. Thus, for any component $\alpha = x, y, z$ we have:

$$\boxed{\frac{\partial}{\partial r_\alpha}\left(\frac{1}{r}\right) \equiv \partial_\alpha\left(\frac{1}{r}\right) = -\frac{r_\alpha}{r^3}.}$$

9.12. Legendre Transformation in Thermodynamics

The Legendre transformation is a very useful tool in mathematics and the physical sciences. It transforms convex functions on a vector space to convex functions on the dual space while preserving the convexity. Thus, it goes beyond a simple "change-of-variable" by maintaining the local shapes of the surfaces, loosely speaking. This is useful if we are trying to optimize a function, such as maximizing the entropy or finding the minimum in the free energy surface, as we often do in thermodynamics.

In chemistry, it is used to define some thermodynamic potentials. For example, we may go from the internal energy $U(S, V, N)$, whose differential is

$$dU = TdS - pdV + \mu dN$$

to the Helmholtz free energy $A(T, V, N) = U - TS$,

$$dA = dU - SdT - TdS = -SdT - pdV + \mu dN$$

or to the enthalpy $H(S, p, N) = U + pV$, whose differential is

$$dH = TdS + Vdp + \mu dN$$

or to the free enthalpy (Gibbs' potential) $G(T, p, N) = U - TS + pV$, whose differential is

$$dG = dU - TdS - SdT + pdV + Vdp = -SdT + Vdp + \mu dN.$$

9.12.1. Classical Mechanics. In classical mechanics, the Hamiltonian function is obtained from the Lagrangian through a Legendre transformation. The Hamiltonian is convex in the momenta because of the kinetic energy term:

$$\mathcal{H}(\mathbf{p}, \mathbf{q}) = \sum_i \frac{p_i^2}{2m_i} + U(\mathbf{q}).$$

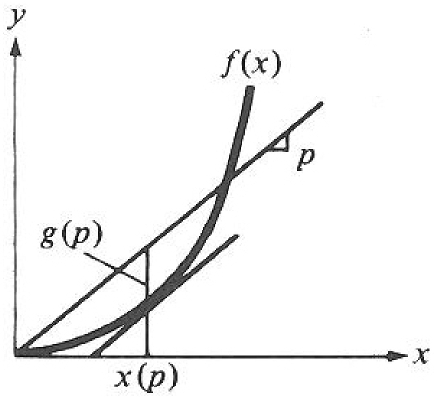

Figure 9.1. Legendre transformation.

The Lagrangian, which is obtained by switching from the p variables to the velocities, $\dot{q}_i$, is convex in these new variables:

$$L(\mathbf{q}, \dot{\mathbf{q}}) = \sum_i \frac{1}{2} m_i \dot{q}_i^2 - U(\mathbf{q}).$$

It can also be used as a tool to solve differential equations that would otherwise be impossible to solve. An example of this is given at the end of this supplement.

9.12.2. How to Compute It. In this section, we give an intuitive definition of the Legendre transform based on the treatment found in Arnold:

- V.I. Arnold, *Mathematical Methods of Classical Mechanics*, 2nd edition, Springer-Verlag (1997).

Another good reference, with a different set of examples, is the book by Honerkamp:

- J. Honerkamp, *Statistical physics: an advanced approach with applications*, 2nd edition, Springer-Verlag (2004).

Definition 9.6. Let $y = f(x)$ be a convex function, $f''(x) > 0$. The Legendre transformation of the function f is a new function g of a new variable p, which is constructed in the following way (Figure 9.1). We draw the graph of f in the x, y plane. Let p be a given number. Consider the straight line $y = px$. We take the point $x = x(p)$ at which the curve is farthest from the straight line in the vertical direction: for each p the function $px - f(x) = F(p, x)$ has a maximum with respect to x at the point $x(p)$. Now we define $g(p) = F(p, x(p))$. The point $x(p)$ is defined by the extremal condition $\partial F/\partial x = 0$, i.e. $f'(x) = p$. Since f is convex, the point $x(p)$ is unique (if it exists).

9.12.3. Examples.

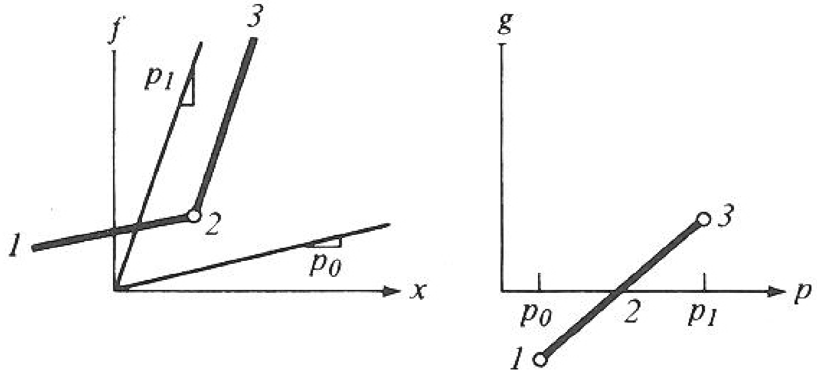

Figure 9.2. Legendre transformation taking an angle to a line segment.

Example 9.7. Let $f(x) = x^2$. Then $F(p, x) = px - x^2$, $x(p) = (1/2)p$, $g(p) = (1/4)p^2$.

Example 9.8. Let $f(x) = mx^2/2$. Then $g(p) = p^2/2m$.

Example 9.9. Let $f(x) = x^\alpha/\alpha$. Then $g(p) = p^\beta/\beta$, where $(1/\alpha) + (1/\beta) = 1$ ($\alpha > 1$, $\beta > 1$).

Example 9.10. Let $f(x)$ be a convex polygon. Then $g(p)$ is also a convex polygon, in which the vertices of $f(x)$ correspond to the edges of $g(p)$, and the edges of $f(x)$ to the vertices of $g(p)$. For example, the corner depicted in Fig. 9.2 is transformed to a line segment under the Legendre transformation.

9.12.4. Involutivity. Let us illustrate what it means for the Legendre transform to be involutive. Consider a function f which is differentiable as many times as necessary, with $f''(x) > 0$. It is easy to verify that a Legendre transformation takes convex functions to convex functions. Therefore, we can apply it twice.

Theorem 9.11. *The Legendre transformation is involutive, i.e., its square is the identity: if under the Legendre transformation f is taken to g, then the Legendre transform of g will again be f.*

Proof. In order to apply the Legendre transform to g, with variable p, we must by definition look at a new independent variable (which we call x), construct the function

$$G(x, p) = xp - g(p),$$

and find the point $p(x)$ at which G attains its maximum: $\partial G/\partial p = 0$, i.e., $g'(p) = x$. Then the Legendre transform of $g(p)$ will be the function of x equal to $G(x, p(x))$.

We will show that $G(x, p(x)) = f(x)$. To this end we notice that $G(x, p) = xp - g(p)$ has a simple geometric interpretation: it is the ordinate of the point with abscissa x on the line

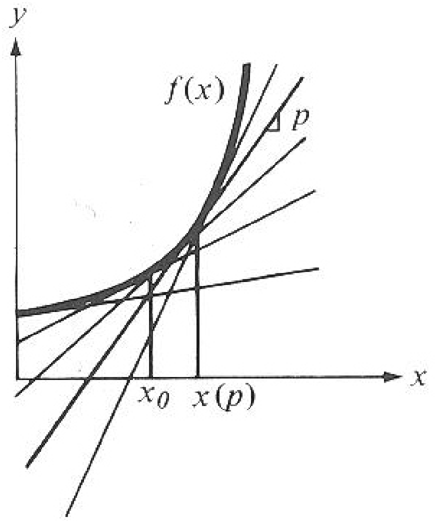

Figure 9.3. Involutivity of the Legendre transformation

tangent to the graph of $f(x)$ with slope p (Figure 9.3). For fixed p, the function $G(x, p)$ is a linear function of x, with $\partial G/\partial x = p$, and for $x = x(p)$ we have $G(x, p) = xp - g(p) = f(x)$ by the definition of $g(p)$.

Let us now fix $x = x_0$ and vary p. Then the values of $G(x, p)$ will be the ordinates of the points of intersection of the line $x = x_0$ with the line tangent to the graph of $f(x)$ with various slopes p. By the convexity of the graph it follows that all these tangents lie below the curve, and therefore the maximum of $G(x, p)$ for a fixed $x(p_0)$ is equal to $f(x)$ (and is achieved for $p = p(x_0) = f'(x_0)$).

□

9.12.5. Inequalities. By definition of the Legendre transform, $F(x, p) = px - f(x)$ is less than or equal to $g(p)$ for any x and p. From this we have Young's inequality:

$$px \leq f(x) + g(p).$$

Example 9.12. If $f(x) = \frac{1}{2}x^2$, then $g(p) = \frac{1}{2}p^2$ and we obtain the well-known inequality $px \leq \frac{1}{2}x^2 + \frac{1}{2}p^2$ for all x and p.

Example 9.13. If $f(x) = x^\alpha/\alpha$, $g(p) = p^\beta/\beta$, where $(1/\alpha) + (1/\beta) = 1$, and we obtain Young's inequality $px \leq (x^\alpha/\alpha) + (p^\beta/\beta)$ for all $x > 0$, $p > 0$, $\alpha > 1$, $\beta > 1$ and $(1/\alpha) + (1/\beta) = 1$.

Problem 136. Let f by a quadratic form $f(\mathbf{x}) = \sum f_{ij}x_ix_j$. Show that its Legendre transform is again a quadratic form $g(\mathbf{p}) = \sum g_{ij}p_ip_j$, and that the values of both forms at corresponding points coincide:

$$f(\mathbf{x}(\mathbf{p})) = g(\mathbf{p}) \text{ and } g(\mathbf{p}(\mathbf{x})) = f(\mathbf{x}).$$

Solution. The Legendre transform of f is (see next section below for notation):

$$f^*(\mathbf{p}) = \max_{\mathbf{x}}\{\mathbf{p}\cdot\mathbf{x} - f(\mathbf{x})\}$$

The max is found by setting the derivative equal to zero:

$$\frac{\partial}{\partial\mathbf{x}}(\mathbf{p}\cdot\mathbf{x} - f(\mathbf{x})) = 0,$$

which implies:

$$\mathbf{p} = \frac{\partial f(\mathbf{x})}{\partial\mathbf{x}} = 2\mathsf{F}\mathbf{x}.$$

where $f(\mathbf{x}) = \mathbf{x}^t\mathsf{F}\mathbf{x}$, with F the matrix with entries f_{ij}. Solving for $\mathbf{x}$ in terms of $\mathbf{p}$ gives $\mathbf{x} = \frac{1}{2}\mathsf{F}^{-1}\mathbf{p}$. Substituting this special value of $\mathbf{x}$ corresponding to $\mathbf{p}$ into $\mathbf{p}\cdot\mathbf{x} - f(\mathbf{x})$. This gives:

$$\begin{aligned} g(\mathbf{p}) = \{\mathbf{p}\cdot\mathbf{x} - f(\mathbf{x})\}_{\mathbf{x}=\frac{1}{2}\mathsf{F}^{-1}\mathbf{p}} &= \frac{1}{2}\mathbf{p}\cdot\mathsf{F}^{-1}\mathbf{p} - \frac{1}{4}(\mathsf{F}^{-1}\mathbf{p})^t\mathsf{F}\mathsf{F}^{-1}\mathbf{p} \\ &= \frac{1}{2}\mathbf{p}\cdot\mathsf{F}^{-1}\mathbf{p} - \frac{1}{4}(\mathsf{F}^{-1}\mathbf{p})^t\mathbf{p} = \frac{1}{4}\mathbf{p}^t\mathsf{F}^{-1}\mathbf{p} \end{aligned}$$

from which we see that the matrix $[g_{ij}]$ is $\frac{1}{4}\mathsf{F}^{-1}$. ■

9.12.6. Convexity of Legendre Transform. Here we follow Evans:

- L. Evans, *Partial Differential Equations*, American Mathematical Society (1998).

Let's call the function we wish to transform, L, the Lagrangian[2]. Its Legendre transform will be denoted L^*. The conjugate variables will be denoted $\vec{q}$ and $\vec{p}$, both of which are vectors.

Definition 9.14 (Convex function)**.** A function L is convex over some domain U if its value is never greater than its average slope (between $\vec{q}_1$ and $\vec{q}_2$):

$$L(t\vec{q}_1 + (1-t)\vec{q}_2) \le tL(\vec{q}_1) + (1-t)L(\vec{q}_2)$$

where $\vec{q}_1, \vec{q}_2 \in U$, $t \in [0,1]$.

Suppose that the Lagrangian $L : \mathbb{R}^n \to \mathbb{R}$ satisfies the following conditions: 1) the mapping $q \to L(\vec{q})$ is convex, 2) $\lim_{|\vec{q}|\to\infty} L(\vec{q})/|\vec{q}| = +\infty$. The convexity implies L is continuous.

Definition 9.15 (Legendre transform)**.** The *Legendre transform* of L is

$$L^*(\vec{p}) := \max_{\vec{q}\in\mathbb{R}^n}\{\vec{p}\cdot\vec{q} - L(\vec{q})\} \quad (\vec{p}\in\mathbb{R}^n). \tag{9.10}$$

---

[2] There is a slight difference in notation with classical mechanics, which uses $\dot{q}$ as the velocity and q for the position. The Legendre transform eliminates $\dot{q}$ in favor of p. In this section we eliminate q instead of $\dot{q}$ to keep the notation simple.

Remark 9.16. The "max" means that for every $\vec{p}$ there exists some $\vec{q}^* \in \mathbb{R}^n$ for which

$$L^*(\vec{p}) = \vec{p} \cdot \vec{q}^* - L(\vec{q}^*)$$

and the mapping $\vec{q} \to \vec{p} \cdot \vec{q} - L(\vec{q})$ has a maximum at $\vec{q} = \vec{q}^*$. But then $\vec{p} = \nabla_{\vec{q}} L(\vec{q}^*)$, provided L is differentiable at $\vec{q}^*$. Hence the equation $\vec{p} = \nabla_{\vec{q}} L(\vec{q})$ is solvable (although perhaps not uniquely) for $\vec{q}$ in terms of $\vec{p}$, $\vec{q}^* = \mathbf{q}(\vec{p})$. Therefore

$$L^*(\vec{p}) = \vec{p} \cdot \mathbf{q}(\vec{p}) - L(\mathbf{q}(\vec{p})).$$

However, this is exactly the definition of the Hamiltonian associated with L. We consequently write

$$H = L^*. \tag{9.11}$$

Thus, this definition tells us how to obtain the Hamiltonian H from the Lagrangian L.

Now, we ask the converse question: given H, how do we compute L?

Theorem 9.17 (Convex duality of Hamiltonian and Lagrangian)**.** *Assume L satisfies the previous conditions and define H as before. Then the mapping $\vec{p} \to H(\vec{p})$ is convex and*

$$\lim_{|\vec{p}| \to \infty} H(\vec{p})/|\vec{p}| = +\infty.$$

Furthermore, $L = H^*$.

Remark 9.18. Thus H is the Legendre transform of L, and vice versa:

$$L = H^*, \ H = L^*.$$

We say H and L are *dual* convex functions.

Proof. 1. For each fixed $\vec{q}$, the function $\vec{p} \to \vec{p} \cdot \vec{q} - L(\vec{q})$ is linear, and consequently the mapping

$$\vec{p} \to H(\vec{p}) = L^*(\vec{p}) = \max_{\vec{q} \in \mathbb{R}^n} \{\vec{p} \cdot \vec{q} - L(\vec{q})\}$$

is convex. Indeed, if $0 \le t \le 1$, $\vec{p}_1, \vec{p}_2 \in \mathbb{R}^n$,

$$\begin{aligned} H(t\vec{p}_1 + (1-t)\vec{p}_2) =& \max_{\vec{q}} \{(t\vec{p}_1 + (1-t)\vec{p}_2) \cdot \vec{q} - L(\vec{q})\} \\ =& \max_{\vec{q}} \{(t\vec{p}_1 + (1-t)\vec{p}_2) \cdot \vec{q} - (1-t+t)L(\vec{q})\} \\ =& \max_{\vec{q}} \{(t\vec{p}_1 + (1-t)\vec{p}_2) \cdot \vec{q} - (1-t)L(\vec{q}) - tL(\vec{q})\} \\ \le& t\max_{\vec{q}} \{\vec{p}_1 \cdot q - L(\vec{q})\} + (1-t)\max_{\vec{q}} \{\vec{p}_2 \cdot \vec{q} - L(\vec{q})\} \\ =& tH(\vec{p}_1) + (1-t)H(\vec{p}_2), \end{aligned} \tag{9.12}$$

which is the definition of a convex function. $\therefore$ L convex implies that H is convex. Where we used the inequality $\max_{\vec{x}}\{f(\vec{x}) + g(\vec{x})\} \le \max\{f(\vec{x})\} + \max\{g(\vec{x})\}$.

2. Fix any $\lambda > 0$, $\vec{p} \neq 0$. Then

$$\begin{aligned} H(\vec{p}) &= \max_{\vec{q}}\{\vec{p}\cdot\vec{q} - L(\vec{q})\} \geq \lambda|\vec{p}| - L(\lambda\frac{\vec{p}}{|\vec{p}|}) \quad (\vec{q} = \lambda\frac{\vec{p}}{|\vec{p}|}) \\ &\geq \lambda|\vec{p}| - \max_{B(0,\lambda)} L. \end{aligned} \tag{9.13}$$

(The first inequality holds by virtue of the fact that the supremum over all $\vec{q}$ exceeds any particular choice of $\vec{q}$ such as $\vec{q} = \lambda\vec{p}/|\vec{p}|$ which is just some vector of arbitrary magnitude λ pointing in the direction of the unit vector $\vec{p}/|\vec{p}|$. The second inequality is trivial.)

Thus $\liminf_{|\vec{p}|\to\infty} H(\vec{p})/|\vec{p}| \geq \lambda$ for all $\lambda > 0$.

3. In view of (9.11), $H(\vec{p}) + L(\vec{q}) \geq \vec{p}\cdot\vec{q}$ for all $\vec{p}, \vec{q} \in \mathbb{R}^n$. (This follows easily from the application of the definition $L^*(\vec{p}) := \max_{\vec{q}}\{\vec{p}\cdot\vec{q} - L(\vec{q})\}$ to the sum $L^*(\vec{p}) + L(\vec{q})$.) Consequently

$$L(\vec{q}) \geq \max_{\vec{p}}\{\vec{p}\cdot\vec{q} - H(\vec{p})\} = H^*(\vec{q}). \tag{9.14}$$

On the other hand

$$\begin{aligned} H^*(\vec{q}) &= \max_{\vec{p}}\left\{\vec{p}\cdot\vec{q} - \max_{r}\{\vec{p}\cdot\vec{r} - L(\vec{r})\}\right\} \\ &= \max_{\vec{p}}\min_{\vec{r}}\{\vec{p}\cdot(\vec{q}-\vec{r}) + L(\vec{r})\}. \end{aligned} \tag{9.15}$$

Now since $q \to L(\vec{q})$ is convex, there exists $\vec{s} \in \mathbb{R}^n$ such that

$$L(\vec{r}) \geq L(\vec{q}) + \vec{s}\cdot(\vec{r}-\vec{q}) \quad (\vec{r} \in \mathbb{R}^n). \tag{9.16}$$

(If L is differentiable at $\vec{q}$, take $\vec{s} = \nabla_{\vec{q}}(\vec{q})$. See Figure 9.4.) Taking $\vec{p} = \vec{s}$ in (9.15), we compute

$$H^*(\vec{q}) \geq \min_{\vec{r}}\{\vec{s}\cdot(\vec{q}-\vec{r}) + L(\vec{r})\} = L(\vec{q}). \tag{9.17}$$

(The last step follows by "substituting" (9.16) into (9.17). The term $\vec{s}\cdot(\vec{r}-\vec{q})$ cancels $\vec{s}\cdot(\vec{q}-\vec{r})$ while the minimum of $L(\vec{q})$ taken of all $\vec{r}$ is still $L(\vec{q})$.)

$\square$

9.13. Legendre Transformation in Classical Field Theory

Classical field theory provides a framework for describing physical fields, such as electromagnetic fields or gravitational fields. A key mathematical tool in this theory is the Legendre transformation, which allows us to transition from the Lagrangian to the Hamiltonian formalism. This transformation is crucial for understanding the dynamics of fields and plays a significant role in the quantization of fields in quantum field theory.

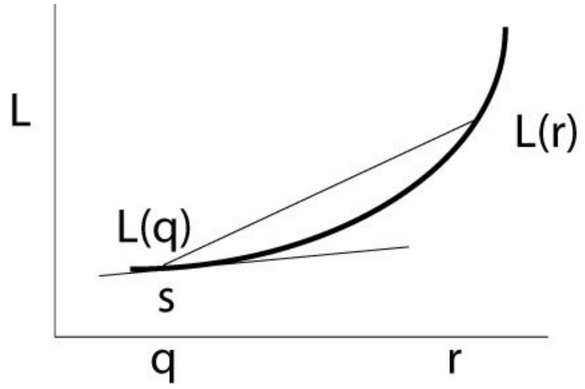

Figure 9.4. For a convex function, its average slope $(L(\vec{r}) - L(\vec{q}))/(\vec{r} - \vec{q})$ is greater than its slope $\vec{s} = \nabla_{\vec{q}}(\vec{q})$ at $\vec{q}$.

9.13.1. Lagrangian and Hamiltonian in Field Theory. The Lagrangian density $\mathcal{L}$ is a function that depends on field variables and their derivatives. It encapsulates the dynamics of the field. The Hamiltonian density $\mathcal{H}$, on the other hand, represents the energy density of the field and is derived from the Lagrangian density through the Legendre transformation.

9.13.2. Mathematical Framework of the Legendre Transformation. Given a Lagrangian density $\mathcal{L}(\phi, \partial_\mu \phi)$, where ϕ represents the field and $\partial_\mu \phi$ its derivatives, the Hamiltonian density is obtained as follows:

$$\mathcal{H} = \sum_i \pi^i \dot{\phi}_i - \mathcal{L}$$

where π^i are the canonical momenta defined by:

$$\pi^i = \frac{\partial \mathcal{L}}{\partial \dot{\phi}_i}$$

Here, $\dot{\phi}_i$ represents the time derivative of the field components ϕ_i.

9.13.3. Energy Stored in a Dielectric Medium. In a dielectric medium, the energy stored in the electromagnetic field can be analyzed using the electric displacement field **D** and the magnetic field **B**. Here, we derive the Hamiltonian density without assuming the Coulomb gauge ($\nabla\phi = 0$).

9.13.3.1. *Lagrangian Density in a Dielectric Medium.* The Lagrangian density for the electromagnetic field in a dielectric medium is:

$$\mathcal{L} = \frac{1}{2}\mathbf{D} \cdot \mathbf{E} - \frac{1}{2\mu}\mathbf{B}^2$$

where $\mathbf{E} = -\nabla\phi - \frac{\partial \mathbf{A}}{\partial t}$, $\mathbf{B} = \nabla \times \mathbf{A}$, and μ is the magnetic permeability of the medium.

9.13.3.2. *Canonical Momenta.* The canonical momentum conjugate to the vector potential $\mathbf{A}$ is given by:

$$\mathbf{\Pi} = \frac{\partial \mathcal{L}}{\partial(\partial \mathbf{A}/\partial t)} = -\mathbf{D}$$

Note that this formulation considers the general expression for $\mathbf{E}$ including both $-\nabla\phi$ and $-\frac{\partial \mathbf{A}}{\partial t}$.

9.13.3.3. *Hamiltonian Density.* Applying the Legendre transformation, we obtain the Hamiltonian density:

$$\mathcal{H} = \mathbf{\Pi} \cdot \frac{\partial \mathbf{A}}{\partial t} - \mathcal{L}$$

Substituting $\mathbf{\Pi}$ and $\mathcal{L}$ and simplifying, we get:

$$\mathcal{H} = \frac{1}{2}\mathbf{D} \cdot \mathbf{E} + \frac{1}{2\mu}\mathbf{B}^2$$

This Hamiltonian density describes the energy density of the electromagnetic field in a dielectric medium.

Note: In the general case, the relation between $\mathbf{D}$ and $\mathbf{E}$ is influenced by the dielectric properties of the medium, typically $\mathbf{D} = \varepsilon\mathbf{E}$, where ε is the permittivity.

9.14. Navier-Stokes Equation and Fluid Mechanics in Classical Field Theory

9.14.1. Lagrangian and Hamiltonian Formulation for an Ideal Fluid. The Navier-Stokes equations are fundamental in describing fluid motion. For an ideal fluid, which is a simplified model neglecting viscous terms (leading to Euler equations), we consider the Lagrangian density defined by the fluid's velocity field $\mathbf{v}$ and density ρ:

$$\mathcal{L}(\mathbf{v}, \rho) = \frac{1}{2}\rho\mathbf{v}^2 - \rho U(\rho)$$

where $U(\rho)$ denotes the internal energy per unit mass.

Applying the Euler-Lagrange equations to this Lagrangian density gives the Euler equations, a subset of the Navier-Stokes equations for an ideal fluid.

9.14.2. Canonical Momentum and Hamiltonian Density. The canonical momentum $\mathbf{\Pi}$ is defined as the derivative of the Lagrangian density with respect to the fluid's velocity:

$$\mathbf{\Pi} = \frac{\partial \mathcal{L}}{\partial \mathbf{v}} = \rho\mathbf{v}$$

This represents the momentum density of the fluid. The Hamiltonian density, indicating the total energy density of the fluid, is obtained via the Legendre transformation:

$$\mathcal{H} = \mathbf{\Pi} \cdot \mathbf{v} - \mathcal{L} = \frac{1}{2}\rho\mathbf{v}^2 + \rho U(\rho)$$

This formulation aligns with the principles of field theory for continuous systems like fluids and is essential for understanding fluid dynamics from a Hamiltonian perspective.

9.14.3. Energy Conservation in the Euler Equations. The Euler equations for an ideal fluid are fundamental in fluid dynamics, describing the conservation of mass and momentum. A key aspect of these equations is the conservation of energy, which we can demonstrate by showing that the total derivative of the Hamiltonian density with respect to time is zero.

9.14.3.1. *Hamiltonian Density for an Ideal Fluid.* The Hamiltonian density for an ideal fluid, representing the total energy density, is given by:

$$\mathcal{H} = \frac{1}{2}\rho\mathbf{v}^2 + \rho U(\rho)$$

where ρ is the mass density, $\mathbf{v}$ is the fluid velocity, and $U(\rho)$ is the internal energy per unit mass.

9.14.3.2. *Proof of Energy Conservation.* To prove energy conservation, we must show that the total derivative of the Hamiltonian density with respect to time is zero:

$$\frac{d\mathcal{H}}{dt} = 0$$

Step 1: Total Time Derivative The total time derivative of $\mathcal{H}$ encompasses both explicit and implicit time dependencies:

$$\frac{d\mathcal{H}}{dt} = \frac{\partial\mathcal{H}}{\partial t} + \frac{\partial\mathcal{H}}{\partial\mathbf{v}} \cdot \frac{d\mathbf{v}}{dt} + \frac{\partial\mathcal{H}}{\partial\rho}\frac{d\rho}{dt}$$

Step 2: Using the Euler Equations[3] The Euler equations are:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$
$$\rho \frac{d\mathbf{v}}{dt} + \rho(\mathbf{v} \cdot \nabla)\mathbf{v} = -\nabla p$$

where p is the pressure.

Step 3: Substituting into the Total Derivative Substituting the Euler equations into the expression for $\frac{d\mathcal{H}}{dt}$ and simplifying, we find that it equals zero:

$$\frac{d\mathcal{H}}{dt} = 0$$

This result indicates that the total energy density of the ideal fluid, as represented by the Hamiltonian density, is conserved over time, including both the fluid's kinetic and internal energies.

9.15. Liouville's Theorem

9.15.1. The Principle of Equal A Priori Probabilities.

The principle of equal chances for each microstate in a nearly isolated system is a key idea in statistical mechanics. This concept is often called the principle of equal *a priori* probabilities. It says that if a system

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[3] For completeness, let's provide a derivation of Euler equations from the Hamiltonian density. The Hamiltonian density for an ideal fluid is given by:

$$\mathcal{H} = \frac{1}{2}\rho \mathbf{v}^2 + \rho U(\rho)$$

where ρ is the mass density, $\mathbf{v}$ is the fluid velocity, and $U(\rho)$ is the internal energy per unit mass.

Hamilton's equations for a fluid with field variables $\mathbf{v}$ (velocity) and ρ (density) are:

$$\frac{\partial \mathbf{v}}{\partial t} = \frac{\partial \mathcal{H}}{\partial \mathbf{\Pi}}$$

where $\mathbf{\Pi}$ is the momentum density.

Step 1: Momentum Density Evolution Using the Hamiltonian density, the evolution of momentum density $\mathbf{\Pi} = \rho \mathbf{v}$ is given by:

$$\frac{\partial \mathbf{\Pi}}{\partial t} = -\nabla \mathcal{H}$$

Expanding this and substituting the Hamiltonian density, we get the momentum conservation equation.

Step 2: Mass Density Evolution The continuity equation for mass conservation is derived from the time derivative of the density:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$

This equation ensures mass conservation in the fluid.

Step 3: Deriving the Euler Equations Combining the equations from Steps 1 and 2, we arrive at the Euler equations for an ideal fluid:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$
$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho(\mathbf{v} \cdot \nabla)\mathbf{v} = -\nabla p$$

where p is the pressure related to the internal energy density. These Euler equations describe the dynamics of an ideal fluid, encapsulating the conservation of mass and momentum.

has a specific energy, each of the microstates that make up that energy level is equally likely to occur.

Liouville's theorem is important in this context. It comes from classical mechanics and suggests that the volume of phase space – the space where all possible states of a system are represented – stays constant over time for an isolated system. This theorem allows us to say that the density of a statistical ensemble, which is a collection of all the states the system can possibly be in, depends only on the system's energy.

The statistical ensemble we talk about here is known as Gibbs' ensemble. It is a group of microstates that are in agreement with the laws of mechanics and do not change over time. In this ensemble, the probability of a system being in any particular microstate is directly related to the phase space volume it occupies.

Quantum mechanics echoes this principle by stating that every quantum state with the same energy has the same statistical weight. This means that the likelihood of a system being in any quantum state is the same for all states at the same energy level.

The ergodic hypothesis is another concept that supports this principle. It suggests that the time average of a quantity – what you get if you measure something many times over a long period and then average it – is the same as the ensemble average – the average you would get if you could measure all possible states at once. This hypothesis is important because it implies that over time, a nearly isolated system will naturally explore all of its microstates, which means that its time average will represent an ensemble average.

The ergodic problem is about trying to understand these ideas using the rules of mechanics. It has been studied more from a mathematical standpoint, but it's still a fundamental question in statistical mechanics. It's about connecting the dots between the predictable nature of classical mechanics and the probabilistic nature of statistical ensembles.

The principle of equal *a priori* probabilities is grounded on classical mechanical principles, quantum mechanical rules, and the ergodic hypothesis. They provide the basis for us to use probability theory in statistical mechanics in a way that matches up with the mechanical behavior of physical systems.

To learn more, see the books by Kubo & Toda, Arnold and Khinchin:

- V.I. Arnold, *Mathematical Methods of Classical Mechanics*, Second Edition, Springer-Verlag (1989), pp. 68-70.
- A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics*, Dover (1960)
- M. Toda, R. Kubo, N. Saito, *Statistical physics I*, 2nd edition, Springer (1998)

9.15.2. Proof of Liouville's Theorem. Recall Hamilton's equations of motion, for a Hamiltonian $\mathcal{H}(\mathbf{p}, \mathbf{q}, t)$:

$$\dot{\mathbf{p}} = -\frac{\partial \mathcal{H}}{\partial \mathbf{q}}, \qquad \dot{\mathbf{q}} = \frac{\partial \mathcal{H}}{\partial \mathbf{p}}. \tag{9.18}$$

In this course on equilibrium statistical mechanics, we will mostly consider time-independent Hamiltonians $\mathcal{H}(\mathbf{p}, \mathbf{q})$. The coordinates $(\mathbf{p}, \mathbf{q})$ have their usual meaning, e.g.

$$\begin{aligned} \mathbf{p} &= (\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N), \\ \mathbf{q} &= (\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N), \\ (\mathbf{p}, \mathbf{q}) &= (\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{q}_1, \dots, \mathbf{q}_N). \end{aligned}$$

where $\mathbf{p}_1 = (p_{1x}, p_{2x}, p_{3x})$ etc. The phase flow is defined by the transformation

$$g^t : (\mathbf{p}(0), \mathbf{q}(0)) \to (\mathbf{p}(t), \mathbf{q}(t)),$$

where $\mathbf{p}(t)$ and $\mathbf{q}(t)$ are solutions of Hamilton's equations. In previous lectures, we used the shorthand notation $\mathbf{x} = (\mathbf{p}, \mathbf{q})$. The Liouville theorem is the statement that, for any region D of phase space we have (see Figure 9.5):

$$\text{volume of } g^t D = \text{volume of } D.$$

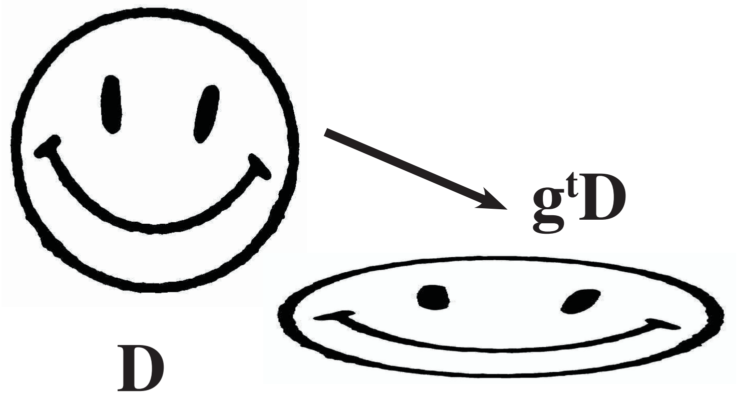

Figure 9.5. Liouville's theorem is the statement that the volume of a set of points in phase space remains constant. Thus, if the heigh of the "object" is reduced, its width increases such that its volume remains unchanged.

Consider a system of ODEs:

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x})$$

where $\mathbf{x} = (x_1, \dots, x_n)$. The solution of this ODE can be expanded in a Taylor series:

$$g^t\mathbf{x} = \mathbf{x} + \mathbf{f}(\mathbf{x})t + \mathcal{O}(t^2). \tag{9.19}$$

At time $t = 0$, let $D(0)$ be a region in phase space and $v(0)$ its volume. Let:

$$v(t) = \text{volume of } D(t), \qquad D(t) = g^t D(0).$$

We now proceed to show that: if $\nabla \cdot \mathbf{f} = \sum_i \partial f_i/\partial x_i = 0$ then g^t preserves volume: $v(t) = v(0)$. This result follows because:

$$\left.\frac{dv(t)}{dt}\right|_{t=0} = \int_{D(0)} \nabla \cdot \mathbf{f}\, d\mathbf{x},$$

and if $\nabla \cdot \mathbf{f} = 0$ then $dv/dt = 0$. To show that $\left.\frac{dv(t)}{dt}\right|_{t=0} = \int_{D(0)} \nabla \cdot \mathbf{f}\, d\mathbf{x}$, we note that the formula for changing variables in a multiple integral gives ($\mathbf{y} = g^t\mathbf{x}$)

$$v(t) = \int_{D(t)} d\mathbf{y} = \int_{D(t)} \det\left|\frac{\partial \mathbf{y}}{\partial \mathbf{x}}\right| d\mathbf{x}.$$

Differentiating Eq. (9.19) with respect to $\mathbf{x}$, and expanding in powers of t, we find:

$$\frac{\partial \mathbf{y}}{\partial \mathbf{x}} = \frac{\partial g^t\mathbf{x}}{\partial \mathbf{x}} = \mathbf{1} + \frac{\partial \mathbf{f}}{\partial \mathbf{x}} t + \mathcal{O}(t^2),$$

where $\mathbf{1}$ is the unit matrix and the first order term $\frac{\partial \mathbf{f}}{\partial \mathbf{x}}$ is the derivative of $g^t\mathbf{x}$ with respect to $\mathbf{x}$ evaluated at the point $t = 0$. The latter can be read directly from Eq. (9.19). The determinant of this expression is:

$$\det \frac{\partial g^t\mathbf{x}}{\partial \mathbf{x}} = 1 + \mathrm{Tr}\left[\frac{\partial \mathbf{f}}{\partial \mathbf{x}}\right] t + \mathcal{O}(t^2).$$

The formula $\det(\mathbf{1} + At) = 1 + t\mathrm{Tr}(A) + \mathcal{O}(t^2)$ follows from the direct expansion of the determinant: all terms are $\mathcal{O}(t^2)$ except for the product of diagonal elements:

$$(1 + ta_{11})(1 + ta_{22}) \ldots (1 + ta_{nn}) = 1 + t\mathrm{Tr}(A) + \mathcal{O}(t^2).$$

Using the fact that $\mathrm{Tr}[\partial \mathbf{f}/\partial \mathbf{x}] = \sum_i \partial f_i/\partial x_i = \nabla \cdot \mathbf{f}$, we arrive at:

$$v(t) = \int_{D(0)} \left[1 + t\nabla \cdot \mathbf{f} + \mathcal{O}(t^2)\right] d\mathbf{x}.$$

Differentiating with respect to t gives the desired result. In the case of Hamilton's equations of motion, we have [taking $\mathbf{f} = (\dot{\mathbf{p}}, \dot{\mathbf{q}})$ and $\mathbf{x} = (\mathbf{p}, \mathbf{q})$]:

$$\nabla \cdot \mathbf{f} = (\partial_{\mathbf{p}}, \partial_{\mathbf{q}}) \cdot (\dot{\mathbf{p}}, \dot{\mathbf{q}}) = \frac{\partial}{\partial \mathbf{p}} \cdot \dot{\mathbf{p}} + \frac{\partial}{\partial \mathbf{q}} \cdot \dot{\mathbf{q}} = \frac{\partial}{\partial \mathbf{p}} \cdot \left(-\frac{\partial H}{\partial \mathbf{q}}\right) + \frac{\partial}{\partial \mathbf{q}} \cdot \left(\frac{\partial H}{\partial \mathbf{p}}\right) = 0.$$

Thus, the velocity field $(\dot{\mathbf{p}}, \dot{\mathbf{q}})$ in phase space has zero divergence. This is analogous to the case of an incompressible fluid[4].

9.15.2.1. *Application of the Liouville theorem in classical mechanics.* In classical mechanics, the Liouville theorem says that $dv/dt = 0$ for Hamiltonian flow. It makes sense to take $v(t)$ to represent a probabiliy density $\rho(\mathbf{x})d\mathbf{x}$ of finding a particle inside a volume element $d\mathbf{x}$ at $\mathbf{x}$. This density may evolve over time due to the Hamiltonian flow, so we write $\rho(\mathbf{x}, t) \equiv \rho(g^t\mathbf{x})$ because it is the points $\mathbf{x} \to g^t\mathbf{x}$ that evolve under the flow. The

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[4] In fluid mechanics, a fluid is incompressible if its velocity field $\mathbf{v} = \dot{\mathbf{x}}$ has zero divergence $\nabla \cdot \mathbf{v} = 0$. In Hamiltonian mechanics, the velocity field is $\mathbf{f} = (\dot{\mathbf{p}}, \dot{\mathbf{q}})$. It is incompressible if $\nabla \cdot \mathbf{f} = 0$.

total number of particles N in our system at any given time should remain constant:

$$N = \int \rho(g^t \mathbf{x}) d\mathbf{x}.$$

Thus, the Liouville theorem tell us that the density of points in phase space remains invariant:

$$\frac{d\rho}{dt}(\mathbf{x}, t) = \frac{\partial \rho}{\partial t} + \nabla_{\mathbf{x}} \rho \cdot \underbrace{\frac{d\mathbf{x}}{dt}}_{(\dot{\mathbf{p}}, \dot{\mathbf{q}})} = \frac{\partial \rho}{\partial t} + \left(\frac{\partial \rho}{\partial \mathbf{q}} \cdot \frac{\partial H}{\partial \mathbf{p}} - \frac{\partial \rho}{\partial \mathbf{p}} \cdot \frac{\partial H}{\partial \mathbf{q}} \right) = 0,$$

where $\mathbf{x} = (\mathbf{p}, \mathbf{q})$. The equation $d\rho/dt$ says that the *convective derivative*[5] of ρ is zero, i.e. the derivative along the flow does not change, although at a fixed location in space it may change (the partial derivative $\partial \rho / \partial t$ is not necessarily zero). This situation is illustrated in Fig. (9.6), where the density of representative points in some small region between the surfaces E and $E + \delta E$ demains constant in time, as the system moves along the strip of constant energy (Hamiltonian flow). In other words, the distribution function is constant along any trajectory in phase space.

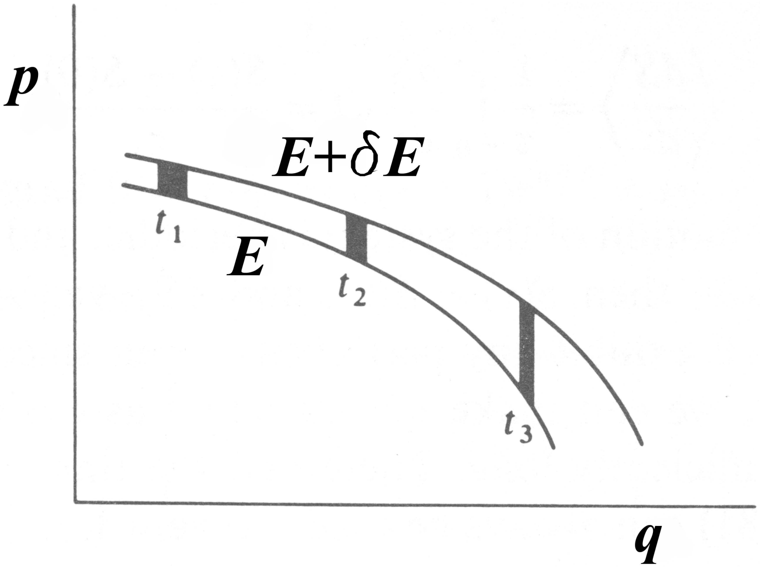

Figure 9.6. Hamiltonian flow for a system of constant energy E. The distribution of points (phase space volume) always remains constant along the trajectory of the flow. This is seen by the volume (dark region) at time t_1 becoming narrower at later times (t_3) but also taller, such that its volume is unchanged.

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[5] In fluid mechanics, a differential operator of the form $d/dt = \partial/\partial t + \dot{\mathbf{x}} \cdot \nabla$ is called convective derivative. It arises because of the chain rule of calculus, when the *total derivative* d/dt acts on a function of time and space, such as $\rho(\mathbf{x}, t)$, and space itself is a function of time, i.e. $\mathbf{x} \equiv \mathbf{x}(t)$.

Therefore, rewriting the last equality in component form, we get:

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right) = 0$$

The summation term is called the Poisson bracket of H and ρ and this is often written in shorthand notation as:

$$\frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\} = 0.$$

This equation is also called the Liouville equation of classical mechanics. It is sometimes written $\partial \rho / \partial t = -\hat{L}\rho$ where $\hat{L}$ is the Liouvillian operator, $\hat{L} = \sum_{i=1}^{N} \left(\frac{\partial \mathcal{H}}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial \mathcal{H}}{\partial q_i} \frac{\partial}{\partial p_i} \right)$. The formal solution is

$$\rho(g^t \mathbf{x}) = e^{-\hat{L}t} \rho(\mathbf{x}).$$

The exponential operator is computed with the Liouvillian utilizing variables $(\mathbf{p}, \mathbf{q})$ evaluated at time $t = 0$. There exists also a Liouville equation in quantum mechanics (Sakurai, p. 181),

$$\frac{\partial \hat{\rho}}{\partial t} + \frac{1}{i\hbar} [\hat{\rho}, \hat{\mathcal{H}}] = 0,$$

but where $\hat{\rho}$ is the density matrix and $[\hat{\mathcal{H}}, \hat{\rho}]$ is the commutator of $\hat{\mathcal{H}}$ and $\hat{\rho}$. This is also often written in terms of the Liouvillian superoperator: $\partial \hat{\rho} / \partial t = -\hat{\hat{L}} \hat{\rho}$, where $\hat{\hat{L}} \equiv (i/\hbar)[\hat{\mathcal{H}}, \cdot]$. We will not make explicit use of this theorem in this course, apart from using it to justify the probabilistic structure of the microcanonical ensemble. Its importance to statistical mechanics is great. To learn more about the classical Liouville theorem, see Goldstein:

- H. Goldstein, *Classical Mechanics* Second Edition, Addison Wesley (1980).

9.15.3. Ergodic Theorems. In statistical mechanics, ergodic theorems basically say that time averages can be equated to phase space averages under appropriate conditions. This is important to us because experimental measurements, which almost always are time averages, can be predicted by calculation of ensemble averages. It is generally an easier task to calculate ensemble averages than time averages. We look at a few of these theorems but we omit the proofs, which are of a rather technical nature. They can be found in the book by Khinchin:

- A.I. Khinchin, *Mathematical Foundations of Statistical Mechanics*, Dover Publications (1960).

9.15.3.1. *Birkhoff's Theorem (Toda p.179).* Since the volume V of a subspace in phase space is invariant under the transformation $g^t V$, i.e. $g^t V = V$, then for almost all points $\mathbf{x}$ in phase space, the long-time average of f exists (Birkhoff's first theorem):

$$\overline{f} = \lim_{T \to \infty} \frac{1}{T} \int_0^T f(g^t \mathbf{x}) dt.$$

Birkhoff's second theorem states that this average has the same value for all $\mathbf{x}$ along the path of the flow. In other words, the time average is independent of the choice of point $\mathbf{x}$ as long as $\mathbf{x}$ is along the trajectory.

The implications of these theorems are that the time-evolution g^t is ergodic iff all the invariant functions f are constant. This constant equals the ensemble average $\langle f \rangle$. The concepts of *metric transitivity* and *mixing* (Toda, pp. 182-183) are sometimes used to prove ergodicity. The concept of metric transitivity is hard to prove. Instead, it is easier to use the following theorem by Khinchin, which requires only to compute a time-correlation function.

9.15.3.2. *Khinchin's Theorem (Toda p.183).* If the time-correlation function

$$R(u) = \frac{1}{\langle f^2(\mathbf{x}) \rangle} \langle f(g^t\mathbf{x}) f(g^{t+u}\mathbf{x}) \rangle \to 0 \qquad \text{as} \qquad u \to \infty.$$

where $\langle \dots \rangle$ denotes a phase average - recall that it is an average over a surface of constant energy E:

$$\langle f \rangle = \langle f \rangle_E = \frac{1}{W_{\delta E}(E)} \int_\Gamma \delta(H(\mathbf{x}) - E) f(\mathbf{x}) d\mathbf{x} = \frac{1}{W_{\delta E}(E)} \int_{H(\mathbf{x})=E} f(\mathbf{x}) \frac{d\mathbf{s}}{|\nabla \mathcal{H}(\mathbf{x})|},$$

then the phase function $f(\mathbf{x})$ is ergodic, i.e. its phase average equals its time average:

$$\langle f \rangle_E = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau f(g^t\mathbf{x}) dt.$$

9.15.3.3. *Proof of the Volume to Surface Integral Formula via the Coarea Formula.* Let $\mathbb{R}^n$ denote the n-dimensional Euclidean space, and let $g : \mathbb{R}^n \to \mathbb{R}$ be a continuously differentiable function such that $\nabla g(\mathbf{x}) \neq 0$ for all $\mathbf{x} \in \mathbb{R}^n$. The level set $g^{-1}(0)$ is then a smooth $(n-1)$-dimensional manifold. The formula is given by:

$$\int_{\mathbb{R}^n} f(\mathbf{x}) \, \delta(g(\mathbf{x})) \, d\mathbf{x} = \int_{g^{-1}(0)} \frac{f(\mathbf{x})}{|\nabla g(\mathbf{x})|} \, d\sigma(\mathbf{x})$$

Proof: First we recall the Dirac delta δ centered at zero, which is defined by the property that for any test function ϕ:

$$\int_{\mathbb{R}^n} \phi(\mathbf{x}) \, \delta(g(\mathbf{x})) \, d\mathbf{x} = \phi(\mathbf{0})$$

when $g(\mathbf{0}) = 0$ and $\nabla g(\mathbf{0}) \neq 0$. Next, we invoke Sard's Theorem, which states that the set of critical values of g has measure zero. This implies that almost every level set $g^{-1}(c)$ is a smooth manifold, and in particular, $g^{-1}(0)$ is a smooth manifold since ∇g is nowhere zero. Secondly, we invoke the Coarea formula, which states that for any integrable function h:

$$\int_{\mathbb{R}^n} h(\mathbf{x}) \, d\mathbf{x} = \int_{-\infty}^{\infty} \left(\int_{g^{-1}(c)} \frac{h(\mathbf{x})}{|\nabla g(\mathbf{x})|} \, d\sigma_c(\mathbf{x}) \right) dc$$

where $d\sigma_c$ is the surface measure on the level set $g^{-1}(c)$. Finally, we apply to f and δ: Let $h(\mathbf{x}) = f(\mathbf{x})\delta(g(\mathbf{x}))$. Since the delta function is nonzero only when $g(\mathbf{x}) = 0$, the coarea formula reduces to:

$$\int_{\mathbb{R}^n} f(\mathbf{x})\delta(g(\mathbf{x}))\,d\mathbf{x} = \int_{g^{-1}(0)} \frac{f(\mathbf{x})}{|\nabla g(\mathbf{x})|}\,d\sigma(\mathbf{x})$$

where $d\sigma$ is the surface measure on $g^{-1}(0)$. This concludes the proof. The delta function effectively collapses the entire integral to the level set $g^{-1}(0)$, and the coarea formula relates the volume integral to the integral over this level set, accounting for the gradient ∇g to ensure the correct "density" of the integral is maintained.

9.15.3.4. *Justification of the basic assumptions in microcanonical statistics.* We summarize the previous observations/results:

- Time averages are constant on trajectories. (Birkhoff's theorem.)
- Time averages are constant on the energy surfaces. (This is a consequence of the previous point, and the fact that trajectories move along energy surfaces.)
- Time averages equal microcanonical averages. (We need to show that trajectories do not "linger" in some regions of the energy surface.)
  - Liouville's theorem told us that the microcanonical ensemble was time independent.
  - So the ensemble average equals its time average, which equals the ensemble average of the time average.
  - *But the time average is constant.*
  - So in an ergodic system the ensemble average equals the time average everywhere.

9.15.3.5. *Non-ergodic systems of statistical mechanics.* It turns out to be very difficult to prove ergodicity of a dynamical system. There are a lot of real systems which are not ergodic. The following systems have been shown to be non-ergodic:

- Glasses
- Fermi, Pasta, Ulam and KdV
- Broken symmetry phases
- KAM tori and the three-body problem

9.16. Properties of the Laplace Transform

Definition of the Laplace Transform. The Laplace transform of a function $f(t)$, defined for all real numbers $t \geq 0$, is given by the integral

$$\mathcal{L}\{f(t)\} = F(s) = \int_0^\infty e^{-st} f(t)\,dt,$$

where s is a complex number for which the integral converges.

Inversion Formula. The original function $f(t)$ can be recovered from its Laplace transform $F(s)$ using the inverse Laplace transform, provided certain conditions are met:

$$f(t) = \mathcal{L}^{-1}\{F(s)\} = \frac{1}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} e^{st} F(s)\, ds,$$

where γ is a real number greater than the real part of all singularities of $F(s)$.

Properties and Theorems

Linearity. For constants a and b and functions $f(t)$ and $g(t)$,

$$\mathcal{L}\{af(t) + bg(t)\} = aF(s) + bG(s).$$

Proof: Follows directly from the linearity of the integral.

Time-Delay. For a time delay $\tau > 0$,

$$\mathcal{L}\{f(t-\tau)u(t-\tau)\} = e^{-\tau s} F(s).$$

Proof: Apply the definition with a change of variable $z = t - \tau$.

First Derivative. If $f(t)$ has a first derivative $f'(t)$,

$$\mathcal{L}\{f'(t)\} = sF(s) - f(0).$$

Proof: Integrate by parts, using the definition of the Laplace transform.

Second Derivative. For the second derivative $f''(t)$,

$$\mathcal{L}\{f''(t)\} = s^2 F(s) - sf(0) - f'(0).$$

Proof: Apply the first derivative property twice.

Initial Value Theorem. If $\lim_{t \to 0^+} f(t)$ exists,

$$\lim_{s \to \infty} sF(s) = f(0^+).$$

Proof: Consider the limit as s goes to infinity in the Laplace integral.

Time Scaling. For a scaling factor $a > 0$,

$$\mathcal{L}\{f(at)\} = \frac{1}{a} F\left(\frac{s}{a}\right).$$

Proof: Use the substitution method in the definition with $z = at$.

Multiplication by Time.

$$\mathcal{L}\{t^n f(t)\} = (-1)^n \frac{d^n}{ds^n} F(s).$$

Proof: Differentiate under the integral sign n times with respect to s.

Complex Shift. For a complex number a,

$$\mathcal{L}\{e^{at} f(t)\} = F(s-a).$$

Proof: Apply the definition with the exponential function as part of the integrand.

Convolution Theorem. The Laplace transform of the convolution of $f(t)$ and $g(t)$ is

$$\mathcal{L}\{f * g\} = F(s)G(s).$$

Proof: Use Fubini's theorem to interchange the order of integration in the convolution integral.

Parseval's Theorem. For functions $f(t)$ and $g(t)$ with Laplace transforms $F(s)$ and $G(s)$, respectively,

$$\int_0^\infty f(t)\overline{g(t)}\, dt = \frac{1}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} F(s)\overline{G(\overline{s})}\, ds.$$

Proof: Derive from the inversion formula and properties of complex conjugates.

9.17. Properties of Fourier Transforms

Parseval's theorem (conservation of total energy).

$$\int_{-\infty}^{\infty} |f(x)|^2 dx = \int_{-\infty}^{\infty} |\hat{f}(\omega)|^2 d\omega.$$

Proof:

$$\int_{-\infty}^{\infty} |f(x)|^2 dx = \int_{-\infty}^{\infty} f(x)\overline{f(x)} dx = \int_{-\infty}^{\infty} \hat{f}(\omega)\overline{\hat{f}(\omega)} d\omega = \int_{-\infty}^{\infty} |\hat{f}(\omega)|^2 d\omega.$$

Utilizing the Fourier transform and its inverse, the proof follows from the definition of the Fourier transform and the complex conjugate.

Convolution of f and g.

$$h(x) = (f * g)(x) = \int_{-\infty}^{\infty} f(y) g(x-y) dy.$$

In Fourier space, the convolution is a product of their Fourier transforms

$$\hat{h}(\omega) = \hat{f}(\omega) \cdot \hat{g}(\omega).$$

i.e.,

$$\hat{h}(\omega) = \int_{-\infty}^{\infty} h(x)e^{-i\omega x}dx = \hat{f}(\omega)\cdot\hat{g}(\omega).$$

Proof: Let $f(x)$ and $g(x)$ be two functions with their respective Fourier transforms defined as:

$$\hat{f}(\omega) = \int_{-\infty}^{\infty} f(x)e^{-i\omega x}dx, \qquad \hat{g}(\omega) = \int_{-\infty}^{\infty} g(x)e^{-i\omega x}dx.$$

The convolution $h(x)$ of $f(x)$ and $g(x)$ is given by:

$$h(x) = (f*g)(x) = \int_{-\infty}^{\infty} f(y)g(x-y)dy$$

Taking the Fourier transform of $h(x)$:

$$\hat{h}(\omega) = \int_{-\infty}^{\infty} h(x)e^{-i\omega x}dx = \int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty} f(y)g(x-y)dy\right]e^{-i\omega x}dx = \int_{-\infty}^{\infty} f(y)\left[\int_{-\infty}^{\infty} g(x-y)e^{-i\omega x}dx\right]dy$$

Let $u = x - y$, then $dx = du$ and the inner integral becomes:

$$\int_{-\infty}^{\infty} g(u)e^{-i\omega(u+y)}du = e^{-i\omega y}\int_{-\infty}^{\infty} g(u)e^{-i\omega u}du = e^{-i\omega y}\hat{g}(\omega)$$

Substituting back into the integral for $\hat{h}(\omega)$:

$$\hat{h}(\omega) = \int_{-\infty}^{\infty} f(y)e^{-i\omega y}\hat{g}(\omega)dy = \hat{g}(\omega)\int_{-\infty}^{\infty} f(y)e^{-i\omega y}dy = \hat{g}(\omega)\hat{f}(\omega)$$

Hence, we have shown that the Fourier transform of the convolution $h(x)$ is the product of the Fourier transforms of $f(x)$ and $g(x)$, i.e., $\hat{h}(\omega) = \hat{f}(\omega)\cdot\hat{g}(\omega)$.

Functions defined in a 3D Box (finite region). Functions in a finite region (3D box with side lengths L_x, L_y, L_z and volume $\mathcal{V} = L_xL_yL_z$), and periodic, e.g. $f(\mathbf{r} + L_x\mathbf{e}_x) = f(\mathbf{r} + L_y\mathbf{e}_y) = f(\mathbf{r} + L_z\mathbf{e}_z) = f(\mathbf{r})$,

$$f(\mathbf{r}) = \frac{1}{\mathcal{V}}\sum_{\mathbf{k}} f_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}, \qquad \Big\{k_x = \tfrac{2\pi n_x}{L_x}, n_x = 0, \pm1, \pm2, \ldots,$$

where

$$f_{\mathbf{k}} = \int_{\mathcal{V}} d^3\mathbf{r} f(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}.$$

Proof: Consider a function $f(\mathbf{r})$ defined within a three-dimensional box with side L and volume $V = L^3$, which obeys periodic boundary conditions. The function can be expanded as a Fourier series:

$$f(\mathbf{r}) = \sum_{\mathbf{n}} c_{\mathbf{n}}e^{i\mathbf{k}_{\mathbf{n}}\cdot\mathbf{r}}$$

where $\mathbf{k}_{\mathbf{n}} = \frac{2\pi}{L}\mathbf{n}$ and $\mathbf{n}$ is a vector of integers (n_x, n_y, n_z), representing the quantization of wave vectors due to boundary conditions. The coefficients $c_{\mathbf{n}}$ can be determined by the inverse Fourier series:

$$c_{\mathbf{n}} = \frac{1}{V}\int_V f(\mathbf{r})e^{-i\mathbf{k_n}\cdot\mathbf{r}}d^3\mathbf{r}.$$

This integral extends over the volume V of the box. The periodic boundary conditions ensure that the function $f(\mathbf{r})$ and its Fourier series representation are identical on opposite faces of the box. This leads to a discrete set of $\mathbf{k_n}$ values.

The orthogonality of the exponential functions over the box volume is given by:

$$\int_V e^{i(\mathbf{k_n}-\mathbf{k_m})\cdot\mathbf{r}}d^3\mathbf{r} = V\delta_{\mathbf{n},\mathbf{m}}$$

where $\delta_{\mathbf{n},\mathbf{m}}$ is the Kronecker delta, which is 1 if $\mathbf{n} = \mathbf{m}$ and 0 otherwise. This property allows us to isolate each coefficient $c_{\mathbf{n}}$ when we multiply the Fourier series by $e^{-i\mathbf{k_m}\cdot\mathbf{r}}$ and integrate over the volume V.

Thus, the Fourier series expansion is a valid representation of $f(\mathbf{r})$ within a 3D box with periodic boundary conditions. The set of wave vectors $\mathbf{k_n}$ forms a discrete lattice in reciprocal space, which is a direct consequence of the finite spatial domain and periodicity of the function.

Important theorems:

$$\int d^3\mathbf{r}e^{-i\mathbf{k}\cdot\mathbf{r}} = \mathcal{V}\delta_{\mathbf{k},0}, \qquad \frac{1}{\mathcal{V}}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} = \delta(\mathbf{r}).$$

Proof: These identities follow directly from the orthogonality relations of the complex exponentials in a finite volume and their delta function representation.

Infinite Region. In an infinite region, we may let $\mathcal{V} \to \infty$ and obtain:

$$f(\mathbf{r}) = \int \frac{d^3\mathbf{k}}{(2\pi)^3} f_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}, \qquad f_{\mathbf{k}} = \int d^3\mathbf{r} f(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}.$$

Proof: In an infinite region, we may let $\mathcal{V} \to \infty$, and in the limit of infinite volume, summations become integrals and we recover the continuous Fourier transform relations.

FT theorems, continuous versions.

$$\int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}} = \delta(\mathbf{r}), \qquad \int d^3\mathbf{r}e^{-i\mathbf{k}\cdot\mathbf{r}} = (2\pi)^3\delta(\mathbf{k}).$$

Proof: These are derived from the properties of the Dirac delta function in three dimensions and the inverse relations of the Fourier transform.

Time and frequency transforms. These differ by a sign (in line with the usual phase factor of a propagating wave $e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$)

$$f(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f_\omega e^{-i\omega t}, \quad f_\omega = \int_{-\infty}^{\infty} dt f(t)e^{i\omega t},$$

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega t}=\delta(t),\quad \int_{-\infty}^{\infty}dte^{i\omega t}=2\pi\delta(\omega).$$

Proof:

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega t}=\delta(t),\quad \int_{-\infty}^{\infty}dte^{i\omega t}=2\pi\delta(\omega). \tag{9.20}$$

These results are a special case of the Fourier transform applied to time-dependent functions and their frequencies.

Fourier transforms of differential operators.

$$\nabla_{\mathbf{r}}\leftrightarrow i\mathbf{k}\quad \nabla_{\mathbf{r}}^2\leftrightarrow -\mathbf{k}^2,\quad \partial_t\leftrightarrow -i\omega,\quad \nabla\times\leftrightarrow i\mathbf{k}\times$$

Proof:

$$\mathcal{F}\left\{\frac{\partial^n f}{\partial x^n}\right\}=\int_{-\infty}^{\infty}\frac{\partial^n f}{\partial x^n}e^{-i\omega x}dx=(i\omega)^n\hat{f}(\omega).$$

This result is obtained by applying integration by parts and assuming the boundary terms vanish, leading to the multiplication of the Fourier transform of the function by $(i\omega)^n$. We used the time-frequency transform ($t\leftrightarrow\omega$), but this also applies to spatial coordinates ($\mathbf{x}\leftrightarrow\mathbf{k}$).

Fourier transform of the function $f=1$.

$1_{\mathbf{r}}\leftrightarrow\mathcal{V}\delta_{\mathbf{k},0}$	$1_{\mathbf{k}}\leftrightarrow\delta(\mathbf{r})$	discrete k
$1_{\mathbf{r}}\leftrightarrow(2\pi)^3\delta(\mathbf{k})$	$1_{\mathbf{k}}\leftrightarrow\delta(\mathbf{r})$	continuous k
$1_t\leftrightarrow 2\pi\delta(\omega)$	$1_\omega\leftrightarrow\delta(t)$	continuous ω

Convolution integrals (multidimensional case).

$$f(\mathbf{r})=\int d^3\mathbf{s}\,h(\mathbf{r}-\mathbf{s})g(\mathbf{s})=\int d^3\mathbf{s}\frac{1}{\mathcal{V}^2}\sum_{\mathbf{k},\mathbf{k}'}h_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{s})}g_{\mathbf{k}'}e^{i\mathbf{k}'\cdot\mathbf{s}}=\frac{1}{\mathcal{V}}\sum_{\mathbf{k}}h_{\mathbf{k}}g_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

Therefore,

$$\int d\mathbf{s}h(\mathbf{r}-\mathbf{s})g(\mathbf{s})\leftrightarrow h_{\mathbf{k}}g_{\mathbf{k}}$$

Proof:

$$\hat{f}(\mathbf{k})*\hat{g}(\mathbf{k})=\int d^3\mathbf{k}'\hat{f}(\mathbf{k}')\hat{g}(\mathbf{k}-\mathbf{k}')=\int d^3\mathbf{r}\,f(\mathbf{r})g(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}.$$

The proof exploits the Fourier transform properties to convert the convolution of two functions in the spatial domain to a multiplication in the Fourier (k-space) domain.

Invariance of inner products going from r to k.

$$\int d^3\mathbf{r}h(\mathbf{r})g^*(\mathbf{r}) = \int \frac{d^3\mathbf{k}}{(2\pi)^3}h_{\mathbf{k}}g^*_{\mathbf{k}}$$
$$\int d^3\mathbf{r}h(\mathbf{r})g(\mathbf{r}) = \int \frac{d^3\mathbf{k}}{(2\pi)^3}h_{\mathbf{k}}g_{-\mathbf{k}}$$
$$\int d^3\mathbf{r}h(\mathbf{r})g(-\mathbf{r}) = \int \frac{d^3\mathbf{k}}{(2\pi)^3}h_{\mathbf{k}}g_{\mathbf{k}}$$

Proof:

$$\int d^3\mathbf{r}\, f^*(\mathbf{r})g(\mathbf{r}) = \int d^3\mathbf{k}\, \hat{f}^*(\mathbf{k})\hat{g}(\mathbf{k}) = \langle f|g\rangle = \langle \hat{f}|\hat{g}\rangle.$$

(Note: we used the symmetric version of the Fourier transform, so the factor $(2\pi)^3$ isn't needed.) This demonstrates the inner product (or the 'dot product' in function space) is preserved under the Fourier transform, which is a crucial property for maintaining the physical interpretation of quantum mechanical states in both position and momentum spaces.

Translationally invariant systems. If a function depends only on the difference of its arguments, i.e. $f(\mathbf{r}, \mathbf{r}') = f(\mathbf{r} - \mathbf{r}')$, then it is easy to show from the definitions that its Fourier transform has the property $f(\mathbf{r}, \mathbf{r}') \leftrightarrow f_{\mathbf{k},-\mathbf{k}}$.

Proof:

$$\mathcal{F}\{f(\mathbf{r} - \mathbf{r}_0)\} = \int d^3\mathbf{r}\, f(\mathbf{r} - \mathbf{r}_0)e^{-i\mathbf{k}\cdot\mathbf{r}} = e^{-i\mathbf{k}\cdot\mathbf{r}_0}\hat{f}(\mathbf{k}).$$

The proof follows from a change of variable in the integral, which highlights that a translation in real space results in a phase shift in Fourier space, reflecting the invariance of the system's properties under translation.

9.18. Fock Space

We explore the fundamental concepts of Fock space and how it is used to derive the Fermi-Dirac and Bose-Einstein distributions. Fock space is a concept used in quantum mechanics to describe a quantum state of a variable number of particles. It is constructed as a direct sum of Hilbert spaces, each corresponding to a different number of particles.

9.18.1. Basis States. In Fock space, the basis states can be represented as occupation number states, which are denoted by kets like $|n_1, n_2, \ldots\rangle$. Each n_i in the ket represents the number of particles in the i-th quantum state. The basis states include:

- The vacuum state $|0, 0, \ldots\rangle$, indicating no particles in any state.
- One-particle states such as $|1, 0, \ldots\rangle$, $|0, 1, \ldots\rangle$, indicating a single particle in one of the quantum states.
- Two-particle states like $|2, 0, \ldots\rangle$, $|1, 1, \ldots\rangle$, and so on.

- Higher occupation number states representing more particles in various configurations.

9.18.2. Operators. Operators in Fock space can be one-body or two-body operators, and their action can be understood by considering the structure of Fock space.

9.18.2.1. *One-Body Operators.* For one-body operators, we only need to consider states with a single particle ($N = 1$). These operators act on kets with one particle, and their matrix elements can be written as:

$$O^{(1)}_{ij} = \langle 1; i|\hat{O}^{(1)}|1; j\rangle,$$

where $|1; i\rangle$ and $|1; j\rangle$ are shorthand for one-particle states in specific quantum states (i and j, respectively).

9.18.2.2. *Two-Body Operators.* For two-body operators, we consider states with two particles ($N = 2$). The action of two-body operators on kets with two particles is expressed as:

$$O^{(2)}_{ijkl} = \langle 2; ij|\hat{O}^{(2)}|2; kl\rangle,$$

where $|2; ij\rangle$ and $|2; kl\rangle$ are two-particle states (for states ij and kl, respectively).

9.18.2.3. *Resolution of the Identity.* The identity operator in Fock space, considering the structure of Fock space, can be expressed using a double summation:

$$\hat{I} = \sum_{N=0}^{\infty} \sum_{\{n_k\}, \sum n_k = N} |N; n_1, n_2, \ldots\rangle\langle N; n_1, n_2, \ldots|.$$

9.18.2.4. *Matrix Elements.* The resolution of the identity allows us to express the matrix elements of an operator $\hat{O}$ by sandwiching $\hat{O}$ between these identity operators, accounting for all possible particle numbers:

$$\begin{aligned}O_{ij} &= \langle i|\hat{I}\hat{O}\hat{I}|j\rangle\\ &= \sum_{N=0}^{\infty} \sum_{\{n_k\}, \sum n_k = N} \sum_{N'=0} \sum_{\{m_k\}, \sum m_k = N'}\\ &\qquad \langle i|N; n_1, n_2, \ldots\rangle\langle N; n_1, n_2, \ldots|\hat{O}|N'; m_1, m_2, \ldots\rangle\langle N'; m_1, m_2, \ldots|j\rangle.\end{aligned}$$

where i and j denote two arbitrary kets of our choosing. The matrix representation of an operator in Fock space takes into account the different possible numbers of particles. For a general operator $\hat{O}$, its matrix representation would involve summing over all possible occupation numbers, reflecting the infinite-dimensional nature of Fock space.

Example: The matrix representation of the outer product of vacuum states $|0\rangle\langle 0|$ is a matrix with all zero elements except for a 1 in the top-left corner. This matrix is infinite-dimensional and can be written as:

$$|0\rangle\langle 0| = \begin{pmatrix} 1 & 0 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

9.18.3. Trace of Operators.

9.18.3.1. *Trace of One-Body Operators.* For one-body operators, which act on individual particles, the trace in Fock space simplifies significantly. Considering a one-body operator $\hat{O}^{(1)}$, the trace over Fock space can be expressed as:

$$\mathrm{Tr}(\hat{O}^{(1)}) = \sum_{N=0}^{\infty} \sum_{\{n_k\}} \langle N; n_1, n_2, \ldots | \hat{O}^{(1)} | N; n_1, n_2, \ldots \rangle.$$

However, since $\hat{O}^{(1)}$ is a one-body operator, it only has a non-zero effect on the states with $N = 1$. Thus, the trace reduces to:

$$\mathrm{Tr}(\hat{O}^{(1)}) = \sum_i \langle 1; i | \hat{O}^{(1)} | 1; i \rangle,$$

where the summation is over all one-particle states.

9.18.3.2. *Trace of Two-Body Operators.* For two-body operators, which involve interactions between pairs of particles, the trace calculation is slightly more complex but still simplifies from the general form. For a two-body operator $\hat{O}^{(2)}$, the trace in Fock space is:

$$\mathrm{Tr}(\hat{O}^{(2)}) = \sum_{N=0}^{\infty} \sum_{\{n_k\}} \langle N; n_1, n_2, \ldots | \hat{O}^{(2)} | N; n_1, n_2, \ldots \rangle.$$

However, $\hat{O}^{(2)}$ only affects two-particle states, meaning the trace collapses to consider only states with $N = 2$:

$$\mathrm{Tr}(\hat{O}^{(2)}) = \sum_{i,j} \langle 2; ij | \hat{O}^{(2)} | 2; ij \rangle,$$

where the summation is over all pairs of two-particle states.

Trace Contributions of One-Body and Two-Body Operators in Fock Space. In the formalism of second quantization, the action of one-body and two-body operators on states in Fock space is governed by the algebra of creation and annihilation operators. We explore why one-body operators only contribute to the trace for single-particle states ($N = 1$) and two-body operators for two-particle states ($N = 2$).

One-Body Operators A one-body operator $\hat{O}^{(1)}$ in second quantization can be expressed as:

$$\hat{O}^{(1)} = \sum_{ij} O_{ij}^{(1)} \hat{a}_i^\dagger \hat{a}_j$$

Consider a Fock state $|n_1, n_2, \ldots\rangle$ with more than one particle ($N > 1$). The action of $\hat{O}^{(1)}$ on this state yields a linear combination of states where at most one particle's state is changed (e.g., a particle in state j is destroyed whereas one in state i is created). The inner product with any other N-particle state will vanish unless it differs by at most one single-particle state. Therefore, the trace contribution of $\hat{O}^{(1)}$ over states with $N > 1$ vanishes.

Example: For a two-particle state $|0, 2, \ldots\rangle$, the operator $\hat{a}_1^\dagger \hat{a}_2$ acting on it will produce a state $|1, 1, \ldots\rangle$ (if particles are distinguishable). The inner product of this state with any other two-particle state, like $|0, 2, \ldots\rangle$, will be zero, showing the vanishing trace contribution.

Two-Body Operators A two-body operator $\hat{O}^{(2)}$ can be written as:

$$\hat{O}^{(2)} = \frac{1}{2} \sum_{ijkl} O_{ijkl}^{(2)} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l$$

In the case of states with $N > 2$ or $N < 2$, the two-body operator either creates or annihilates more than two particles, resulting in states that have no overlap (non-zero inner product) with the original N-particle states. Consequently, the trace contributions from states with $N > 2$ or $N < 2$ are zero.

Example: For a three-particle state $|3\rangle$, the action of a two-body operator like $\hat{a}_1^\dagger \hat{a}_2 \hat{a}_3 \hat{a}_4$ will create or annihilate particles, leading to states with a different number of particles. These states will have zero overlap with any three-particle state, leading to a vanishing trace contribution.

Fermions: The trace of an operator in Fock space can be computed using a double summation over the total number of particles and over all kets with occupation numbers that add up to that total number. For fermions, the trace is computed using the eigenvalue relation of the number operator. The partition function Z for fermions is given by:

$$Z = \prod_i (1 + e^{-\beta \epsilon_i})$$

where β is $1/(k_B T)$ and ϵ_i are single-particle energies.

Bosons: For bosons, the trace is computed as:

$$Z = \prod_i \frac{1}{1 - e^{-\beta \epsilon_i}}$$

This is derived by summing over all possible occupation numbers for each state.

Fermi-Dirac Distribution: The Fermi-Dirac distribution gives the average number of fermions in a given energy state. It is derived from the partition function and given by:

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}$$

Bose-Einstein Distribution: The Bose-Einstein distribution gives the average number of bosons in a given energy state. It is derived from the partition function for bosons and is expressed as:

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}$$

Single Mode in Fock Space: The trace of an operator $\hat{O}$ in Fock space is calculated by summing the expectation values of $\hat{O}$ in all basis states:

$$\mathrm{Tr}(\hat{O}) = \sum_{N=0}^{\infty} \sum_{\{n_i\}} \langle n_1, n_2, \ldots | \hat{O} | n_1, n_2, \ldots \rangle$$

where $\{n_i\}$ denotes all possible sets of occupation numbers for N-photon states.

Consider a simplified Fock space with only one mode. The space is spanned by states $|n\rangle$ for n photons in this mode. For an operator $\hat{O}$, the trace is:

$$\mathrm{Tr}(\hat{O}) = \sum_{n=0}^{\infty} \langle n | \hat{O} | n \rangle.$$

Particularly for the number operator $\hat{n} = \hat{a}^\dagger \hat{a}$, this becomes:

$$\mathrm{Tr}(\hat{n}) = \sum_{n=0}^{\infty} n \langle n | n \rangle = \sum_{n=0}^{\infty} n.$$

This sum diverges, reflecting the unbounded nature of the photon number in this idealized scenario.

9.18.4. Structure of Fock Space. Fock space is the Hilbert space used to describe quantum states of a system with a variable number of identical particles, such as photons. In the case of photons, which are bosons, the Fock space is the direct sum of Hilbert spaces for each possible photon number. Fock space provides a framework for understanding the quantum states of such systems, including those of identical particles like bosons and fermions.

Mathematical Definition. Technically, Fock space $\mathcal{F}_\nu(H)$ is defined as the Hilbert space completion of the direct sum of symmetric or antisymmetric tensors in the tensor powers of a single-particle Hilbert space H:

$$\mathcal{F}_\nu(H) = \overline{\bigoplus_{n=0}^{\infty} S_\nu H^{\otimes n}}$$

where S_ν is the symmetrization (for bosons, $\nu = +$) or antisymmetrization (for fermions, $\nu = -$) operator, and $H^{\otimes n}$ represents the n-fold tensor product of H.

Fock Space for Bosons and Fermions. For bosons (resp. fermions), Fock space is constructed from the symmetric (resp. antisymmetric) tensors:

$$\mathcal{F}_+(H) = \overline{S^* H} \quad \text{(Bosons)}$$

$$\mathcal{F}_-(H) = \overline{\bigwedge^* H} \quad \text{(Fermions)}$$

Structure and States. The structure of Fock space can be described as follows:

- The space $\mathbb{C}$ consists of states corresponding to no particles (the vacuum state).
- H represents the states of one particle.
- $S_\nu(H \otimes H)$ represents the states of two identical particles, and so on.

A general state in Fock space is an infinite sum:

$$|\Psi\rangle_\nu = a|0\rangle \oplus \sum_i a_i |\psi_i\rangle \oplus \sum_{ij} a_{ij} |\psi_i, \psi_j\rangle_\nu \oplus \cdots$$

where $|\psi_i\rangle$ is a state in the single-particle Hilbert space, and a, a_i, a_{ij} are complex coefficients.

Inner Product and Norm. The inner product on Fock space is defined as:

$$\langle \Psi | \Phi \rangle_\nu := \sum_n \langle \Psi_n | \Phi_n \rangle_\nu$$

where $|\Psi_n\rangle, |\Phi_n\rangle$ are states in the n-particle Hilbert spaces. The n-particle norm is defined by the inner product, ensuring that the norm of the entire state is finite.

Orthogonality of Subspaces. The n-particle subspaces are orthogonal for different n, meaning states with different numbers of particles are orthogonal to each other in Fock space.

Worked Examples

Example 1: Vacuum State and Single Particle States
Consider a Fock space for a system of fermions. The vacuum state, denoted by $|0\rangle$, represents a state with no particles. It is the simplest element in Fock space.
Now, let's introduce a single-particle state $|\psi\rangle$ in the Hilbert space H. In Fock space, this state is represented simply by $|\psi\rangle$ itself, indicating the presence of one particle in state ψ. If we have another orthogonal single-particle state $|\phi\rangle$, the two-particle state formed by these particles would be represented by the antisymmetrized state $\frac{1}{\sqrt{2}}(|\psi\rangle \otimes |\phi\rangle - |\phi\rangle \otimes |\psi\rangle)$.

Example 2: Two Bosons in Different States
Consider a Fock space for bosons. Let $|\psi\rangle$ and $|\phi\rangle$ be two orthogonal single-particle states. The state with one particle in $|\psi\rangle$ and another in $|\phi\rangle$ is represented by the symmetrized state $\frac{1}{\sqrt{2}}(|\psi\rangle \otimes |\phi\rangle + |\phi\rangle \otimes |\psi\rangle)$. This state reflects the indistinguishable nature of the bosons and the requirement that their joint state must be symmetric under particle exchange.

Example 3: Inner Product in Fock Space
To illustrate the inner product in Fock space, consider two simple states: $|\Psi\rangle = |0\rangle \oplus |\psi\rangle$ and $|\Phi\rangle = |0\rangle \oplus |\phi\rangle$, where $|\psi\rangle$ and $|\phi\rangle$ are orthogonal single-particle states. The inner product $\langle\Psi|\Phi\rangle$ in Fock space is calculated as:

$$\langle\Psi|\Phi\rangle = \langle 0|0\rangle + \langle\psi|\phi\rangle = 1 + 0 = 1$$

since $\langle\psi|\phi\rangle = 0$ due to orthogonality.

Example 4: Two Fermions in a Superposition State
Consider a Fock space for fermions with two single-particle states $|\psi_1\rangle$ and $|\psi_2\rangle$. We construct a two-fermion state where each fermion is in a superposition of $|\psi_1\rangle$ and $|\psi_2\rangle$. The state is given by:

$$|\Psi\rangle = \frac{1}{2}\left(|\psi_1\rangle + |\psi_2\rangle\right) \otimes \left(|\psi_1\rangle - |\psi_2\rangle\right).$$

Antisymmetrizing this state results in:

$$|\Psi\rangle = \frac{1}{2\sqrt{2}}\left(|\psi_1, \psi_2\rangle - |\psi_2, \psi_1\rangle\right).$$

This example illustrates the complexity of constructing antisymmetrized states for fermions in superposition.

Example 5: Annihilation Operator Acting on a Two-Boson State
In the Fock space of bosons, consider the annihilation operator $\hat{a}$ associated with a single-particle state $|\phi\rangle$. Let's apply this operator to a two-boson state $|\Psi\rangle = |\phi, \phi\rangle$. The action of $\hat{a}$ is given by:

$$\hat{a}|\Psi\rangle = \sqrt{2}|\phi\rangle.$$

This demonstrates the effect of the annihilation operator in reducing the number of particles in a given state, along with the accompanying normalization factor.

Example 6: Particle Number Operator in a Mixed State
Consider a mixed state in the Fock space of fermions, described by a density matrix ρ. Suppose the system has a probability p of being in the one-fermion state $|\psi\rangle$ and $1-p$ in the two-fermion state $|\psi_1, \psi_2\rangle$. The density matrix is:

$$\rho = p|\psi\rangle\langle\psi| + (1-p)|\psi_1, \psi_2\rangle\langle\psi_1, \psi_2|.$$

The expectation value of the particle number operator $\hat{N}$ in this state is:

$$\langle\hat{N}\rangle = \mathrm{Tr}(\hat{N}\rho) = p\langle\psi|\hat{N}|\psi\rangle + (1-p)\langle\psi_1, \psi_2|\hat{N}|\psi_1, \psi_2\rangle$$

This example illustrates the calculation of expectation values in mixed states within Fock space.

The particle number operator $\hat{N}$ in Fock space is defined as the sum of the number operators for each mode or state. If $\hat{a}_i^\dagger$ and $\hat{a}_i$ are the creation and annihilation operators for the i-th mode, respectively, then the number operator for that mode is $\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i$. The total number operator is then given by:

$$\hat{N} = \sum_i \hat{n}_i = \sum_i \hat{a}_i^\dagger \hat{a}_i$$

This operator counts the total number of particles across all modes in the state it acts upon.

Example 7: Inner Product of Phonon States
Consider two phonon states in mode k, $|\phi_k\rangle = \hat{a}_k^\dagger|0\rangle$ and $|\phi'_k\rangle = \hat{a}_k^\dagger|0\rangle$. The inner product is:

$$\begin{aligned}
\langle\phi'_k|\phi_k\rangle &= \langle 0|\hat{a}_k \hat{a}_k^\dagger|0\rangle \\
&= \langle 0|(\hat{a}_k^\dagger \hat{a}_k + 1)|0\rangle \quad \text{(using commutation relation)} \\
&= \langle 0|0\rangle + \langle 0|\hat{a}_k^\dagger \hat{a}_k|0\rangle \\
&= 1 \quad (\text{since } \hat{a}_k|0\rangle = 0)
\end{aligned}$$

This calculation illustrates the orthonormality of single-phonon states.
Now, for different states:

$$\langle\phi_l|\phi_k\rangle = \langle 0|\hat{a}_l \hat{a}_k^\dagger|0\rangle = \langle 0|0\rangle = 0 \quad (\text{since } \hat{a}_l \hat{a}_k^\dagger = 0 \text{ for } l \neq k).$$

This illustrates the orthonormality of single-phonon states in different modes.

Example 8: Inner Product of Cooper Pair States
Consider two Cooper pair states, $|\text{Cooper}\rangle = \hat{b}^\dagger|0\rangle$ and $|\text{Cooper}'\rangle = \hat{b}^\dagger|0\rangle$, with $\hat{b}^\dagger = \hat{a}^\dagger_{k\uparrow}\hat{a}^\dagger_{-k\downarrow}$. The inner product is:

$$\begin{aligned}\langle\text{Cooper}'|\text{Cooper}\rangle &= \langle 0|\hat{b}\hat{b}^\dagger|0\rangle \\ &= \langle 0|\hat{a}_{-k\downarrow}\hat{a}_{k\uparrow}\hat{a}^\dagger_{k\uparrow}\hat{a}^\dagger_{-k\downarrow}|0\rangle \\ &= \langle 0|\hat{a}_{-k\downarrow}\hat{a}^\dagger_{-k\downarrow}|0\rangle \quad (\text{since } \hat{a}_{k\uparrow}\hat{a}^\dagger_{k\uparrow} = 1) \\ &= \langle 0|0\rangle = 1\end{aligned}$$

This demonstrates the orthonormality of Cooper pair states.
Now, for different states:

$$\langle\text{Cooper}_l|\text{Cooper}_k\rangle = \langle 0|\hat{b}_l\hat{b}^\dagger_k|0\rangle = 0 \quad (\text{as } \hat{b}_l \text{ and } \hat{b}^\dagger_k \text{ commute for } l \neq k).$$

This demonstrates the orthogonality of Cooper pair states in different momentum pairs.

Example 9: Inner Product in Fermionic Coherent States
Fermionic coherent states are given by $|\alpha\rangle = e^{\alpha\hat{a}^\dagger}|0\rangle$, where α is a Grassmann number. For fermions, the square of the creation operator is zero. Therefore, the state simplifies to $|\alpha\rangle = (1 + \alpha\hat{a}^\dagger)|0\rangle$.
Considering two different fermionic coherent states $|\alpha\rangle$ and $|\beta\rangle$, the inner product is:

$$\begin{aligned}\langle\beta|\alpha\rangle &= \langle 0|(1 + \beta^*\hat{a})(1 + \alpha\hat{a}^\dagger)|0\rangle \\ &= \langle 0|1 + \beta^*\alpha\hat{a}\hat{a}^\dagger|0\rangle \\ &= 1 + \beta^*\alpha\langle 0|\hat{a}\hat{a}^\dagger|0\rangle \\ &= 1 + \beta^*\alpha \quad (\text{since } \hat{a}|0\rangle = 0)\end{aligned}$$

This calculation directly uses the properties of fermionic operators and the Fock space inner product.

Example 10: Inner Product in Bosonic Coherent States
Consider two different bosonic coherent states $|\alpha\rangle$ and $|\beta\rangle$ in a single mode, where $|\alpha\rangle$ and $|\beta\rangle$ are generated by displacing the vacuum state by α and β respectively, with $\alpha, \beta \in \mathbb{C}$. The states are given by:

$$|\alpha\rangle = e^{-\frac{|\alpha|^2}{2}} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} (\hat{a}^\dagger)^n |0\rangle, \qquad |\beta\rangle = e^{-\frac{|\beta|^2}{2}} \sum_{n=0}^{\infty} \frac{\beta^n}{\sqrt{n!}} (\hat{a}^\dagger)^n |0\rangle.$$

The inner product between these states is:

$$\begin{aligned}
\langle\beta|\alpha\rangle &= \left(e^{-\frac{|\beta|^2}{2}} \sum_{m=0}^{\infty} \frac{(\beta^*)^m}{\sqrt{m!}} \langle 0|(\hat{a})^m \right) \left(e^{-\frac{|\alpha|^2}{2}} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} (\hat{a}^\dagger)^n |0\rangle \right) \\
&= e^{-\frac{|\alpha|^2}{2} - \frac{|\beta|^2}{2}} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(\beta^*)^m \alpha^n}{\sqrt{m! n!}} \langle 0|(\hat{a})^m (\hat{a}^\dagger)^n |0\rangle \\
&= e^{-\frac{|\alpha|^2}{2} - \frac{|\beta|^2}{2}} \sum_{n=0}^{\infty} \frac{(\beta^*)^n \alpha^n}{n!} \quad (\text{since } \langle 0|(\hat{a})^m (\hat{a}^\dagger)^n|0\rangle = n! \delta_{mn}) \\
&= e^{-\frac{|\alpha|^2}{2} - \frac{|\beta|^2}{2}} e^{\beta^* \alpha} = e^{\beta^* \alpha - \frac{|\alpha|^2 + |\beta|^2}{2}}.
\end{aligned}$$

This result demonstrates the overlap of bosonic coherent states and is a key characteristic in quantum optics.

In this last example, we could also have expressed the bosonic coherent states as $|\alpha\rangle = e^{\alpha \hat{a}^\dagger}|0\rangle$, where α is a complex number. For bosons, the creation operator can be raised to any power. Considering two different bosonic coherent states $|\alpha\rangle$ and $|\beta\rangle$, the inner product is:

$$\langle\beta|\alpha\rangle = \langle 0|e^{\beta^* \hat{a}} e^{\alpha \hat{a}^\dagger}|0\rangle = e^{-\frac{|\alpha|^2}{2} - \frac{|\beta|^2}{2}} \sum_{m,n=0}^{\infty} \frac{(\beta^*)^m \alpha^n}{\sqrt{m! n!}} \langle 0|(\hat{a})^m (\hat{a}^\dagger)^n |0\rangle = e^{\beta^* \alpha - \frac{|\alpha|^2 + |\beta|^2}{2}}.$$

Example 11: Trace of a Density Operator in Quantum Optics
Consider a thermal light field described by the density operator ρ at temperature T. The Hamiltonian $\hat{H}$ of the harmonic oscillator is $\hat{H} = \hbar\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2})$, where $\hat{a}^\dagger$ and $\hat{a}$ are the creation and annihilation operators, and ω is the frequency of the oscillator. The density operator in the thermal state is given by:

$$\rho = \frac{1}{Z}e^{-\beta\hat{H}},$$

with $\beta = \frac{1}{k_B T}$ and Z being the partition function.
To compute the trace of ρ using coherent states, we use the integral representation:

$$\mathrm{Tr}(\rho) = \int \frac{d^2\alpha}{\pi}\langle\alpha|\rho|\alpha\rangle,$$

where $|\alpha\rangle$ are the coherent states of the light field.
The integral is computed as follows:

$$\begin{aligned}\mathrm{Tr}(\rho) &= \int \frac{d^2\alpha}{\pi}\langle\alpha|\frac{1}{Z}e^{-\beta\hat{H}}|\alpha\rangle = \frac{1}{Z}\int\frac{d^2\alpha}{\pi}e^{-\alpha^*\alpha}\langle\alpha|e^{-\beta\hbar\omega(\hat{a}^\dagger\hat{a}+\frac{1}{2})}|\alpha\rangle \\ &= \frac{1}{Z}\int\frac{d^2\alpha}{\pi}e^{-\alpha^*\alpha}e^{-\frac{1}{2}\beta\hbar\omega}\langle\alpha|e^{-\beta\hbar\omega\hat{a}^\dagger\hat{a}}|\alpha\rangle. \quad \text{(disentangling the exponential)}\end{aligned}$$

The remaining integral involves evaluating the matrix element $\langle\alpha|e^{-\beta\hbar\omega\hat{a}^\dagger\hat{a}}|\alpha\rangle$, which can be done using the properties of coherent states and the harmonic oscillator.

Part 2 of Example 11:
We continue from where we left off, calculating the matrix element $\langle\alpha|e^{-\beta\hbar\omega\hat{a}^\dagger\hat{a}}|\alpha\rangle$ for a coherent state $|\alpha\rangle$ in quantum optics.
First, recall that a coherent state $|\alpha\rangle$ is an eigenstate of the annihilation operator $\hat{a}$ with eigenvalue α:

$$\hat{a}|\alpha\rangle = \alpha|\alpha\rangle.$$

Using this property, we can simplify the matrix element as follows:

$$\begin{aligned}\langle\alpha|e^{-\beta\hbar\omega\hat{a}^\dagger\hat{a}}|\alpha\rangle &= \langle\alpha|e^{-\beta\hbar\omega\alpha^*\hat{a}}|\alpha\rangle \quad (\text{since } \hat{a}^\dagger\hat{a}|\alpha\rangle = \alpha^*\hat{a}|\alpha\rangle)\\ &= e^{-\beta\hbar\omega\alpha^*\alpha}\langle\alpha|\alpha\rangle \quad (\text{using the eigenvalue equation})\\ &= e^{-\beta\hbar\omega|\alpha|^2}.\end{aligned}$$

This result reflects the property of coherent states being eigenstates of the annihilation operator.
Substituting this back into the integral for the trace, we get:

$$\mathrm{Tr}(\rho) = \frac{1}{Z}\int\frac{d^2\alpha}{\pi}e^{-\alpha^*\alpha}e^{-\frac{1}{2}\beta\hbar\omega}e^{-\beta\hbar\omega|\alpha|^2} = \frac{1}{Z}e^{-\frac{1}{2}\beta\hbar\omega}\int\frac{d^2\alpha}{\pi}e^{-\alpha^*\alpha(1+\beta\hbar\omega)}.$$

This integral can be evaluated using Gaussian integration techniques, leading to the final result for the trace.

Part 3 of Example 11:
Continuing from the previous steps, we have the integral:

$$\mathrm{Tr}(\rho) = \frac{1}{Z} e^{-\frac{1}{2}\beta\hbar\omega} \int \frac{d^2\alpha}{\pi} e^{-\alpha^*\alpha(1+\beta\hbar\omega)}.$$

This integral is over the complex plane, so we can write $\alpha = x + iy$ and $d^2\alpha = dx\,dy$. The integral becomes:

$$\begin{aligned}\mathrm{Tr}(\rho) &= \frac{1}{Z} e^{-\frac{1}{2}\beta\hbar\omega} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{dx\,dy}{\pi} e^{-(x^2+y^2)(1+\beta\hbar\omega)} \\ &= \frac{1}{Z} e^{-\frac{1}{2}\beta\hbar\omega} \frac{1}{\pi} \int_{-\infty}^{\infty} e^{-x^2(1+\beta\hbar\omega)} dx \int_{-\infty}^{\infty} e^{-y^2(1+\beta\hbar\omega)} dy.\end{aligned}$$

Both integrals are Gaussian integrals of the form $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$ for $a > 0$. Thus, we get:

$$\mathrm{Tr}(\rho) = \frac{1}{Z} e^{-\frac{1}{2}\beta\hbar\omega} \frac{1}{\pi} \left(\sqrt{\frac{\pi}{1+\beta\hbar\omega}}\right)^2 = \frac{1}{Z} e^{-\frac{1}{2}\beta\hbar\omega} \frac{1}{1+\beta\hbar\omega}.$$

Finally, the partition function Z for a single harmonic oscillator is $Z = \mathrm{Tr}(e^{-\beta\hat{H}}) = \frac{1}{1-e^{-\beta\hbar\omega}}$, so the trace of ρ simplifies to:

$$\mathrm{Tr}(\rho) = 1,$$

which is expected, as the trace of a density operator should be 1 in a normalized quantum system.

Example 12: Trace in Path Integral Formulation
In quantum field theory, the partition function Z at finite temperature can be expressed as a trace over coherent states in the path integral formulation. Consider a quantum field described by the Hamiltonian $\hat{H}$.
The partition function is given by:

$$Z = \mathrm{Tr}(e^{-\beta \hat{H}}) = \int \mathcal{D}\phi \, \langle \phi | e^{-\beta \hat{H}} | \phi \rangle,$$

where $|\phi\rangle$ represents coherent states of the field, and $\mathcal{D}\phi$ is a functional integration over all field configurations.
The calculation involves:

$$Z = \int \mathcal{D}\phi \, \langle \phi | e^{-\beta \hat{H}} | \phi \rangle = \int \mathcal{D}\phi \, e^{-\beta \langle \phi | \hat{H} | \phi \rangle} \quad \text{(using the coherent state representation).}$$

This integral sums over all possible field configurations $|\phi\rangle$, weighted by the exponential of the negative Hamiltonian.
This example illustrates the use of coherent states in the path integral formulation to compute the partition function in quantum field theory, providing a bridge between quantum mechanics and statistical mechanics.

Part 2 of Example 12:
The matrix element for the harmonic oscillator Hamiltonian in a coherent state $|\phi\rangle$ is:

$$\langle \phi | e^{-\beta \hat{H}} | \phi \rangle = \langle \phi | e^{-\beta \hbar \omega (\hat{a}^\dagger \hat{a} + \frac{1}{2})} | \phi \rangle.$$

Expanding the exponential and using the property $\hat{a}|\phi\rangle = \phi|\phi\rangle$, we get:

$$\langle \phi | e^{-\beta \hat{H}} | \phi \rangle = e^{-\frac{1}{2}\beta \hbar \omega} \langle \phi | e^{-\beta \hbar \omega \hat{a}^\dagger \hat{a}} | \phi \rangle = e^{-\frac{1}{2}\beta \hbar \omega} e^{-\beta \hbar \omega |\phi|^2}.$$

The partition function Z is then:

$$Z = \int \mathcal{D}\phi \, e^{-\frac{1}{2}\beta \hbar \omega} e^{-\beta \hbar \omega |\phi|^2} = e^{-\frac{1}{2}\beta \hbar \omega} \int \frac{d^2\phi}{\pi} e^{-\beta \hbar \omega |\phi|^2} = e^{-\frac{1}{2}\beta \hbar \omega} \frac{1}{\beta \hbar \omega}.$$

This integral is evaluated in a similar manner to Gaussian integrals, and the result gives the partition function for a single-mode harmonic oscillator in quantum field theory.

Mathematical Proof: Simplification of Path Integral for Harmonic Oscillator

Consider a single-mode quantum harmonic oscillator with Hamiltonian

$$\hat{H} = \hbar\omega(\hat{a}^\dagger \hat{a} + \frac{1}{2}),$$

where $\hat{a}^\dagger$ and $\hat{a}$ are creation and annihilation operators.

Step 1: Time-Independent Hamiltonian and Thermal State

Since the Hamiltonian is time-independent and we are considering a thermal state, the partition function at temperature T (or inverse temperature $\beta = \frac{1}{k_B T}$) is given by

$$Z = \mathrm{Tr}(e^{-\beta \hat{H}}).$$

Step 2: Coherent States as Eigenstates

Coherent states $|\alpha\rangle$ are eigenstates of the annihilation operator $\hat{a}$:

$$\hat{a}|\alpha\rangle = \alpha|\alpha\rangle.$$

Therefore, for a coherent state $|\alpha\rangle$, the action of $e^{-\beta \hat{H}}$ simplifies as

$$\langle\alpha|e^{-\beta\hat{H}}|\alpha\rangle = e^{-\frac{1}{2}\beta\hbar\omega}\langle\alpha|e^{-\beta\hbar\omega\hat{a}^\dagger\hat{a}}|\alpha\rangle = e^{-\frac{1}{2}\beta\hbar\omega}e^{-\beta\hbar\omega|\alpha|^2}.$$

Step 3: Integral Over Coherent States

The partition function becomes

$$Z = \int \frac{d^2\alpha}{\pi}\langle\alpha|e^{-\beta\hat{H}}|\alpha\rangle = e^{-\frac{1}{2}\beta\hbar\omega}\int \frac{d^2\alpha}{\pi}e^{-\beta\hbar\omega|\alpha|^2}.$$

Step 4: Gaussian Integral

The integral over α (a complex number) is a Gaussian integral in the complex plane, which can be evaluated directly without the need for time-slicing:

$$Z = e^{-\frac{1}{2}\beta\hbar\omega}\int \frac{d^2\alpha}{\pi}e^{-\beta\hbar\omega|\alpha|^2} = e^{-\frac{1}{2}\beta\hbar\omega}\frac{1}{\beta\hbar\omega}.$$

This demonstrates that for a time-independent Hamiltonian in a thermal state, particularly for a single-mode quantum harmonic oscillator, the path integral simplifies to a Gaussian integral over coherent states. This simplification bypasses the need for time-slicing, typical in path integrals for time-dependent quantum field theory problems.

9.19. Coherent States

9.19.1. Bosonic Coherent States. Bosonic coherent states are known for their classical-like properties, particularly having well-defined phase and amplitude. This can be mathematically demonstrated by examining the properties of these states.

A coherent state $|\alpha\rangle$ is defined as an eigenstate of the annihilation operator $\hat{a}$:

$$\hat{a}|\alpha\rangle = \alpha|\alpha\rangle$$

where α is a complex number. Coherent states can be expressed in terms of the number basis as:

$$|\alpha\rangle = e^{-\frac{|\alpha|^2}{2}} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle.$$

The complex number α can be written in polar form as $\alpha = |\alpha| e^{i\theta}$, where $|\alpha|$ is the amplitude and θ is the phase.

The expectation values of the position $\hat{x}$ and momentum $\hat{p}$ operators in a coherent state provide insight into its classical-like nature.

The position operator in the harmonic oscillator basis is $\hat{x} = x_0(\hat{a} + \hat{a}^\dagger)$, where $x_0 = \sqrt{\hbar/2m\omega}$. The expectation value of $\hat{x}$ in the coherent state is:

$$\begin{aligned}
\langle \hat{x} \rangle &= \langle \alpha | x_0(\hat{a} + \hat{a}^\dagger) | \alpha \rangle \\
&= x_0(\alpha + \alpha^*) \\
&= 2x_0 |\alpha| \cos(\theta)
\end{aligned}$$

This shows that the position expectation value oscillates with an amplitude of $2x_0|\alpha|$ and a phase of θ, resembling a classical wave.

Similarly, for the momentum operator $\hat{p} = -i\hbar(\hat{a} - \hat{a}^\dagger)/2x_0$, the expectation value is:

$$\begin{aligned}
\langle \hat{p} \rangle &= \langle \alpha | - i\hbar(\hat{a} - \hat{a}^\dagger)/2x_0 | \alpha \rangle \\
&= -i\hbar(\alpha - \alpha^*)/2x_0 \\
&= \hbar |\alpha| \sin(\theta)/x_0
\end{aligned}$$

The momentum expectation value also exhibits oscillatory behavior, consistent with a classical wave.

The above derivation shows that bosonic coherent states are characterized by well-defined phase and amplitude. The expectation values of position and momentum operators oscillate in a manner analogous to a classical wave, thus demonstrating the classical-like properties of coherent states.

9.19.2. Displacement Operator. Bosonic coherent states can be defined in two ways: as an eigenstate of the annihilation operator, and as the result of applying the displacement operator to the vacuum state. We'll show the equivalence of these definitions.

The coherent state $|\alpha\rangle$ is defined as an eigenstate of the annihilation operator $\hat{a}$:

$$|\alpha\rangle = e^{-\frac{|\alpha|^2}{2}} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle$$

The displacement operator $\hat{D}(\alpha)$ is defined as:

$$\hat{D}(\alpha) = \exp(\alpha\hat{a}^\dagger - \alpha^*\hat{a})$$

The coherent state can also be defined as:

$$|\alpha\rangle = \hat{D}(\alpha)|0\rangle$$

where $|0\rangle$ is the vacuum state.

We aim to show that applying the displacement operator to the vacuum state yields the same result as the eigenstate definition.

The displacement operator can be expanded using the Baker-Campbell-Hausdorff formula:

$$\hat{D}(\alpha) = \exp(\alpha\hat{a}^\dagger - \alpha^*\hat{a}) = \exp(-\frac{|\alpha|^2}{2})\exp(\alpha\hat{a}^\dagger)\exp(-\alpha^*\hat{a})$$

Applying $\hat{D}(\alpha)$ to the vacuum state:

$$\begin{aligned}\hat{D}(\alpha)|0\rangle &= \exp(-\frac{|\alpha|^2}{2})\exp(\alpha\hat{a}^\dagger)\exp(-\alpha^*\hat{a})|0\rangle \\ &= \exp(-\frac{|\alpha|^2}{2})\exp(\alpha\hat{a}^\dagger)|0\rangle \quad (\text{since } \exp(-\alpha^*\hat{a})|0\rangle = |0\rangle)\end{aligned}$$

Now, expand $\exp(\alpha\hat{a}^\dagger)$:

$$\begin{aligned}\exp(\alpha\hat{a}^\dagger)|0\rangle &= \sum_{n=0}^{\infty}\frac{(\alpha\hat{a}^\dagger)^n}{n!}|0\rangle \\ &= \sum_{n=0}^{\infty}\frac{\alpha^n}{n!}(\hat{a}^\dagger)^n|0\rangle \\ &= \sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|n\rangle\end{aligned}$$

Combining the results, we get:

$$|\alpha\rangle = e^{-\frac{|\alpha|^2}{2}}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|n\rangle.$$

This matches the eigenstate definition of the coherent state.

Thus, we have shown the equivalence of the two definitions of a bosonic coherent state. The coherent state as defined by the displacement operator acting on the vacuum state indeed yields the same result as the eigenstate definition.

9.19.3. Expansion Using BCH Formula. To expand the displacement operator $\hat{D}(\alpha)$ using the Baker-Campbell-Hausdorff formula, consider:

$$\hat{D}(\alpha) = \exp(\alpha\hat{a}^\dagger - \alpha^*\hat{a})$$

where $\hat{a}$ and $\hat{a}^\dagger$ are the annihilation and creation operators, respectively.

The BCH formula states that for operators A and B, if $[A,[A,B]] = [B,[A,B]] = 0$, then:

$$e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]}.$$

For the creation and annihilation operators, we have:

$$[\hat{a}, \hat{a}^\dagger] = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1$$

since the creation and annihilation operators obey the bosonic commutation relation $[\hat{a}, \hat{a}^\dagger] = 1$.

Let $A = \alpha\hat{a}^\dagger$ and $B = -\alpha^*\hat{a}$. Then, the commutator $[A, B]$ is:

$$[A,B] = [\alpha\hat{a}^\dagger, -\alpha^*\hat{a}] = -\alpha\alpha^*[\hat{a}^\dagger, \hat{a}] = -|\alpha|^2.$$

Applying the BCH formula:

$$\begin{aligned}\hat{D}(\alpha) &= \exp(\alpha\hat{a}^\dagger - \alpha^*\hat{a}) \\ &= \exp(\alpha\hat{a}^\dagger)\exp(-\alpha^*\hat{a})\exp(-\frac{1}{2}[-|\alpha|^2]) \\ &= \exp(\alpha\hat{a}^\dagger)\exp(-\alpha^*\hat{a})\exp(\frac{|\alpha|^2}{2})\end{aligned}$$

Therefore, the displacement operator $\hat{D}(\alpha)$ can be expanded as:

$$\hat{D}(\alpha) = \exp(\frac{|\alpha|^2}{2})\exp(\alpha\hat{a}^\dagger)\exp(-\alpha^*\hat{a}).$$

This expansion is crucial in the context of quantum optics and the study of coherent states.

9.19.4. Quantum Field Operators and Hamiltonian Formulation. Quantum field operators play a crucial role in quantum field theory, facilitating the description of particle creation and annihilation. Here, we define these operators and show how they are used to construct Hamiltonians.

The annihilation operator $\hat{a}_k$ is defined as:

$$\hat{a}_k|n_k\rangle = \sqrt{n_k}|n_k - 1\rangle.$$

It reduces the number of particles in the state k by one.

The creation operator $\hat{a}_k^\dagger$ is defined as:

$$\hat{a}_k^\dagger|n_k\rangle = \sqrt{n_k + 1}|n_k + 1\rangle.$$

It increases the number of particles in the state k by one.

The quantum field operator $\hat{\Psi}(\mathbf{r})$ at position $\mathbf{r}$ is expressed as:

$$\hat{\Psi}(\mathbf{r}) = \sum_k \phi_k(\mathbf{r})\hat{a}_k$$

where $\phi_k(\mathbf{r})$ is the mode function for the state k.

The kinetic energy term in the Hamiltonian is:

$$\hat{H}_{\text{kinetic}} = \int d^3r\, \hat{\Psi}^\dagger(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \hat{\Psi}(\mathbf{r}).$$

For an external potential $V(\mathbf{r})$:

$$\hat{H}_{\text{potential}} = \int d^3r\, V(\mathbf{r})\hat{\Psi}^\dagger(\mathbf{r})\hat{\Psi}(\mathbf{r}).$$

Combining kinetic and potential energy terms:

$$\hat{H} = \hat{H}_{\text{kinetic}} + \hat{H}_{\text{potential}} = \int d^3r\, \hat{\Psi}^\dagger(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right) \hat{\Psi}(\mathbf{r}).$$

Consider the Hamiltonian for a free particle in a box:

$$\hat{H} = \int d^3r\, \hat{\Psi}^\dagger(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \hat{\Psi}(\mathbf{r}).$$

Substituting the field operator expansion:

$$\hat{H} = \int d^3r \left(\sum_k \phi_k^*(\mathbf{r})\hat{a}_k^\dagger\right) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \left(\sum_l \phi_l(\mathbf{r})\hat{a}_l\right).$$

This expression can be further simplified by considering orthonormal mode functions and the properties of creation and annihilation operators.

9.19.5. Free Particle Hamiltonian in Quantum Field Theory. To simplify the Hamiltonian for a free particle in quantum field theory, we consider the orthonormal mode functions and the properties of creation and annihilation operators.

The Hamiltonian for a free particle expressed in terms of quantum field operators is:

$$\hat{H} = \int d^3r \left(\sum_k \phi_k^*(\mathbf{r})\hat{a}_k^\dagger\right) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \left(\sum_l \phi_l(\mathbf{r})\hat{a}_l\right).$$

The mode functions $\phi_k(\mathbf{r})$ are assumed to be orthonormal, satisfying:

$$\int d^3r\, \phi_k^*(\mathbf{r})\phi_l(\mathbf{r}) = \delta_{kl}$$

where δ_{kl} is the Kronecker delta.

Applying the orthonormality condition, the Hamiltonian becomes:

$$\begin{aligned}\hat{H} &= \sum_{k,l} \int d^3r\, \phi_k^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \phi_l(\mathbf{r}) \hat{a}_k^\dagger \hat{a}_l \\ &= \sum_{k,l} \hat{a}_k^\dagger \hat{a}_l \int d^3r\, \phi_k^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \phi_l(\mathbf{r}) \\ &= \sum_k \epsilon_k \hat{a}_k^\dagger \hat{a}_k\end{aligned}$$

where ϵ_k is the energy of mode k.

The final form of the Hamiltonian, representing the total energy of the system, is:

$$\hat{H} = \sum_k \epsilon_k \hat{a}_k^\dagger \hat{a}_k.$$

This expression shows the energy of each mode k multiplied by the number operator $\hat{a}_k^\dagger \hat{a}_k$, which counts the number of particles in that mode.

This derivation illustrates how the use of orthonormal mode functions and the properties of creation and annihilation operators simplify the Hamiltonian of a quantum field. The result is a concise expression that captures the essential quantum nature of the system.

9.19.6. Second Quantization of a Hamiltonian with Coulomb Interaction. In second quantization, a Hamiltonian including a two-body interaction, such as the Coulomb interaction, can be expressed using quantum field operators. This approach is fundamental in many-body quantum mechanics.

Consider field operators $\hat{\Psi}(\mathbf{r})$ and $\hat{\Psi}^\dagger(\mathbf{r})$ which annihilate and create a particle at position $\mathbf{r}$, respectively.

The Coulomb interaction between two charged particles is given by:

$$V(\mathbf{r}, \mathbf{r}') = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}$$

where e is the elementary charge and ϵ_0 is the vacuum permittivity.

The Hamiltonian for a system of particles including the Coulomb interaction can be written as:

$$\hat{H} = \hat{H}_{\text{kinetic}} + \hat{H}_{\text{Coulomb}}$$

where $\hat{H}_{\text{kinetic}}$ is the kinetic energy term.

The kinetic energy term in second quantization is:

$$\hat{H}_{\text{kinetic}} = \int d^3r\, \hat{\Psi}^\dagger(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \hat{\Psi}(\mathbf{r}).$$

The Coulomb interaction term in second quantization is:

$$\hat{H}_{\text{Coulomb}} = \frac{1}{2}\int d^3r \int d^3r' \, \hat{\Psi}^\dagger(\mathbf{r})\hat{\Psi}^\dagger(\mathbf{r'})V(\mathbf{r},\mathbf{r'})\hat{\Psi}(\mathbf{r'})\hat{\Psi}(\mathbf{r}).$$

Expanding the field operators in terms of creation and annihilation operators:

$$\hat{\Psi}(\mathbf{r}) = \sum_k \phi_k(\mathbf{r})\hat{a}_k, \quad \hat{\Psi}^\dagger(\mathbf{r}) = \sum_l \phi_l^*(\mathbf{r})\hat{a}_l^\dagger$$

where $\phi_k(\mathbf{r})$ are the mode functions.

Substituting into the Coulomb term and simplifying:

$$\begin{aligned}\hat{H}_{\text{Coulomb}} &= \frac{1}{2}\sum_{k,l,m,n}\int d^3r \int d^3r' \, \phi_k^*(\mathbf{r})\phi_l^*(\mathbf{r'})V(\mathbf{r},\mathbf{r'})\phi_m(\mathbf{r'})\phi_n(\mathbf{r})\hat{a}_k^\dagger\hat{a}_l^\dagger\hat{a}_m\hat{a}_n \\ &= \frac{1}{2}\sum_{k,l,m,n} V_{klmn}\hat{a}_k^\dagger\hat{a}_l^\dagger\hat{a}_m\hat{a}_n\end{aligned}$$

where V_{klmn} represents the matrix elements of the Coulomb interaction.

This derivation shows the second quantization form of a Hamiltonian including a two-body Coulomb interaction term. The final expression involves sums over creation and annihilation operators for each mode, representing the quantized nature of particle interactions in the system.

9.19.7. Coulomb Interaction Matrix Elements in Plane Wave Basis. In a plane wave basis, particles are described by wavefunctions that are plane waves. This allows for a more tractable calculation of the Coulomb interaction matrix elements V_{klmn}.

In a plane wave basis, the wavefunctions are of the form:

$$\phi_k(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

where $\mathbf{k}$ is the wavevector and V is the normalization volume.

The Coulomb interaction matrix elements are defined as:

$$V_{klmn} = \int d^3r \int d^3r' \, \phi_k^*(\mathbf{r})\phi_l^*(\mathbf{r'})\frac{e^2}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r'}|}\phi_m(\mathbf{r'})\phi_n(\mathbf{r}).$$

Expanding the plane wave states and performing the integration, we have:

$$\begin{aligned}V_{klmn} &= \frac{e^2}{4\pi\epsilon_0 V^2}\int d^3r \int d^3r' \, e^{-i\mathbf{k}\cdot\mathbf{r}}e^{-i\mathbf{l}\cdot\mathbf{r'}}\frac{1}{|\mathbf{r}-\mathbf{r'}|}e^{i\mathbf{m}\cdot\mathbf{r'}}e^{i\mathbf{n}\cdot\mathbf{r}} \\ &= \frac{e^2}{4\pi\epsilon_0 V^2}\int d^3r \int d^3r' \, \frac{e^{i(\mathbf{m}-\mathbf{l})\cdot\mathbf{r'}}e^{i(\mathbf{n}-\mathbf{k})\cdot\mathbf{r}}}{|\mathbf{r}-\mathbf{r'}|}\end{aligned}$$

This integral can be further simplified using Fourier transform techniques.

The Coulomb potential's Fourier transform is:

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} \to \frac{4\pi}{q^2}$$

where $q = |\mathbf{m}-\mathbf{l}| = |\mathbf{n}-\mathbf{k}|$ is the magnitude of the momentum transfer.

Substituting this back into the expression for V_{klmn}, we obtain:

$$V_{klmn} = \frac{e^2}{V^2}\frac{(2\pi)^6\delta(\mathbf{k}+\mathbf{l}-\mathbf{m}-\mathbf{n})}{|\mathbf{m}-\mathbf{l}|^2}$$

This expression represents the Coulomb interaction matrix elements in the plane wave basis, revealing the momentum conservation (through the delta function) and the dependence on the momentum transfer.

The calculation of the Coulomb interaction matrix elements in the plane wave basis illustrates the use of Fourier transform techniques in simplifying the interaction term. It highlights the importance of conservation laws and momentum transfer in quantum interactions.

9.20. Quantization of the Radiation Field

9.20.1. Lagrangian for Electromagnetic Field in SI Units. In SI units, the Lagrangian density for the electromagnetic field is given by the difference between the electric and magnetic field energy densities:

$$\ell = \frac{\varepsilon_0}{2}\mathbf{E}^2 + \frac{1}{2\mu_0}\mathbf{B}^2$$

where $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic fields, respectively, ε_0 is the vacuum permittivity, and μ_0 is the vacuum permeability. Integrating this density over a volume V gives the total Lagrangian:

$$\mathcal{L} = \int_V \left(\frac{\varepsilon_0}{2}\mathbf{E}^2 + \frac{1}{2\mu_0}\mathbf{B}^2\right) dV$$

Expressing E and B in terms of Potentials: In SI units, the electric and magnetic fields can be expressed in terms of the vector potential $\mathbf{A}$ and the scalar potential ϕ as follows:

$$\mathbf{E} = -\nabla\phi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}$$

These expressions allow us to rewrite the fields in the Lagrangian in terms of the potentials. Substituting these into the Lagrangian yields:

$$\mathcal{L} = \int_V \left(\frac{\varepsilon_0}{2}\left(-\nabla\phi - \frac{\partial \mathbf{A}}{\partial t}\right)^2 - \frac{1}{2\mu_0}\left(\nabla \times \mathbf{A}\right)^2\right) dV$$

9.20.2. Applying the Coulomb Gauge. The Coulomb gauge is a specific choice of gauge in electromagnetism that simplifies the mathematical treatment of the electromagnetic fields. This gauge is defined by the condition:

$$\nabla \cdot \mathbf{A} = 0$$

where $\mathbf{A}$ is the vector potential. This condition has significant implications when applied to Maxwell's equations.

Gauss's Law in the Absence of Charges: Gauss's law for electricity, one of Maxwell's equations, in the absence of charges is given by:

$$\nabla \cdot \mathbf{E} = 0$$

In terms of the scalar potential ϕ and the vector potential $\mathbf{A}$, the electric field $\mathbf{E}$ is expressed as $\mathbf{E} = -\nabla\phi - \frac{\partial \mathbf{A}}{\partial t}$. Substituting this expression for $\mathbf{E}$ into Gauss's law gives:

$$\nabla \cdot \left(-\nabla\phi - \frac{\partial \mathbf{A}}{\partial t} \right) = 0$$

Expanding the divergence, we have:

$$-\nabla^2\phi - \nabla \cdot \frac{\partial \mathbf{A}}{\partial t} = 0$$

Applying the Coulomb gauge condition $\nabla \cdot \mathbf{A} = 0$ leads to

$$\nabla^2\phi = 0.$$

This is Laplace's equation, which governs the behavior of the scalar potential ϕ in the absence of charges.

Implications for the Scalar Potential: In many practical electromagnetic problems, especially those involving fields in free space or in a perfect cavity, the scalar potential ϕ can be taken as zero or a constant. This is because the general solution to Laplace's equation in a region without sources (charges) is a constant. Therefore, the scalar potential ϕ effectively drops out of the electromagnetic field expressions, simplifying the analysis and leaving the vector potential $\mathbf{A}$ as the primary contributor to the fields.

In the absence of charges and currents (as in free space or in a perfect cavity), the scalar potential ϕ satisfies the Laplace equation $\nabla^2\phi = 0$. The solution to this equation in a source-free region is a constant, which can be set to zero without loss of generality. Therefore, the scalar potential ϕ effectively drops out of the Lagrangian, leaving us with:

$$\mathcal{L} = \int \left\{ \frac{\varepsilon_0}{2} \left(-\frac{\partial \mathbf{A}}{\partial t} \right)^2 + \frac{1}{2\mu_0} \left(\nabla \times \mathbf{A} \right)^2 \right\} dV$$

Here, ε_0 is the vacuum permittivity and μ_0 is the vacuum permeability. The Lagrangian now depends only on the vector potential $\mathbf{A}$ and its time derivative.

9.20.3. Legendre Transformation to Hamiltonian. The process of obtaining the Hamiltonian from the Lagrangian involves defining the conjugate momentum and then performing the Legendre transformation.

Definition of Conjugate Momentum: The conjugate momentum Π corresponding to the vector potential $\mathbf{A}$ is defined as the derivative of the Lagrangian with respect to the time derivative of $\mathbf{A}$. Given the Lagrangian density for the electromagnetic field is:

$$\ell = \frac{\varepsilon_0}{2}\left(\frac{\partial \mathbf{A}}{\partial t}\right)^2 - \frac{1}{2\mu_0}\left(\nabla \times \mathbf{A}\right)^2$$

where ε_0 is the vacuum permittivity, and μ_0 is the vacuum permeability. The conjugate momentum is then defined as:

$$\Pi = \frac{\partial \ell}{\partial(\frac{\partial \mathbf{A}}{\partial t})} = \varepsilon_0 \frac{\partial \mathbf{A}}{\partial t}$$

Construction of the Hamiltonian: The Hamiltonian $\mathcal{H}$ is constructed using the Legendre transformation:

$$\mathcal{H} = \int \Pi \cdot \frac{\partial \mathbf{A}}{\partial t}\, dV - \mathcal{L}$$

Substituting the expression for Π into the Hamiltonian, we get:

$$\mathcal{H} = \int \left(\varepsilon_0 \frac{\partial \mathbf{A}}{\partial t}\right) \cdot \frac{\partial \mathbf{A}}{\partial t}\, dV - \int \ell \, dV = \int \left(\frac{\varepsilon_0}{2}\left(\frac{\partial \mathbf{A}}{\partial t}\right)^2 + \frac{1}{2\mu_0}\left(\nabla \times \mathbf{A}\right)^2\right) dV.$$

This Hamiltonian represents the total energy of the electromagnetic field in terms of the vector potential $\mathbf{A}$ and its partial time derivative.

9.20.4. Fourier Expansion of A and Π. In quantum field theory, the vector potential $\mathbf{A}$ and its conjugate momentum Π are expanded in terms of Fourier series using complex exponential functions. This method is particularly useful as it simplifies the analysis and is more suitable for describing wave-like phenomena.

Expansion using Exponential Functions: The Fourier expansion of $\mathbf{A}$ and Π in terms of complex exponential functions is given as follows:

The vector potential A is expanded as:

$$\mathbf{A}(\mathbf{x}, t) = \sum_{\mathbf{k},\lambda} \left[a_{\mathbf{k},\lambda}(t)\, e^{i\mathbf{k}\cdot\mathbf{x}} \epsilon_{\mathbf{k},\lambda} + a^{\dagger}_{\mathbf{k},\lambda}(t)\, e^{-i\mathbf{k}\cdot\mathbf{x}} \epsilon^{*}_{\mathbf{k},\lambda}\right]$$

where $\mathbf{k}$ is the wave vector, λ denotes the polarization, and $\epsilon_{\mathbf{k},\lambda}$ are polarization vectors.

Similarly, the conjugate momentum Π, in SI units, is expanded as:

$$\Pi(\mathbf{x}, t) = \varepsilon_0 \sum_{\mathbf{k},\lambda} \left[\dot{a}_{\mathbf{k},\lambda}(t)\, e^{i\mathbf{k}\cdot\mathbf{x}} \epsilon_{\mathbf{k},\lambda} + \dot{a}^{\dagger}_{\mathbf{k},\lambda}(t)\, e^{-i\mathbf{k}\cdot\mathbf{x}} \epsilon^{*}_{\mathbf{k},\lambda}\right]$$

Here, $\dot{a}_{\mathbf{k},\lambda}(t)$ and $\dot{a}^{\dagger}_{\mathbf{k},\lambda}(t)$ represent the time derivatives of the expansion coefficients.

Derivatives $\dot{\mathbf{A}}$ and $\nabla \times \mathbf{A}$: The time derivative of A is given by:

$$\dot{\mathbf{A}}(\mathbf{x},t) = \sum_{\mathbf{k},\lambda} \left[\dot{a}_{\mathbf{k},\lambda}(t)\, e^{i\mathbf{k}\cdot\mathbf{x}} \epsilon_{\mathbf{k},\lambda} + \dot{a}^{\dagger}_{\mathbf{k},\lambda}(t)\, e^{-i\mathbf{k}\cdot\mathbf{x}} \epsilon^{*}_{\mathbf{k},\lambda} \right]$$

And the curl of $\mathbf{A}$ is:

$$\nabla \times \mathbf{A}(\mathbf{x},t) = \sum_{\mathbf{k},\lambda} i\mathbf{k} \times \left[a_{\mathbf{k},\lambda}(t)\, e^{i\mathbf{k}\cdot\mathbf{x}} \epsilon_{\mathbf{k},\lambda} - a^{\dagger}_{\mathbf{k},\lambda}(t)\, e^{-i\mathbf{k}\cdot\mathbf{x}} \epsilon^{*}_{\mathbf{k},\lambda} \right]$$

Substitution and Simplification: Substituting $\dot{\mathbf{A}}$ and $\nabla \times \mathbf{A}$ into the Hamiltonian, we get:

$$\begin{aligned} \mathcal{H} = {} & \frac{\varepsilon_0}{2} \int \left(\sum_{\mathbf{k},\lambda} \left[\dot{a}_{\mathbf{k},\lambda}(t)\, e^{i\mathbf{k}\cdot\mathbf{x}} \epsilon_{\mathbf{k},\lambda} + \dot{a}^{\dagger}_{\mathbf{k},\lambda}(t)\, e^{-i\mathbf{k}\cdot\mathbf{x}} \epsilon^{*}_{\mathbf{k},\lambda} \right] \right)^2 dV \\ & + \frac{1}{2\mu_0} \int \left(\sum_{\mathbf{k},\lambda} i\mathbf{k} \times \left[a_{\mathbf{k},\lambda}(t)\, e^{i\mathbf{k}\cdot\mathbf{x}} \epsilon_{\mathbf{k},\lambda} - a^{\dagger}_{\mathbf{k},\lambda}(t)\, e^{-i\mathbf{k}\cdot\mathbf{x}} \epsilon^{*}_{\mathbf{k},\lambda} \right] \right)^2 dV \end{aligned}$$

The integrals in the Hamiltonian can be simplified using the properties of Fourier series and the orthogonality of the complex exponential functions. After simplification, the Hamiltonian will be expressed in terms of the coefficients $a_{\mathbf{k},\lambda}$ and $a^{\dagger}_{\mathbf{k},\lambda}$.

Evaluating the Integrals: The simplification involves evaluating the integrals over the volume V. The key property used here is the orthogonality of the complex exponential functions, which states that for different wave vectors $\mathbf{k}$ and $\mathbf{k}'$:

$$\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}}\, dV = 0 \quad \text{if} \quad \mathbf{k} \neq \mathbf{k}'$$

This property ensures that when we square the sums in the Hamiltonian, only terms with the same $\mathbf{k}$ and λ will contribute to the integral, as all other cross terms will cancel out.

Squaring the Sums: The Hamiltonian contains squared sums of the Fourier expansions of $\dot{\mathbf{A}}$ and $\nabla \times \mathbf{A}$. We need to square these sums and then simplify. For the time derivative of A, we have:

$$\begin{aligned} \left(\frac{\partial \mathbf{A}}{\partial t} \right)^2 &= \left(\sum_{\mathbf{k},\lambda} \left[\dot{a}_{\mathbf{k},\lambda}(t)\, e^{i\mathbf{k}\cdot\mathbf{x}} \epsilon_{\mathbf{k},\lambda} + \dot{a}^{\dagger}_{\mathbf{k},\lambda}(t)\, e^{-i\mathbf{k}\cdot\mathbf{x}} \epsilon^{*}_{\mathbf{k},\lambda} \right] \right)^2 \\ &= \sum_{\mathbf{k},\lambda} \sum_{\mathbf{k}',\lambda'} \left[\dot{a}_{\mathbf{k},\lambda} \dot{a}_{\mathbf{k}',\lambda'} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{x}} \epsilon_{\mathbf{k},\lambda} \epsilon_{\mathbf{k}',\lambda'} + \cdots \right] \end{aligned}$$

Similarly, for the curl of $\mathbf{A}$, we have:

$$\begin{aligned}(\nabla \times \mathbf{A})^2 &= \left(\sum_{\mathbf{k},\lambda} i\mathbf{k} \times \left[a_{\mathbf{k},\lambda}(t)\, e^{i\mathbf{k}\cdot\mathbf{x}} \epsilon_{\mathbf{k},\lambda} - a^\dagger_{\mathbf{k},\lambda}(t)\, e^{-i\mathbf{k}\cdot\mathbf{x}} \epsilon^*_{\mathbf{k},\lambda}\right]\right)^2 \\ &= \sum_{\mathbf{k},\lambda} \sum_{\mathbf{k}',\lambda'} \left[(i\mathbf{k} \times a_{\mathbf{k},\lambda} e^{i\mathbf{k}\cdot\mathbf{x}} \epsilon_{\mathbf{k},\lambda}) \cdot (i\mathbf{k}' \times a_{\mathbf{k}',\lambda'} e^{i\mathbf{k}'\cdot\mathbf{x}} \epsilon_{\mathbf{k}',\lambda'}) + \cdots\right]\end{aligned}$$

Applying Orthogonality: The simplification of these expressions uses the orthogonality of the complex exponential functions. This orthogonality leads to the cancellation of terms where $\mathbf{k} \neq \mathbf{k}'$, simplifying the sums significantly. We are left with terms where $\mathbf{k} = \mathbf{k}'$ and $\lambda = \lambda'$.

Final Hamiltonian: After applying the orthogonality conditions and performing the necessary integrations, the Hamiltonian becomes:

$$\mathcal{H} = \sum_{\mathbf{k},\lambda} \left[\frac{\varepsilon_0}{2} |\dot{a}_{\mathbf{k},\lambda}(t)|^2 + \frac{1}{2\mu_0} |\mathbf{k} \times \epsilon_{\mathbf{k},\lambda}|^2 |a_{\mathbf{k},\lambda}(t)|^2\right]$$

This expression represents the total energy of the electromagnetic field, summed over all modes indexed by wave vector $\mathbf{k}$ and polarization λ. The terms involving $\dot{a}_{\mathbf{k},\lambda}$ and $a_{\mathbf{k},\lambda}$ correspond to the contributions of the electric and magnetic fields, respectively.

After obtaining the classical Hamiltonian for the electromagnetic field, the next step is to transform it into its second-quantized form. This involves promoting the classical field amplitudes to quantum operators.

Quantization: In the second quantization, the classical field amplitudes $a_{\mathbf{k},\lambda}$ and $a^\dagger_{\mathbf{k},\lambda}$ are replaced by quantum field operators $\hat{a}_{\mathbf{k},\lambda}$ and $\hat{a}^\dagger_{\mathbf{k},\lambda}$. These operators satisfy the commutation relations:

$$\begin{aligned}&[\hat{a}_{\mathbf{k},\lambda}, \hat{a}^\dagger_{\mathbf{k}',\lambda'}] = \delta_{\mathbf{k},\mathbf{k}'}\delta_{\lambda,\lambda'}, \\ &[\hat{a}_{\mathbf{k},\lambda}, \hat{a}_{\mathbf{k}',\lambda'}] = [\hat{a}^\dagger_{\mathbf{k},\lambda}, \hat{a}^\dagger_{\mathbf{k}',\lambda'}] = 0.\end{aligned}$$

Time-Harmonic Assumption: In the classical Hamiltonian, the amplitudes $a_{\mathbf{k},\lambda}(t)$ are assumed to have a time-harmonic form, i.e., they vary as $e^{-i\omega_{\mathbf{k},\lambda}t}$. This assumption simplifies the time derivatives:

$$\dot{a}_{\mathbf{k},\lambda}(t) = -i\omega_{\mathbf{k},\lambda} a_{\mathbf{k},\lambda}(t)$$

Thus, the kinetic energy term $|\dot{a}_{\mathbf{k},\lambda}(t)|^2$ in the classical Hamiltonian becomes proportional to $\omega^2_{\mathbf{k},\lambda} |a_{\mathbf{k},\lambda}(t)|^2$.

Energy of Each Mode: The energy of each mode of the electromagnetic field is related to its frequency. For a mode with wave vector $\mathbf{k}$ and polarization λ, the energy is proportional to the frequency $\omega_{\mathbf{k},\lambda}$, which is related to the magnitude of $\mathbf{k}$.

Second-Quantized Form: The second-quantized form of the Hamiltonian is obtained by substituting these operators into the classical Hamiltonian expression. The final second-quantized Hamiltonian for the electromagnetic field is:

$$\hat{\mathcal{H}} = \sum_{\mathbf{k},\lambda} \left[\frac{\varepsilon_0}{2} \dot{\hat{a}}^\dagger_{\mathbf{k},\lambda} \dot{\hat{a}}_{\mathbf{k},\lambda} + \frac{1}{2\mu_0} |\mathbf{k} \times \epsilon_{\mathbf{k},\lambda}|^2 \hat{a}^\dagger_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda} \right]$$

where $\dot{\hat{a}}_{\mathbf{k},\lambda}$ and $\dot{\hat{a}}^\dagger_{\mathbf{k},\lambda}$ are the time derivatives of the quantum field operators.

In this form, the Hamiltonian describes the energy of the quantized electromagnetic field in terms of photons. Each term in the sum corresponds to the energy contribution of a photon with wave vector $\mathbf{k}$ and polarization λ. The operators $\hat{a}^\dagger_{\mathbf{k},\lambda}$ and $\hat{a}_{\mathbf{k},\lambda}$ can be interpreted as creating and annihilating photons, respectively. This Hamiltonian forms the basis for studying quantum electromagnetic phenomena and the interaction of light and matter at the quantum level.

Final Form: It can be shown that the final form in second quantization is given by:

$$\hat{\mathcal{H}} = \sum_{\mathbf{k},\lambda} \hbar\omega_{\mathbf{k},\lambda} \hat{a}^\dagger_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda} \tag{9.21}$$

This Hamiltonian represents the total energy of the quantized electromagnetic field. Each term in the sum corresponds to the energy of a photon mode with wave vector $\mathbf{k}$ and polarization λ, where $\hat{a}^\dagger_{\mathbf{k},\lambda}$ and $\hat{a}_{\mathbf{k},\lambda}$ are the creation and annihilation operators for the photons in that mode. This can be seen by noting that $|\mathbf{k} \times \epsilon_{\mathbf{k},\lambda}|^2$ is proportional to $\omega^2_{\mathbf{k},\lambda}$. This final form of the Hamiltonian represents the total energy of the quantized electromagnetic field, with each term corresponding to the energy of a photon mode. We recall that the speed of light in vacuum is related to ε_0 (vacuum permittivity) and μ_0 (vacuum permeability) by:

$$c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}.$$

This relationship implies that $\varepsilon_0 \mu_0 = \frac{1}{c^2}$.

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