

Foreword

In the present book we discuss various problems of the existing nucleation theories and a new common microscopic (nonempirical) approach to overcome them. First, basic statements of the classical nucleation theory (CNT) as well as the quasichemical one are reviewed to demonstrate the internal difficulties of these agreed-upon approaches. Furthermore, a lot of experimental results on condensation in nozzles, jets, thermal diffusion chambers etc. are discussed that so far have not been explained in the frame of CNT. This is made in order to introduce our main idea which we discussed for many years with our colleagues that it is impossible (or, at least, very hard) to surmount these problems working at the level of macroscopic description of the condensible gas.

Here we describe a possibility to solve the problems stated accounting for nonequilibrium excitation of the cluster internal degrees of freedom and its influence on condensation kinetics. Below a new approach which we conventionally named a “microscopic condensation theory” (MCT) is presented. The basic statements of the theory proposed are described as well as the comparison with the existing models is given. We demonstrate that there is a natural explanation of the mentioned experimental facts within the frameworks of this new theory of condensation. Comparison with the experiment is made on the basis of scaling relations of the condensation processes, that are also discussed here.

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Dedication

We devote this book to our parents who first inspired us that science as well as the other general human values keep their significance at any time.

Preface

The present work summarizes certain results of the authors' activity on creating a new theory of condensation which makes an impact on consideration of some microscopic effects left aside in the usual nucleation theories. In particular, the main idea of our microscopic condensation theory (MCT) is that it considers the violation of the equilibrium cluster distribution over the internal degrees of freedom due to co-occurring condensation and decay reactions of the clusters.

In this section we would like to give the extended contents of the work and describe its structure. In our opinion, reader should read this section in order to decide which chapter of the book is useful or interesting to him. We could suggest the following scheme:

- for experimenters - chapter ??, sections ??.??, ??.??, ??.??, conclusions;
- for physicians-theoreticians - all sections except Appendices and, perhaps sections ??.??, ??.??;
- for mathematicians - all sections except, perhaps sections ??.??, ??.??;
- for engineers and programmers - sections ??.??, ??.?? and, perhaps, Appendix ??.

For the last group of readers we present the FORTRAN code which makes it possible to compute the condensation processes in various systems and devices based upon our approach.

The structure of the paper logically reproduces stages of the new theory development. The following aspects are discussed consequently:

1. Firstly, a brief review of the quasicheical and classical nucleation theories (CNT) is given that leads to the necessity to elaborate a new one. In addition, we bring a lot of experimental results on condensation in nozzles, jets, thermal diffusion chambers etc. that cannot be explained in the framework of the existing nucleation theories.

2. Further we put in the basis of our new theory governing kinetic equations for populations of the intermolecular vibrations of clusters and explore their equilibrium and quasisteady solutions. The equilibrium distribution obtained here exists both in the stable and metastable areas and describes an equilibrium phase transition at crossing the coexisting curve. In addition, all parameters of our equilibrium function are obviously expressed through microscopic parameters of condensible molecules. In what follows we discussed in detail why our global equilibrium distribution is distinguished from the cluster equilibrium function usually exploited by CNT.
3. In the subsequent chapter an analytical asymptotic solution of the system proposed is obtained both for populations and concentrations of the clusters. In the case of rapid relaxation of monomers all these variables can be expressed in terms of supersaturation S and the gas temperature T . It can be shown that the kinetic equation for concentrations of clusters of size $j < R$ (R being a parameter of MCT) strongly differ from the quasichemical ones. Finally in this way one is allowed to solve the only kinetic equation for S further analytically restoring the cluster size distribution function.
4. In order to make our theory suitable for practical applications we propose a new approach for calculating the rate constant of the unimolecular decay of clusters which appeared in our reduced kinetic equation, developing the RRKM theory for such a case. Based on the result obtained while using the microscopic reversibility law and the expressions for the equilibrium cluster concentrations¹ we have got a rate constant of the reverse process — the growth of cluster gaining a single molecule. The ratio of this constant and a free molecular flux on the cluster surface gives the value of the cluster condensation coefficient α depending upon the cluster size j and T . In the limit of high j we get the extreme value of α . When carrying out this idea a model representation of clusters as “loosen complexes” is employed to account for an anharmonicity of the intermolecular vibrations and free rotations of dissociated fragments around the axis perpendicular to the reaction coordinate. In addition, some physical assumptions are made to obtain an analytical expression of the constants considered. In particular: i) We divide all intermolecular vibrations in the cluster into librational and translational ones replacing all normal mode frequencies of each group with the average one. ii) The activation energy of the molecule leaving the cluster depends upon j be-

cause its average number of bonds $y(j)$ with the other molecules in the cluster depends on j . For instance, for small water clusters having a ring structure $y(j) = 2$ and having a linear structure - $y(j) = 1$ though the maximum number of the hydrogenous bonds for the water molecule in a large cluster is equal to 4. Accounting for this fact we introduce the simplest approximation for $y(j)$. The final expressions for the rate constants of unimolecular decay and formation of the neutral cluster with size j as well as for the condensation coefficients are presented in the book. Note that for the large cluster the condensation coefficient does not depend on j . The explicit expression of R also follows from this method. In addition, in this way the rate constants of formation and decay for cluster's ions can be obtained. In such a case the dissociation energy in addition depends upon the sign and value of the ion charge.

5. In the next chapter in order to verify the theory developed and to understand how it regards to the existing theories we analyze the CNT assumptions from the standpoint of the results obtained. After that we bring a short summary of our main results and the basic formulae which allow the reader which is not interested in these details or has no background in this field to utilize these expressions "as they are" in practical computing left aside all the other material of this work.
6. The next step is concerned with the comparison between our prediction and the experimental data for nozzles, jets, thermal diffusion chambers and mixtures of the vapor with a carrier gas. Certainly, first of all it requires to generalize our method for the condensable vapor flows in such devices that is done at the beginning of that chapter. After that it turns out that the comparison made shows a good agreement of our prediction with the gas parameters in the Wilson point for water, argon, nitrogen, moist air especially for regimes where the existing theories were failed. In addition it is shown that the experimental data obtained at the condensation study in nozzles, jets and thermal diffusion chambers can be quite naturally interpreted within the framework of MCT ²⁻⁷. The comparison with the experiment was made using the scaling of condensation processes the basic statements of which are given in ⁸⁻¹¹.

It should be noted that in the framework of MCT there is no so-called "Lothe-Pound paradox". Indeed, we determine the equilibrium cluster distribution in a similar manner like Lothe and Pound based upon the micromolecular approach. However, our prediction of the condensable

gas parameters made with the help of MCT which uses our equilibrium function, demonstrates a good agreement with the experimental data for many substances. Moreover, the most important fact is that these substances include those for which the Lothe and Pound theory prediction strongly differs from the available data of experiments.

7. As a consequent generalization of MCT we describe a new theory of heterogeneous condensation on charged particles — ions and electrons. Since 1899 when Wilson observed this phenomenon it has been well known that the rate of water vapor condensation is dramatically accelerated in the presence of free electrons. So far the adequate theory of such processes was absent but in the existing attempts to describe it based on the classical nucleation theory all restrictions of CNT are presented. Therefore, we demonstrate the effectiveness of developing the heterogeneous condensation theory on the basis of the consistent theory of homogeneous condensation.

In doing that we consider the kinetic equation describing simultaneously condensation and relaxation processes as well as recombination and ionization of molecules and clusters. However, the cluster ions having two or more charges were left aside. In addition, we take into account only formation and decay of clusters gaining or losing a single molecule or ion. We derive common expressions for the equilibrium cluster concentrations and populations of the energetic levels of intermolecular vibrations both for the neutral and charged clusters as well as for monomers, free ions and electrons. To reduce them to the explicit form within the simplest model the charged particle is assumed to be located in the center of the cluster, all clusters are suggested to have a shape close to a sphere, the influence of the electric field of an ion on frequencies of the intermolecular vibrations and the gas polarization is omitted but the contribution of the spontaneous polarization of the cluster molecules is taken into account.

The analysis of the results obtained follows the well known phenomenon that there is a situation when the vapor in an equilibrium state without ions and electrons becomes the supersaturated one in their presence. Using the ideas of MCT we have managed to find an analytical representation for all populations and concentrations of the neutral and charged clusters through the gas temperature and three supersaturations of the neutral molecules, free ions and electrons, respectively^{12,13}. For these variables the closed system of the ordinary differential equations is derived admitting both a numerical solution and a qualitative analysis. In

particular, an example of the test calculations of the gas flow with heterogeneous condensation is given. The analysis of the equations obtained gave an interesting result. It turns out that the condensation process on ions is extraordinary different from condensation on electrons. It can be shown that the rate of condensation depends upon the sign of the spontaneous polarization. For water vapor this sign coincides with the sign of the electron charge and condensation elapses immediately after the moment when the vapor becomes supersaturated. The typical value of supersaturation in the Wilson point in such a case is about 1.1 although in the absence of electrons it is about 5–6. This result is in good agreement with the Wilson data. On the contrary the positive ions weakly influence the water condensation.

8. The subsequent chapter is devoted to the generalization of the model for photonucleation. In such a case clusters with different electronic and vibrational states have to be taken into account. It is shown that the common approach of MCT allows one to interpret the experimental data qualitatively.
9. Another aspect of the problem — how to control the condensation process. For example, for modern technologies it is very important to produce clusters of certain sizes and properties for many substances. The well known source of clusters is the gas streams in nozzles and jets. So far there was a complexity to measure experimentally the cluster size distribution function (CSDF) especially for the large clusters. However, the possibility to predict the CSDF form theoretically is also very limited in the framework of both CNT (because of some of its artificial assumptions) and the quasichemical model (a numerical calculation of the time-dependent CSDF for a multidimensional flow requires very powerful computers). In the present report we demonstrate the advantage of our model for computing the condensable gas flows in nozzles and jets. As a typical example results of numerical simulation of the two-dimensional water vapor flow with condensation in a supersonic nozzle with a wall bend are presented that allow one, in principle, to draw mass fractions for any size of clusters existing in the stream. It turns out that the shock wave created by the wall's bend considerably affects the condensation. Thus, there appears a new possibility to control CSDF varying the nozzle contour in a certain manner.

Let us mention that besides the experiments described here there exists an

extensive available but non-systematized experimental material on nucleation in thermal diffusion chambers. The generalization of theoretical representations of MCT for TDC and the comparison of our prediction obtained in such a way with the experimental results ¹⁴⁻¹⁶ was given in ⁷ in detail and in the present book we only describe these results briefly.

In conclusion we should recommend the readers who are only interested in applications to skip the chapters where the equilibrium and quasisteady solutions are considered.

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Chapter 1

Kinetic theory of ion-induced nucleation

In this chapter we describe briefly a new theory of ion-induced nucleation. Since 1899 when Wilson observed this phenomenon it has been well known that the rate of water vapor condensation is dramatically accelerated in the presence of free electrons, however so far there has been no adequate theory of such processes. In the existing attempts to describe it based on CNT all restrictions of CNT are presented.

Heterogeneous condensation accompanies a number of processes because real condensing gases not subject by a special purification always contain contaminants (dust particles, ions, ionic complexes, aerosols, etc.). Generally speaking, the number of admixture types may be high enough, and hence conceivable mechanisms of heterogeneous condensation are very diverse. An adequate theory of these processes is not complete yet. One of the possible reason is that this macroscopic theory must describe a great variety of the processes caused by interactions between the condensible molecules and a surface of heterogeneous centers, namely: adsorption, desorption, surface diffusion, relaxation of various degrees of freedom etc. Thus, heterogeneous condensation on ions can be considered as one of the rare fairly simple cases.

Our approach which is described below is a generalization of MCT. In what follows the main principles of the theory are formulated (see also ^{12,17,13}) and a diversity between heterogeneous condensation on positive and negative ions is explained.

1. Short review of the existing approaches

Heterogeneous condensation on ions has been studied in several works (see reviews ¹⁸ and ^{19–23}). We shall briefly discuss their main results. It is commonly accepted in these works that an individual cluster can be considered as a thermodynamic system. Vapor condensation on an ion results in formation of a cluster whose core is an ion of a given radius r_a , and the work of formation of this cluster is

$$\Delta G_i = \frac{4\pi}{3v_1} (r^3 - r_a^3) (\mu_v - \mu_l) + 4\pi (r^2 - r_a^2) \sigma + \frac{e^2}{2} \left(\frac{1}{\epsilon_v} - \frac{1}{\epsilon_l} \right) \left(\frac{1}{r} - \frac{1}{r_a} \right). \quad (1.1)$$

Here e is the charge of the electron, i is the number of molecules incorporated in the cluster, r is the cluster radius, μ_v and μ_l are the chemical potentials of the vapor and liquid, σ is the surface tension, v_1 is the effective volume of a molecule in the liquid and ϵ_v and ϵ_l are the dielectric permittivities of the vapor and liquid, respectively. The heterogeneous nucleus of the size equilibrated with the surrounding vapor is defined by the condition $\partial \Delta G_i / \partial i = 0$, or

$$\mu_v - \mu_l + \frac{2\sigma v_1}{r} - \frac{e^2 v_1}{8\pi r^4} \left(\frac{1}{\epsilon_v} - \frac{1}{\epsilon_l} \right) = 0. \quad (1.2)$$

This equation has two roots: r_a and $r_* > r_a$. Values of r_* and the rate of formation of these critical nuclei I can be found based on the concept of the classical homogeneous condensation theory

$$\begin{aligned} I &= 4\pi r_*^2 Z_c \alpha_c P_v (2\pi m_1 k_B T)^{-1/2} \frac{P_v}{k_B T} \exp\left(-\frac{\Delta G_*}{k_B T}\right), \\ \Delta G_* &= \frac{4\pi}{3} (r_*^3 - r_a^3) \sigma + \frac{2e^2}{3} \left(\frac{1}{\epsilon_v} - \frac{1}{\epsilon_l} \right) \left(\frac{1}{r_*} - \frac{1}{r_a} \right), \\ Z_c &= \left\{ \frac{1}{9\pi k_B T i_*^2} \left[4\pi \sigma r_*^2 - \frac{e^2}{r_*} \left(\frac{1}{\epsilon_v} - \frac{1}{\epsilon_l} \right) \right] \right\}^{1/2}, \\ i_* m_1 &= \frac{4\pi r_*^2}{3v_1}. \end{aligned} \quad (1.3)$$

Here α_c is the condensation coefficient, m_1 is the molecular weight, P_v and T are the vapor pressure and temperature, and k_B is the Boltzmann constant. Equation (1.3) is insensitive to the sign of the ion charge. To remove this disadvantage White and Kasner ²⁴ modified the electrostatic term to take into account dipole–dipole and dipole–quadrupole interactions between molecules

being condensed. Numerical calculations carried out in ²⁴ qualitatively describe the effect of the ion charge sign on the nucleation rate.

The above cited approaches developed to solve the problem of heterogeneous nucleation are based on the classical ideas of the crucial role played by the critical nucleus in the condensation kinetics. Because of this, they suffer all the shortcomings of the classical nucleation theory primarily associated with difficulties in substantiating the basic assumptions introduced in the theory and with the procedure used to derive the formula for the rate of formation of the critical nuclei Eq. (1.3). These shortcomings were discussed in the previous sections of this book. For this reason, of importance is the development of more consistent theoretical models of heterogeneous condensation. One of such approaches based on the quasichemical model was suggested in ²³. The appropriate kinetic equations were solved assuming a linear dependence of the rate constant for formation and decomposition of clusters on the number of molecules in them and the final solution was written as a series in terms of the Wittaker functions. The author of ²³ studied a particular class of canonically invariant solutions obtained with specially selected initial size distribution of the clusters.

Despite the attractiveness of the approach suggested in ²³, it should be emphasized that its results are valid only within the applicability limits of the quasichemical condensation model that disregards nonequilibrium distribution of the cluster internal energy. Moreover, the case with a linear correlation between the rate constant and the number of molecules in the cluster is of purely academic interest whereas an extension of the procedure proposed in ²³ for solving the kinetic equations to dependencies of other types causes difficulties. Finally, no allowance was made in ²³ for the formation of homogeneous clusters along with heterogeneous aggregates. An attempt to overcome these disadvantages leads to an idea of developing a theory of heterogeneous condensation on ions based on generalization of our microscopic condensation theory. These problems are discussed in the following sections of this chapter.

2. Formulation of the problem

We consider a spatially uniform system consisting of N molecules confined in volume V . The system is a mixture of ideal molecular and cluster gases. The volume also contains Ω admixture positive ions that are either present as free particles or may be incorporated in some clusters. We assume that the system is quasineutral, i.e. it also contains Ω electrons which either exist in the form of

free particles or are incorporated in some clusters. The ensemble of these ions, electrons and mixed clusters is assumed to be an ideal gas. We consider the cases in which translational and rotational relaxation of all molecular and ion components is so fast that we can introduce a single translational-rotational temperature of the mixture T . This supposition may not hold for very large clusters or nucleation centers. But the concentration of such clusters is low, therefore the single-temperature approximation must at least not affect the integral characteristics of the system. As for the electron gas, its temperature T_e may significantly differ from T . We also assume that T and T_e vary with time slowly.

The vibrational energy distribution in clusters may be essentially nonequilibrium when the rate of vibrational transitions between the upper levels is comparable with the rate of the cluster formation and decomposition. The problems relevant to description of the vibrational degrees of freedom of clusters have already been discussed in the previous chapters. We use the results reported there which demonstrate that with no admixture particles the state of the particles in the studied system can be specified by their total vibrational energy, and the state of the whole system — by a set of number densities $x_j(k) = N_j(k)/V$, where $N_j(k)$ with $j = 1, \dots, N$ and $k = 0, \dots, G_j$, is the number of homogeneous clusters comprising j molecules and possessing the vibrational energy $E_j(k)$. In what follows, the term “homogeneous cluster” means a cluster consisting of only vapor molecules. Clusters containing admixture particles (ions and electrons) will be referred to as heterogeneous ones. In the presence of ions and electrons one should obviously take into account the mixed clusters comprising j vapor molecules and several admixture species. In this work for the sake of simplicity we confine ourselves to a model which considers only those heterogeneous clusters that contain either an admixture ion or an electron. Their populations are denoted by $y_j(k)$ and $z_j(k)$, where $y_0(k)$ is the populations of the vibrational states of free ions, $z_0(0) = z_0$ is the number density of free electrons and $z_0(k) = 0$ at $k \neq 0$.

In further calculations we neglect collisions between the clusters and a possible formation (or decomposition) of a cluster by attaching a dimer, trimer etc. The three-body collisions are also disregarded. Furthermore, we assume that the probability of an ion or electron attachment to a heterogeneous cluster is low²⁰. Finally, we consider only the case where the processes of recombination and ionization can be neglected for all particles.

Based on the results obtained earlier let the mixture of clusters be characterized by a set of numerical densities $x_j^\nu(k)$ where superscript $\nu = 0$ denotes the homogeneous clusters, $\nu = e$ — the heterogeneous ones including an ad-

ditional electron (electronic clusters) and $\nu = i$ — the heterogeneous clusters with an additional positive ion (ionic clusters), G_j^ν denotes the topmost energetic level of the corresponding cluster. In particular, $x_1^i(k)$ is a population of the vibrational states of free ions, $x_1^e(0) \equiv x_1^e$ — a concentration of free electrons; by definition $x_1^e(k) \equiv 0$ if $k \neq 0$. Governing equations describing the evolution of the mixture are the following

$$\frac{dx_j^\nu(k)}{dt} = J_j^\nu(k) + I_j^\nu(k), \quad j \geq 2. \quad (1.4)$$

In Eq. (1.4) the first term describes processes of collisional relaxation of the cluster vibrational energy, the second one — a variation of the cluster populations due to condensation and evaporation. In detail they can be written as follows

$$\begin{aligned} J_j^\nu(k) &= \sum_{\mu} J_j^{\nu\mu}(k) \equiv \sum_{\mu} \sum_{l,i,m} J_j^{\nu\mu}(l,i|k,m) \\ I_j^\nu(k) &= I_{j-1}^{\nu 0}(k) - I_j^{\nu 0}(k) + I_j^{0\nu}(k)(1 - \delta_{\nu 0}) - \sum_{\mu=e,i} I_j^{\nu\mu}(k)\delta_{0\nu}, \end{aligned} \quad (1.5)$$

where

$$\begin{aligned} I_{j-1}^{\nu\mu}(k) &= \sum_{l,i} I_{j-1}^{\nu\mu}(l,i|k)(1 + \delta_{j1}\delta_{li}) \\ J_j^{\nu\mu}(l,i|k,m) &= R_j^{\nu\mu}(l,i|k,m)\bar{x}_j^\nu(l)\bar{x}_1^\mu(i) - R_j^{\nu\mu}(k,m|l,i)\bar{x}_j^\nu(k)\bar{x}_1^\mu(m) \\ I_{j-1}^{\nu 0}(l,i|k) &= C_{j-1}^{\nu 0}(l,i|k)\bar{x}_{j-1}^\nu(l)\bar{x}_1^0(i) - E_j^{\nu 0}(k|i,l)\bar{x}_j^\nu(k), \quad \nu = 0, e, i \\ I_j^{0\mu}(l,i|k) &= C_j^{0\mu}(l,i|k)\bar{x}_j^0(l)\bar{x}_1^\mu(i) - E_{j+1}^{0\mu}(k|i,l)\bar{x}_{j+1}^\mu(k), \quad \mu = i, e. \end{aligned} \quad (1.6)$$

Equations for monomers, free ions and electrons can be written in the form

$$\begin{aligned} \frac{dx_1^0(k)}{dt} &= - \sum_j \sum_{\nu} \bar{I}_j^{\nu 0}(k) - \sum_j \sum_{\nu} \bar{J}_j^{\nu 0}(k) \\ \frac{dx_1^\mu(k)}{dt} &= - \sum_j \bar{I}_j^{0\mu}(k) - \sum_j \sum_{\nu} \bar{J}_j^{\nu\mu}(k), \quad \mu = e, i \\ \bar{J}_j^{\nu\mu}(k) &= \sum_{l,i,m} J_j^{\nu\mu}(l,k|i,m)(1 + \delta_{lk}\delta_{j1}\delta_{\nu\mu}) \\ \bar{I}_{j-1}^{\nu\mu}(k) &= \sum_{l,i} I_{j-1}^{\nu\mu}(l,k|i)(1 + \delta_{j1}\delta_{lk}). \end{aligned} \quad (1.7)$$

Here t is the time; $C_{j-1}^{00}(l,i|k)$ is the rate of formation of the homogeneous j -mer with energy $E_j(k)$ from the homogeneous $(j-1)$ -mer with energy $E_{j-1}(l)$

by the monomer attachment with energy $E_1(i)$; $E_j^{00}(k, | l, i)$ is the rate of the reverse process; $R_j^{00}(l, i | k, m)$ is the rate of relaxation of the homogeneous j -mer from the state with energy $E_j(l)$ into that with energy $E_j(k)$ together with the relaxation of the monomer from the state with energy $E_1(i)$ into that with energy $E_1(m)$; $\bar{x}_j^\nu(k) = x_j^\nu(k)/s_j^\nu(k)$, $s_j^\nu(k)$ is a statistical weight of the k -th vibrational level of the cluster, $C_j^\nu, E_j^\nu, R_j^{\nu 0}, \nu = i, e$ are the respective constants for ionic and electronic clusters describing the processes of their interaction with monomers, $R_j^{\nu\mu}, \nu, \mu = i, e$ is the relaxation constant describing the interaction between the heterogeneous clusters and ions or electrons.

The populations $x_j^\nu(k)$ are to be normalized by the condition

$$\sum_{j=1}^N j \sum_{\nu} \sum_{k=0}^{G_j} x_j^\nu(k) \equiv \sum_{j=1}^N j \sum_{\nu} x_j^\nu = n \equiv N^0/V,$$

$$\sum_{j=1}^{N+1} \sum_{k=0}^{G_j} x_j^i(k) \equiv \omega \equiv N^i/V, \quad \sum_{j=0}^{N+1} \sum_{k=0}^{G_j} x_j^e(k) \equiv \omega \equiv N^e/V, \quad (1.8)$$

where for a quasineutral mixture $N^i = N^e$ and x_j^ν are concentrations of the corresponding clusters. ^a

3. Equilibrium solutions

An equilibrium state of the system is attained at those values of populations that make all the right hand sides of Eq. (1.4) vanish. Clearly, the equilibrium populations are related to the equilibrium concentrations $x_j^\nu = \sum_k x_j^\nu(k)$ by the relationships

$$x_{je}^\nu(k) = x_{je}^\nu s_j^\nu(k) Z_j^\nu(k). \quad (1.9)$$

Here $Z_j^\nu(k)$, $\nu = 0, i, e$ are the Boltzmann factors of the k -th level in homogeneous and heterogeneous clusters.

^awe introduce notation $x_j^\nu = \sum_k x_j^\nu(k)$ for concentrations because it is easy to distinguish these concentrations from populations where the number of the vibrational level is presented in parentheses.

3.1. Equations for determining the equilibrium concentrations

To calculate the equilibrium concentrations x_{je}^ν we use the procedure described in section ???. Since Eqs. (1.9) make all fluxes $J_j^{\nu\lambda}$ vanish, the vanishing of all the right hand sides of Eqs. (1.4) reduces to a set of algebraic equations

$$I_j^{00} = I_j^{0i} = I_j^{0e} = 0, \quad j = 1, \dots, N. \quad (1.10)$$

This condition also makes fluxes I_j^{i0} and I_j^{e0} vanish. Indeed, these fluxes characterize not the appearance of new clusters, but another channel of formation of heterogeneous clusters. However, the number of the reaction channels is of no importance for the equilibrium state. It is easy to ascertain (see below) that the introduction of an additional channel is equivalent to the existence of some additional relations between the reaction rate constant.

In what follows in order to make the physical sense of some formulae more transparent we introduce a special notation $x_j \equiv x_j^0$, $y_j \equiv x_j^i$, $z_j \equiv x_j^e$, $M_j \equiv G_j^0$, $L_j \equiv G_j^i$, $O_j \equiv G_j^e$. To derive the closed set of equations for concentrations we sum up all the equations for $x_j^0(k)$ with respect to $k = 0, \dots, M_j$, for $x_j^i(l)$ with respect to $l = 0, \dots, L_j$ and for $x_j^e(m)$ with respect to $m = 0, \dots, O_j$. Then from the equations

$$\sum_{i,l,k} I_j^{00}(i, l | k) = \sum_{i,l,k} I_j^{0i}(i, l | k) = \sum_{i,l,k} I_j^{0e}(i, l | k) = 0, \quad j = 1, \dots, N \quad (1.11)$$

we obtain the following relations

$$\begin{aligned} x_{je} &= K_j^0(T) x_{j-1,e} x_{1e} \\ y_{je} &= K_j^i(T) y_{0e} x_{je} \\ z_{je} &= K_j^e(T, T_e) z_{0e} x_{je}, \\ K_j^0 &= \frac{\sum_{i,k,l} C_{j-1}^{00}(l, i | k) Z_{j-1}^0(l) Z_1^0(i)}{\sum_{i,k,l} E_j^{00}(k | l, i) Z_j^0(k)}, \\ K_j^i &= \frac{\sum_{i,k,l} C_{j-1}^{0i}(l, i | k) Z_{j-1}^0(l) Z_0^i(i)}{\sum_{i,k,l} E_j^{0i}(k | l, i) Z_j^i(k)}, \end{aligned}$$

$$K_j^e = \frac{\sum_{i,k,l} C_{j-1}^{0e}(l, i | k) Z_{j-1}^0(l) Z_1^e(i)}{\sum_{i,k,l} E_j^{0e}(k | l, i) Z_j^e(k)}. \quad (1.12)$$

To find x_{1e} , y_{0e} and z_{0e} we express x_{je} , y_{je} and z_{je} through these variables using Eq. (1.12). Then we obtain

$$\begin{aligned} x_{je} &= (x_{1e})^j \prod_{i=1}^j K_i^0, \quad j \geq 2, \\ y_{je} &= y_{0e} (x_{1e})^j K_j^i \prod_{i=1}^j K_i^0, \quad j \geq 1, \\ z_{je} &= z_{0e} (x_{1e})^j K_j^e \prod_{i=1}^j K_i^0, \quad j \geq 1 \end{aligned} \quad (1.13)$$

with $K_1^0 = 1$. Substituting these equalities into the normalizing condition Eq. (1.8) yields equations for determining x_{1e} , y_{0e} , and z_{0e} :

$$\begin{aligned} \sum_{j=1}^N j(x_{je} + y_{je} + z_{je}) &= n \\ &= \sum_{j=1}^N j(x_{1e})^j \prod_{i=1}^j K_i^0 (1 + y_{0e} K_j^i + z_{0e} K_j^e) \\ \sum_{j=0}^N y_{je} &= \omega = \sum_{j=1}^N y_{0e} (x_{1e})^j \prod_{i=1}^j K_i^0 K_j^i + y_{0e}, \\ \sum_{j=0}^N z_{je} &= \omega = \sum_{j=1}^N z_{0e} (x_{1e})^j \prod_{i=1}^j K_i^0 K_j^e + z_{0e}. \end{aligned} \quad (1.14)$$

Expressing y_{0e} and z_{0e} through x_{1e} from the second and third equations of Eq. (1.14)

$$\begin{aligned} y_{0e} &= \omega \left[1 + \sum_{j=1}^N (x_{1e})^j \prod_{i=1}^j K_i^0 K_j^i \right]^{-1}, \\ z_{0e} &= \omega \left[1 + \sum_{j=1}^N (x_{1e})^j \prod_{i=1}^j K_i^0 K_j^e \right]^{-1}, \end{aligned} \quad (1.15)$$

and substituting Eq. (1.15) into the first of Eqs. (1.14) we find a closed equation

for x_{1e} :

$$\sum_{j=1}^N j (x_{1e})^j F_j \left\{ 1 + \omega K_j^i \left[1 + \sum_{k=1}^N (x_{1e})^k F_k K_k^i \right]^{-1} + \omega K_j^e \left[1 + \sum_{k=1}^N (x_{1e})^k F_k K_k^e \right]^{-1} \right\} = n, \quad (1.16)$$

$$F_j = \prod_{i=1}^j K_i^0. \quad (1.16)$$

At $\omega = 0$ (no heterogeneous centers are present) this equation is identical with Eq. (??). If we disregard the formation of homogeneous and negatively charged clusters, unity in the brackets in Eq. (1.16) should be replaced by δ_{j1} and the third term should be omitted ($K_j^e = 0$), and then Eq. (1.16) is transformed into the equation derived in ²³.

By solving Eq. (1.16) we may determine the equilibrium concentration of monomers x_{1e} , then from Eq. (1.15) — the equilibrium concentration of free ions and electrons, and finally all the equilibrium concentrations of homogeneous and heterogeneous clusters can be calculated from Eq. (1.13).

3.2. Equilibrium constants K_j^ν , $\nu = 0, i, e$

To find the explicit solution of Eq. (1.16) we should express the equilibrium constants K_j^ν , $\nu = 0, i, e$ through the partition functions of the corresponding ideal gas. In accordance with Eqs. (??) and (1.16) we get

$$F_j = (\lambda_1^0)^{3j} Z_j^0 / (\lambda_j^0)^3 (Z_j^0)^j. \quad (1.17)$$

By analogy for the equilibrium constants K_j^ν , $\nu = i, e$ it is possible to write

$$K_j^\nu = \left(\frac{\lambda_0^\nu \lambda_j^0}{\lambda_j^\nu} \right)^3 \left(\frac{Z_j^\nu}{Z_j^0 Z_0^\nu} \right), \quad \nu = i, e, \quad (1.18)$$

where $\lambda_j^e = \lambda_j^e(T_e)$, $\lambda_j^i = \lambda_j^i(T)$. Further we can use the well known representation $Z_j^\nu = \exp(-\Psi_j^\nu/k_B T)$, $\nu = 0, i, e$, $Z_0^e \equiv 1$ that with allowance for the following definition

$$\begin{aligned} \lambda_j^0 &= (h^2/2\pi m_j k_B T)^{1/2} = j^{-1/2} \lambda_1^0 \\ \lambda_0^i &= (h^2/2\pi m_0 k_B T)^{1/2} \\ \lambda_j^i &= [h^2/2\pi (m_j + m_0) k_B T]^{1/2} = \lambda_j^0 (1 + m_0/m_j)^{-1/2} \end{aligned}$$

$$\begin{aligned}
&= \lambda_j^0 (1 + m_0/m_1j)^{-1/2}, \quad j \geq 1, \\
\lambda_j^e &= (h^2/2\pi m_j k_B T)^{1/2} = j^{-1/2} \lambda_1^0, \\
\lambda_0^e &= (h^2/2\pi m_e k_B T_e)^{1/2}, \quad j \geq 1,
\end{aligned}$$

yields

$$\begin{aligned}
K_j^i &= (\lambda_1^0)^3 \left(\frac{1}{j} + \frac{m_1}{m_0} \right)^{3/2} \exp \left(-\frac{\Delta\Psi_j^i}{k_B T} \right) \\
K_j^e &= (\lambda_1^0)^3 \left[\frac{T}{T_e} \left(\frac{1}{j} + \frac{m_1}{m_e} \right) \right]^{3/2} \exp \left(-\frac{\Delta\Psi_j^e}{k_B T} \right), \\
\Delta\Psi_j^i &= \Psi_j^i - \Psi_j^0 - \Psi_0^i, \quad \Delta\Psi_j^e = \Psi_j^e - \Psi_j^0,
\end{aligned} \tag{1.19}$$

where m_0 is the ion mass and h is the Planck constant.

We must specify the cluster model more precisely in order to derive explicit expressions for F_j , $\Delta\Psi_j^i$ and $\Delta\Psi_j^e$. Let us assume that:

1. the charge of an ion (or electron) incorporated in the heterogeneous cluster is located at the cluster center;
2. all the clusters have a spherical shape;
3. in the first approximation we may neglect the effect of the electric field on the vibrational frequencies of the molecules incorporated in the cluster;
4. the gas polarization by the ion and electron fields is insignificant since the vapor is assumed to be ideal;
5. the electrostatic interactions between the ions (electrons) can be neglected since free energy corresponding to such an interaction drops as $1/r$.

As in the preceding chapters we divide all molecular vibrations into two groups, translational and librational ones, and consider these vibrations within the harmonic approximation assuming the corresponding normal frequencies within each group to be identical. Then for the free energy of homogeneous clusters Ψ_j^0 the previously obtain representation Eq. (??) is valid as well as the expression for F_j following from Eq. (??)

$$\begin{aligned}
(x_{1e})^j F_j &= (\lambda_1^0)^{-3} D j^{3/2+\mu} \exp \left(Aj - bj^{2/3} \right) \\
&= \bar{A}_j \exp \left(Aj - bj^{2/3} \right).
\end{aligned} \tag{1.20}$$

As far as the free energy of heterogeneous clusters Ψ_j^i and free ions are concerned they can be written as follows

$$\begin{aligned}\Psi_0^i &= \Psi_{1i}^0 + \frac{2e^2}{3e_v} \left(\frac{1}{r_a} - \frac{1}{R} \right) \\ \Psi_j^i &= j\Psi_1^0(T) + \Psi_{1i}^0 + \frac{2e^2}{3e_l} \left(\frac{1}{r_a} - \frac{1}{r} \right) + \frac{2e^2}{3e_v} \left(\frac{1}{r} - \frac{1}{R} \right) \\ &\quad + \alpha_j^i S_j^i + \Psi_{i0} - k_B T \ln (Z_{jR}^i Z_{jV}^0)\end{aligned}\quad (1.21)$$

where according to ²¹

$$\begin{aligned}\alpha_j^i &= \sigma + \frac{Be^2}{r^3} - \frac{e}{r^2} \mathcal{P}(r), \quad B = \frac{1}{16\pi} \left(\frac{1}{\epsilon_l} - \frac{1}{\epsilon_v} \right), \\ r &= (\eta^3 j + r_a^3)^{1/3}, \quad \eta = (3m_0/4\pi\rho_l)^{1/3}, \quad S_j^i = 4\pi r^2.\end{aligned}$$

Here R is the radius of the system under consideration, ρ_l is the liquid phase density, \mathcal{P} is polarization, Ψ_{i0} is the free energy of vibrations along the ion — neutral molecule bond in heterogeneous clusters, Ψ_{1i}^0 is the free energy of the recombined ion, Z_{jR} and Z_{jV} are the rotational and vibrational partition function. Substituting these expressions into Eq. (1.19) we obtain

$$\begin{aligned}\Delta\Psi_j^i &= \frac{2e^2}{3} \left(\frac{1}{\epsilon_l} - \frac{1}{\epsilon_v} \right) \left(\frac{1}{r_a} - \frac{1}{r} \right) + \alpha_j^i S_j^i - \alpha_j^0 S_j^0 + \Psi_{i0} \\ &\quad - k_B T \ln (Z_{jR}^i / Z_{jR}^0), \\ \Psi_{i0} &= -k_B T \ln Z_{i0} = -k_B T \ln \prod_{i=1}^6 \exp \left(\frac{h\nu_i - \varepsilon_0}{2k_B T} \right) \left[1 - \exp \left(\frac{h\nu_i}{k_B T} \right) \right]^{-1}, \\ S_j^0 &= 4\pi\eta^2 j^{2/3}, \quad Z_{jR}^i / Z_{jR}^0 = \left(\frac{m_0 j}{m_0 j + m_i} \frac{r^2}{\eta^2 j^{2/3}} \right)^{3/2},\end{aligned}\quad (1.22)$$

where ε_0 is the depth of the potential well of the interaction between two molecules, ν_i is the frequencies of intracuster translational and librational oscillations.

By analogy it is possible to obtain an explicit representation of $\Delta\Psi_j^e$ if one has in mind that $m_e \ll m_0$, $r_e \ll r_0 \equiv \eta$ and hence $Z_{jR}^e \approx Z_{jR}^0$, $S_j^e \approx S_j^0$. Furthermore, in a physical sense $\Psi_{e0} = 0$. Thus

$$\begin{aligned}\Delta\Psi_j^e &= -\frac{2e^2}{3} \left(\frac{1}{\epsilon_l} - \frac{1}{\epsilon_v} \right) \left(\frac{1}{r_e} - \frac{1}{r} \right) + 4\pi e \left[\frac{Be}{r} - \mathcal{P}(r) \right], \\ r &\equiv \eta j^{1/3}.\end{aligned}\quad (1.23)$$

Thus, we have determined all the thermodynamic functions appearing in Eq. (1.16). Further on we may show in full accordance with section ??, that

in the thermodynamic limit $N \rightarrow \infty$, $V \rightarrow \infty$, $N/V = n = \text{const}$ the solution of Eq. (1.16) at $n > x_{1e,s}$ is $x_{1e} \approx x_{1e,s}$ where $x_{1e,s}$ is exactly identical with the Clapeyron–Clausius formula. In this case

$$\begin{aligned}
x_{je} &= \bar{A}_j \exp(-bj^{2/3}), \quad j \geq 2, \\
y_{je} &= y_{0e} \bar{A}_j \exp(-bj^{2/3}) K_j^+, \quad j \geq 1, \\
z_{je} &= z_{0e} \bar{A}_j \exp(-bj^{2/3}) K_j^-, \quad j \geq 1, \\
y_{0e} &= \omega \left[1 + \sum_{j=1}^N \bar{A}_j \exp(-bj^{2/3}) K_j^+ \right]^{-1}, \\
z_{0e} &= \omega \left[1 + \sum_{j=1}^N \bar{A}_j \exp(-bj^{2/3}) K_j^- \right]^{-1}. \quad (1.24)
\end{aligned}$$

At $n < x_{1e,s}$ the major contribution to the sum in Eq. (1.16) is made by the term with $j = 1$. Then, instead of Eq. (1.16), we approximately have

$$x_{1e} \left[1 + \frac{\omega K_1^i}{1 + x_{1e} K_1^i} + \frac{\omega K_1^e}{1 + x_{1e} K_1^e} \right] \approx n. \quad (1.25)$$

The exact solution of this equation may be found from the Cardano formula. For some limiting values of the parameters of Eq. (1.25) we may obtain even simpler estimates suitable for a qualitative analysis. Thus, if $n \gg \omega$ then $x_{1e} = n$ that is identical to the result of section ???. If $\omega \gg n$ then

$$x_{1e} \approx (n/\omega) (K_1^i + K_1^e)^{-1}. \quad (1.26)$$

This solution is valid at $n / [\omega (K_1^i + K_1^e)] < x_{1e,s}$.

Note also that for many substances (such as water vapor and nitrogen) $x_{1e} K_1^i \ll 1$ and $x_{1e} K_1^e \ll 1$, so that from Eq. (1.25) at $(n/\omega) (K_1^+ + K_1^-)^{-1} \leq x_{1e,s}$ we have

$$x_{1e} \approx n / [1 + \omega (K_1^i + K_1^e)]. \quad (1.27)$$

An analysis of Eqs. (1.25)–(1.27) shows that a vapor saturated in the absence of ions and electrons may be converted into a supersaturated one by adding heterogeneous nucleation centers. Hence, an introduction of charged particles shifts the phase equilibrium point. Indeed, let the whole vapor phase initially consists of monomers with a density $n < x_{1e,s}$ with no heterogeneous nucleation centers present. Then, it follows from Eqs. (1.26)–(1.27) that $x_{1e} \approx$

n , i.e. $S = n/x_{1e} < 1$. Addition of ions or electrons to the vapor reduces x_{1e} , so that S becomes greater than unity.

4. Solution of the kinetic equations. Quasisteady states

In this section we derive analytical expressions for the quasisteady solutions of these kinetic equations. As usual the quasisteady-state method as applied to the problem at issue can be divided into two stages. Within the first stage we look for the analytical expressions of the quasisteady populations of the vibrational states of clusters that reduce the original kinetic equations to a closed set of equations for concentrations of the clusters of all sizes and types. In the second stage, this set is reduced to three equations describing the evolution of the concentrations of monomers and free ions (i.e. positively and negatively charged molecules).

4.1. The first stage of the quasisteady-state method

To solve Eq. (1.4) we employ the quasisteady-state method developed in the previous chapters. The method is essentially as follows. First we replace the variables. The populations of the ground state $x_j(0)$, $y_j(0)$ and $z_j(0)$ are eliminated from the equations and replaced by concentrations x_j , y_j and z_j . Populations $x_j(0)$, $y_j(0)$ and $z_j(0)$ are related to x_j , y_j and z_j according to the relationship

$$\begin{aligned} x_j &= \sum_k x_j(k), & y_j &= \sum_k y_j(k), & z_j &= \sum_k z_j(k), \\ x_j(0) &= x_j - \sum_{k \neq 0} x_j(k), & y_j(0) &= y_j - \sum_{k \neq 0} y_j(k), \\ z_j(0) &= z_j - \sum_{k \neq 0} z_j(k). \end{aligned} \quad (1.28)$$

Equations for x_j are obtained from Eq. (1.4) by summing up all the equations for populations $x_j(k)$ over k . Equations for y_j and z_j are derived in a similar way. All relaxation terms thus drop out from the final equations, and these equations take the following form

$$\frac{dx_j}{dt} = \sum_{k=0}^{M_1} \left\{ \sum_{i=0}^{M_1} \left[\sum_{l=0}^{M_{j-1}} I_{j-1}^{00}(l, i | k) - \sum_{l=0}^{M_{j+1}} I_j^{00}(k, i | l) (1 - \delta_{jN}) \right] \right\}$$

$$\begin{aligned}
& - \left. \sum_{i=0}^{L_0} \sum_{l=0}^{L_j} I_j^{0i}(k, i | l) - \sum_{i=0}^{O_0} \sum_{l=0}^{O_j} I_j^{0e}(k, i | l) \right\}, \quad j = 2, \dots, N, \\
\frac{dy_j}{dt} &= \sum_{k=0}^{L_1} \left\{ \sum_{i=0}^{M_1} \left[\sum_{l=0}^{L_{j-1}} I_{j-1}^{i0}(l, i | k) - \sum_{l=0}^{L_{j+1}} I_j^{i0}(k, i | l) (1 - \delta_{jN}) \right] \right. \\
& \left. + \sum_{i=0}^{L_0} \sum_{l=0}^{M_j} I_j^{0i}(l, i | k) (1 - \delta_{j1}) \right\}, \quad j = 1, \dots, N, \\
\frac{dz_j}{dt} &= \sum_{k=0}^{O_1} \left\{ \sum_{i=0}^{M_1} \left[\sum_{l=0}^{O_{j-1}} I_{j-1}^{e0}(l, i | k) - \sum_{l=0}^{L_{j+1}} I_j^{e0}(k, i | l) (1 - \delta_{jN}) \right] \right. \\
& \left. + \sum_{i=0}^{O_0} \sum_{l=0}^{M_j} I_j^{0e}(l, i | k) (1 - \delta_{j1}) \right\}, \quad j = 1, \dots, N. \tag{1.29}
\end{aligned}$$

As it has been shown earlier when no heterogeneous clusters present in the system all the $x_j(k)$, $k = 1, \dots, M_j$, $j = 2, \dots, N$ variables are fast as compared to the slow variables x_j , $j = 1, \dots, N$ and $x_1(k)$, $k = 1, \dots, M_1$. A similar conclusion applies to $y_j(k)$, $k = 1, \dots, L_j$, $j = 1, \dots, \Omega$ (fast variables with respect to y_j , $j = 0, \dots, \Omega$, $y_0(k)$, $k = 1, \dots, L_0$) and to $z_j(k)$, $k = 1, \dots, O_j$, $j = 1, \dots, \Omega$ (fast variables with respect to z_j , $j = 0, \dots, \Omega$, $z_0(k)$, $k = 1, \dots, O_0$). Now, in accordance with general methods of solving singularly perturbed ordinary differential equations to obtain the quasisteady solutions, instead of the ordinary differential equations we may use for $x_j(k)$, $k = 1, \dots, M_j$, $j = 2, \dots, N$, $y_j(k)$, $k = 1, \dots, L_j$, $j = 1, \dots, \Omega$, $z_j(k)$, $k = 1, \dots, O_j$, $j = 1, \dots, \Omega$ so-called ‘‘reduced’’ ones which follow from the original differential equations by setting the respective R.H.S. equal to zero. Solving these reduced algebraic equations it is possible to express all the quasisteady populations through the slow variables which appear in the reduced equations due to the second line of Eq. (1.28). If one further substitutes these quasisteady populations into Eq. (1.29) then the closed system of equations for concentrations x_j , y_j , z_j follows. This idea is a core of the proposed approach.

Now we proceed to realization of the above mentioned approach. To find the quasisteady populations one should solve the truncated equations derived from Eqs. (1.4). These equations are algebraic, rather than differential, however, it is hardly possible to solve them analytically. We find an approximate solution using the method suggested in chapter ?? and based on some simplifying assumptions.

Attachment of ions and electrons to a cluster. The original equations take into account formation of heterogeneous clusters due to attachment of ions and electrons to the homogeneous clusters. However, the rate constant of this process is much lower than that for the growth of the homogeneous cluster via the attachment of a monomer to it. In order to give some evidence to this point let us consider a reverse process — detachment of one molecule or ion from a heterogeneous cluster. Let this cluster contain j molecules and one ion. Then the probability of detachment of a molecule from the cluster is j times more than that of an ion. Moreover, the dissociating ion is tied by the polarization forces with all the molecules in the cluster, whereas the molecule is bound only with the ion. Finally, we assume that the ion is solvated at the cluster center, whereas the cluster dissociates predominantly via the detachment of the surface molecules. All these considerations suggest the following inequality

$$E_j^{0i}(k | i, l) \ll E_j^{0i}(k | i, l) \ll E_{j+1}^{00}(k | i, l), \quad (1.30)$$

and hence

$$I_j^{0i}(l, i | k) \ll I_j^{i0}(k | i, l) \ll I_j^{00}(l, i | k). \quad (1.31)$$

The higher the number j , the more confidently we may assert that inequalities Eq. (1.31) hold. At low j the validity of Eq. (1.31) should also be proved. We accept a model which assumes that the inequality Eq. (1.31) holds up to $j \geq 2$, and that at $j = 1$ constants $E_1^{0i}(k | i, l)$, $E_1^{i0}(k | i, l)$ and $E_2^{00}(k | i, l)$ are of the same order of magnitude ($I_1^{0i}(k | i, l)$, $I_1^{i0}(k | i, l)$ and $I_2^{00}(k | i, l)$, respectively).

Now we proceed to a heterogeneous cluster comprising j molecules and an electron. As a rule, the electron is localized on one of the cluster monomers, therefore we assume that the overall cluster consists of $j - 1$ monomeric units and one negative ion formed from a monomer molecule by the electron attachment. Then, based on the above consideration we may write

$$\begin{aligned} E_j^{0e}(k | i, l) &\ll E_j^{e0}(k | i, l) \ll E_j^{00}(k | i, l), & j \geq 3, \\ I_j^{0e}(l, i | k) &\ll I_j^{e0}(l, i | k) \ll I_{j-1}^{00}(l, i | k), & j \geq 3, \\ E_2^{0e}(k | i, l) &\ll E_2^{e0}(k | i, l) \sim E_2^{00}(k | i, l), \\ I_2^{0e}(l, i | k) &\ll I_2^{e0}(l, i | k) \ll I_1^{00}(l, i | k). \end{aligned} \quad (1.32)$$

We do not specify the constant $E_1^{0i}(k | i, l)$ so far and retain the appropriate terms in the truncated equations.

Parameter r . We introduced number r for homogeneous clusters such that the rate of relaxation of the clusters with a number of molecules $j > r$ at high levels is much higher than the rate of their dissociation from the same levels; at $j < r$ the ratio of these rates reverses, whereas at $j = r$ the relaxation and dissociation rates of the clusters at high levels are of the same order of magnitude. The expressions for r as a function of P, T and individual properties of condensible molecules are presented in section ???.

In the case of a mixture of heterogeneous and homogeneous clusters we may obviously introduce numbers r^0 , r^i and r^e . They are defined by equations

$$\Theta_j^\nu(k) = \sum_{i,l} E_j^{0\nu}(k | i, l) / \sum_{i,l,p} [R_j^{\nu i}(k, p | l, i) Z_0^i(p) y_{0e} + R_j^{\nu 0}(k, p | l, i) Z_0^0(p) x_{1e} + R_j^{\nu e}(k, p | l, i) Z_0^e(p) z_{0e}], \quad \nu = 0, i, e, \quad (1.33)$$

$$\Theta_j^\nu(G_\nu) = \begin{cases} < 1, & j > r^\nu, \\ 1, & j = r^\nu, \\ > 1, & j < r^\nu, \end{cases} \quad \begin{matrix} \nu = 0, i, e, \\ G_0 = M, G_i = L, G_e = O. \end{matrix} \quad (1.34)$$

The presence of an ion or electron in a heterogeneous complex enhances the attraction forces binding the condensible molecule with the complex (due to polarization of this molecule), i.e. it reduces the dissociation rate constant. The relaxation rates $R_j^{ii}(k, p | l, i)$, $R_j^{ee}(k, p | l, i)$ and $R_j^{00}(k, p | l, i)$ can be assumed to be of the same order. Hence, r^i and r^e are lower than r^0 .

The relaxation rate of monomers and ions. Here we consider Eq. (1.4) for the populations of monomers $x_1(k)$, $k = 1, \dots, M_1$ and ions $y_0(k)$, $k = 1, \dots, L_0$, and formulate a number of additional simplifying assumptions based on an analysis of these relations. First, as shown in chapter ?? inequality $I_0^{00} \ll I_j^{00}$, $j \geq 2$ takes place. This inequality follows from the fast decay of the equilibrium distribution function x_{je} . Similar relations for I_j^{e0} and I_j^{i0} follow from Eq. (1.19), (1.22), thus $I_0^{e0} \ll I_j^{e0}$, $I_0^{i0} \ll I_j^{i0}$, $j \geq 1$.

Using just the same procedure (see Appendix ??) we obtain the following inequalities

$$\begin{aligned} J_1^{00} &\gg J_j^{00}, \quad j \geq 2, \\ J_0^{e0} &\gg J_j^{e0}, \quad J_0^{i0} \gg J_j^{i0}, \quad j \geq 1, \\ J_1^{0e} &\gg J_j^{0e}, \quad J_1^{0i} \gg J_j^{0i}, \quad j \geq 1. \end{aligned} \quad (1.35)$$

Thus, the terms responsible for the relaxation and condensation of the ions, monomers, and electrons in their collisions with each other dominate in Eq. (1.4) for $x_1(k)$, $k = 1, \dots, M_1$, $y_0(k)$, $k = 1, \dots, L_0$ and z_0 .

The above discussion has been concerned with the ratio between the rate of dissociation of the clusters and that of relaxation of intermolecular vibrations in the cluster. As for the ratio between the characteristic rate of intramolecular relaxation of monomers and ions and that of dimerization, it may be different for various types of molecules. Because of this we introduce the second assumption in this paragraph, i.e. that the intramolecular relaxation is much faster than dimerization. Some physical ideas that support this assumption for water molecules has been discussed in chapter ???. Rejection of this assumption implies that one should consider monomers and ions being in a certain vibrational state as an individual particle. This case was studied in chapter ??? as applied to the homogeneous condensation.

The assumptions made allow us to omit all the terms in Eqs. (1.4) for $x_1(k)$, $k = 1, \dots, M_1$, $y_0(k)$, $k = 1, \dots, L_0$ and z_0 except those pertaining to relaxation of monomers and ions in collisions between each other and with electrons. Moreover, the populations $x_1(k)$ and $y_0(k)$ are fast variables as compared to concentrations x_1 , y_0 and z_0 , since only flows $I_j^{\mu\nu}$ describing condensation appear in the equations for concentrations that contain no relaxation terms under these conditions. Thus, the number of fast variables in Eq. (1.4) increases, and the corresponding truncated equations for the $x_1(k)$, $k = 1, \dots, M_1$ and $y_0(k)$, $k = 1, \dots, L_0$ variables must be solved together with the above truncated set of equations.

Quasisteady equations. With due regard for the assumptions introduced above we can rewrite the truncated equations supplemented by equations for $x_1(k)$, $k = 1, \dots, M_1$ and $y_0(k)$, $k = 1, \dots, L_0$ as follows

Monomers and ions

$$\sum_{p=0}^{M_1} \left[\sum_{l,i=0}^{M_j} J_1^{00}(l, k | i, p)(1 + \delta_{lk}) + \sum_{l,i=0}^{L_j} J_0^{i0}(l, k | i, p) + \sum_{l,i=0}^{O_j} J_0^{e0}(l, k | i, p) \right] = 0, \quad k = 1, \dots, M_1;$$

$$\sum_{p=0}^{L_0} \left[\sum_{l,i=0}^{L_j} J_1^{ii}(l, k | i, p)(1 + \delta_{lk}) + \sum_{l,i=0}^{M_j} J_0^{0i}(l, k | i, p) + \sum_{l,i=0}^{O_j} J_0^{ei}(l, k | i, p) \right]$$

$$\begin{aligned}
& \left. + \sum_{l,i=0}^{O_j} J_1^{ei}(l, k | i, p) \right] = 0, \quad k = 1, \dots, L_0; \\
x_1(0) &= x_1 - \sum_{k=1}^{M_1} x_1(k), \quad y_0(0) = y_0 - \sum_{k=1}^{L_0} y_0(k); \\
\sum_{l=0}^{O_j} \left[\sum_{i,p=0}^{M_1} J_1^{e0}(l, i | k, p) + \sum_{i,p=0}^{L_0} J_1^{ei}(l, i | k, p) + \sum_{i,p=0}^{O_0} J_1^{ee}(l, i | k, p) \right] &= 0, \\
& k = 1, \dots, O_1. \tag{1.36}
\end{aligned}$$

Neutral clusters ($k = 1, \dots, K_j$)

$$\begin{aligned}
\sum_{i=0}^{M_1} \left[\sum_{l=0}^{M_{j-1}} I_{j-1}^{00}(l, i | k) - \sum_{l=0}^{M_{j+1}} I_j^{00}(k, l | i) \right] &= 0, \quad j = 2, \dots, r^0 - 1; \\
\sum_{l=0}^{M_j} \left[\sum_{i,p=0}^{M_1} J_j^{00}(l, i | k, p) + \sum_{i,p=0}^{L_0} J_j^{0i}(l, i | k, p) + \sum_{i,p=0}^{M_0} J_j^{0e}(l, i | k, p) \right] \\
&+ \sum_{i=0}^{M_1} \left[\sum_{l=0}^{M_{j-1}} I_{j-1}^{00} - \sum_{l=0}^{M_{j+1}} I_j^{00}(k, i | l) \right] = 0, \quad j = r^0; \\
\sum_{l=0}^{M_j} \left[\sum_{i,p=0}^{M_1} J_j^{00}(l, i | k, p) + \sum_{i,p=0}^{L_0} J_j^{0i}(l, i | k, p) + \sum_{i,p=0}^{O_0} J_j^{0e}(l, i | k, p) \right] &= 0, \\
& j = r^0 + 1, \dots, N. \tag{1.37}
\end{aligned}$$

Ionic clusters ($k = 1, \dots, L_j$)

$$\begin{aligned}
\sum_{i=0}^{M_1} \left[\sum_{l=0}^{L_{j-1}} I_{j-1}^{i0}(l, i | k) - \sum_{l=0}^{L_{j+1}} I_j^{i0}(k, l | i) \right] &= 0, \quad j = 1, \dots, r^i - 1; \\
\sum_{l=0}^{L_j} \left[\sum_{i,p=0}^{M_1} J_j^{i0}(l, i | k, p) + \sum_{i,p=0}^{L_0} J_j^{ii}(l, i | k, p) + \sum_{i,p=0}^{O_0} J_j^{ie}(l, i | k, p) \right] \\
&+ \sum_{i=0}^{M_1} \left[\sum_{l=0}^{L_{j-1}} I_{j-1}^{i0}(l, i | k) - \sum_{l=0}^{L_{j+1}} I_j^{i0}(k, l | i) \right] = 0, \quad j = r^i;
\end{aligned}$$

$$\sum_{l=0}^{L_j} \left[\sum_{i,p=0}^{M_1} J_j^{i0}(l, i | k, p) + \sum_{i,p=0}^{L_0} J_j^{ii}(l, i | k, p) + \sum_{i,p=0}^{O_0} J_j^{ie}(l, i | k, p) \right] = 0, \quad j = r^i + 1, \dots, N. \quad (1.38)$$

Electronic clusters ($k = 1, \dots, M_j$)

$$\begin{aligned} \sum_{i=0}^{M_1} \left[\sum_{l=0}^{O_{j-1}} I_{j-1}^{e0}(l, i | k) - \sum_{l=0}^{O_{j+1}} I_j^{e0}(k, i | l) \right] &= 0, \quad j = 2, \dots, r^e - 1; \\ \sum_{l=0}^{O_j} \left[\sum_{i,p=0}^{M_1} J_j^{e0}(l, i | k, p) + \sum_{i,p=0}^{L_0} J_j^{ei}(l, i | k, p) + \sum_{i,p=0}^{O_0} J_j^{ee}(l, i | k, p) \right] \\ \sum_{i=0}^{M_1} \left[\sum_{l=0}^{O_{j-1}} I_{j-1}^{e0}(l, i | k) - \sum_{l=0}^{O_{j+1}} I_j^{e0}(k, i | l) \right] &= 0, \quad j = r^e; \\ \sum_{l=0}^{O_j} \left[\sum_{i,p=0}^{M_1} J_j^{e0}(l, i | k, p) + \sum_{i,p=0}^{L_0} J_j^{ei}(l, i | k, p) + \sum_{i,p=0}^{O_0} J_j^{ee}(l, i | k, p) \right] &= 0, \quad j = r^e + 1, \dots, N. \end{aligned} \quad (1.39)$$

Now we resort to solving Eqs. 1.36)–(1.39). Equations (1.36) are obviously the easiest to be solved because quasi-equilibrium values of populations are among their solutions

$$\begin{aligned} x_1(k) &= x_1 Z_j^0(k) s_j^0(k), & y_0(k) &= y_0 Z_j^i(k) s_j^i(k), \\ z_1(k) &= z_1 Z_j^e(k) s_j^e(k). \end{aligned} \quad (1.40)$$

As far as the subsets specified by Eqs. (1.37)–(1.39) are concerned they are independent and their structure is precisely identical with those considered in chapter ???. The only distinction is that in this case molecular vibrations in the clusters relax due to collisions of the clusters with monomers, ions and electrons whereas in chapter ??? only one relaxation term presents in the corresponding equations. This diverse, however, does not prevent us from utilizing the method developed in chapter ??? to solve Eqs. (1.37)–(1.39). Note that two models of the relaxation kinetics (single-quantum transitions and BGK models) were used in chapter ??? to find the solution at $j = r$. It turns out that the structure of the solution thus found is identical in both cases and the corresponding terms in the solution differ only in the coefficients. Moreover, these coefficients drop out from the final expressions for the quasisteady concentrations. Bearing this in mind here for the sake of simplicity we use the BGK model in which the

relaxation times for each level are equal and the relaxation terms are written as follows

$$\sum_{l,i,p} J_j^{\nu\mu}(l, i | k, p) = -\frac{\bar{H}_j^\nu(k) - H_j Z_j^\nu(k)}{\tau_j^{\nu\mu}}, \quad \mu = 0, i, e, \quad \nu = 0, i, e, \quad (1.41)$$

where $H_j^0(k) \equiv x_j(k)$, $H_j^i(k) \equiv y_j(k)$, $H_j^e(k) \equiv z_j(k)$, $H_j^\nu \equiv \sum_k H_j^\nu(k)$. By analogy with chapter ?? the solution of Eqs. (1.36)–(1.39) is written as follows.

at $j = r^\nu + 1, \dots, N$

$$\bar{H}_j^\nu(k) = H_j Z_j^\nu(k), \quad k = 1, \dots, G_\nu, \quad \nu = 0, i, e;$$

at $j = 2, \dots, r^\nu - 1$

$$\begin{aligned} \bar{H}_j^\nu(G_\nu) &= [\xi_j^\nu + \alpha_j^\nu \mathcal{C}_{r^\nu, G_\nu, G_\nu}^\nu \bar{H}_{r^\nu}^\nu(G_\nu) \\ &\quad + (\xi_j^\nu \alpha_{r^\nu-1}^\nu - \alpha_j^\nu \xi_{r^\nu-1}^\nu) \mathcal{C}_{r^\nu-1, G_\nu, G_\nu}^\nu x_1] / \kappa_\nu, \\ \bar{H}_j^\nu(k) &= \bar{H}_{j+1}^\nu(G_\nu) \mathcal{E}_{j+1, G_\nu, k}^\nu / \mathcal{C}_{j, k, G_\nu}^\nu x_1, \quad k = 1, \dots, G_\nu - 1; \\ H_j^\nu(0) &= H_j^\nu - \sum_{k=1}^{G_\nu} H_j^\nu(k), \quad \xi_j^\nu = H_{j_e}^\nu Z_j^\nu(G_\nu) S^j, \\ \mathcal{E}_{j, G_\nu, k}^\nu &= \sum_i E_j^{\nu 0}(G_\nu | i, k), \quad \mathcal{C}_{j, G_\nu, k}^\nu = \sum_i C_j^{\nu 0}(k, i | G_\nu) Z_1^\nu(i), \\ \alpha_j^\nu &= [1 + \mathcal{C}_{j-1, G_\nu, G_\nu}^\nu x_1 \alpha_{j-1}^\nu] / \mathcal{E}_{j, G_\nu, G_\nu}^\nu, \\ \alpha_2^\nu &= \left[\sum_{i,l} E_2^{\nu 0}(G_\nu | i, k) \right]^{-1}, \\ \kappa_\nu &= 1 + \mathcal{C}_{r^\nu-1, G_\nu, G_\nu}^\nu x_1 \alpha_{r^\nu-1}^\nu, \quad S = x_1 / x_{1e}, \end{aligned}$$

at $j = r^\nu$

$$\begin{aligned} \bar{H}_j^\nu(k) &= -H_j^\nu (1 - f_j^\nu) \frac{\mathcal{C}_{j, k, G_\nu}^\nu x_1 Z_j^\nu(k)}{\mathcal{C}_{j, k, G_\nu}^\nu x_1 + \tau_j^{\nu-1}} + H_j^\nu Z_j^\nu(k), \\ \frac{\bar{H}_j^\nu(G_\nu)}{H_{j_e}^\nu Z_j^\nu(G_\nu)} &= [\mathcal{C}_{j, G_\nu, G_\nu}^\nu x_{1e} \bar{H}_{j+1}^\nu + \mathcal{C}_{j-1, G_\nu, G_\nu}^\nu x_1 \xi_{j-1}^\nu / \kappa_\nu H_{j_e}^\nu Z_j^\nu(k) \\ &\quad + \bar{H}_j^\nu(\tau_j)^{-1}] [\mathcal{C}_{j, G_\nu, G_\nu}^\nu x_1 + \mathcal{E}_{j, G_\nu, G_\nu}^\nu / \kappa_\nu + (\tau_j)^{-1}]^{-1}, \\ (\tau_j)^{-1} &\equiv (\tau_j^{\nu 0})^{-1} + (\tau_j^{\nu i})^{-1} + (\tau_j^{\nu e})^{-1}, \quad f_j^\nu = \bar{H}_{j+1}^\nu / (S \bar{H}_j^\nu), \\ \bar{H}_j^\nu &\equiv H_j^\nu / H_{j_e}^\nu. \end{aligned} \quad (1.42)$$

4.2. The second stage of the quasisteady-state method

Equations for the slow variables can be obtained by substituting solutions Eq. (1.41) into Eq. (1.29). As in chapter ?? we find

$$\begin{aligned}
\frac{dH_j^\nu}{dt} &= I_j^{\nu(2)} + \frac{d_{je}^\nu \gamma_2 S}{H_{re}^\nu} H_r^\nu (1 - f_r) - d_{je}^\nu \gamma_2^\nu \theta^\nu \tau_r^\nu \left(1 - \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu}{\kappa_\nu \theta^\nu} \right) I_{r+1}^{\nu(2)}, \\
& \quad j = 2, \dots, r-1, \quad \nu = 0, i, e, \\
\frac{dH_r^\nu}{dt} &= \gamma_1^\nu H_r^\nu (1 - f_r) - \gamma_2^\nu I_{r+1}^{\nu(2)}, \\
\gamma_1^\nu &= \frac{1}{\tau_r^\nu} \left[\frac{Z_r^\nu(G_\nu)(1 - \tau_r^\nu \theta^\nu)}{\tau_r^\nu \theta^\nu} - \sum_{k=1}^{G_\nu-1} Z_r^\nu(k) \frac{\mathcal{C}_{r,kG_\nu,e}^\nu x_1}{\mathcal{C}_{r,kG_\nu}^\nu x_1 + (\tau_r^\nu)^{-1}} \right], \\
\gamma_2^\nu &= \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu H_{re}^\nu Z_r^\nu(G_\nu)}{\kappa_\nu S \theta^\nu \tau_r^\nu}, \\
\frac{dH_{r+1}^\nu}{dt} &= -\frac{\gamma_2^\nu S}{H_{re}^\nu} H_r^\nu (1 - f_r) + \gamma_2^\nu \theta^\nu \tau_r^\nu \left(1 - \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu}{\kappa_\nu \theta^\nu} \right) I_{r+1}^{\nu(2)} - I_{r+1}^{\nu(1)} - \frac{dH_r^\nu}{dt} \\
\frac{dH_j^\nu}{dt} &= I_j^{\nu(1)} - I_{j+1}^{\nu(1)} (1 - \delta_{jN}), \quad j > r+1, \tag{1.43}
\end{aligned}$$

where by analogy with chapter ?? $I_j^{\nu(1)}$ and $I_j^{\nu(2)}$ are the fluxes that can be generally represented as

$$\begin{aligned}
I_j^{\nu(1)} &= K_j^{\nu+} H_{j-1}^\nu x_1 - K_j^{\nu-} H_j^\nu, \\
I_{j+1}^{\nu(2)} &= L_j^{\nu+} x_1^{j+1} - L_j^{\nu-} H_j^\nu x_1. \tag{1.44}
\end{aligned}$$

Coefficient d_{je}^ν arises when substituting the steady-state monomer distribution in the definition of d_j that yields

$$\begin{aligned}
d_{je}^\nu &= \frac{\mathcal{C}_{j,0G_\nu}^\nu x_{1e} \alpha_{j+1}^\nu}{s_j^\nu(0) Z_{j+1}^\nu(G_\nu)} \frac{H_{je}^\nu}{H_{j+1,e}^\nu} - \frac{\mathcal{C}_{j,0G_\nu}^\nu s_j^\nu(G_\nu)}{\mathcal{C}_{j,G_\nu,G_\nu}^\nu s_j^\nu(0)} \\
&= \frac{\mathcal{C}_{j,0G_\nu}^\nu}{\mathcal{C}_{j,G_\nu,G_\nu}^\nu s_j^\nu(0) Z_j^\nu(G_\nu)} (1 + \mathcal{C}_{j,G_\nu,G_\nu}^\nu x_1 \alpha_j^\nu - s_j^\nu(G_\nu) Z_j^\nu(G_\nu)) \\
&\approx \frac{\mathcal{C}_{j,0G_\nu}^\nu}{\mathcal{C}_{j,G_\nu,G_\nu}^\nu s_j^\nu(0) Z_j^\nu(G_\nu)} (1 + \mathcal{C}_{j,G_\nu,G_\nu}^\nu x_1 \alpha_j^\nu),
\end{aligned}$$

and the definition of α is given in Appendix B.

Equations for $H_1^i \equiv y_1$ and $H_1^e \equiv z_1$ are not presented in Eq. (1.43). The corresponding equation for y_1 has the same form as the first equation in Eq. (1.43) while for z_1 one could get

$$\frac{dz_1}{dt} = I_1^{e(1)} - K_2^{e+} z_{1e} x_1 (\bar{z}_1 - S) - \hat{I}^e, \tag{1.45}$$

and \hat{I}^ν is the linear combinations of fluxes $I_j^{\nu(1)}$ and $I_j^{\nu(2)}$ which can be written by analogy with Eq. (??)

$$\begin{aligned} \hat{I}^\nu &= -H_r^\nu (1 - f_r^\nu) \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu Z_r^\nu(G_\nu)}{\tau_r^\nu \kappa_\nu \theta^\nu} \\ &\quad - \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu \omega_{r+1}^\nu(G_\nu) \bar{H}_{r+1}^\nu}{\kappa_\nu S \theta^\nu} H_{re}^\nu(G_\nu) Z_r^\nu(G_\nu) (\mathcal{C}_{r,G_\nu,G_\nu,e}^\nu - \mathcal{C}_{r,G_\nu,G_\nu}^\nu) x_1 \\ &\quad + \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu H_{re}^\nu Z_r^\nu(G_\nu)}{\kappa_\nu S} I_{r+1}^{\nu(2)} \left(1 - \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu}{\kappa_\nu \theta^\nu} \right) \end{aligned} \quad (1.46)$$

and throughout this formula $r = r^\nu$.

Substituting the quasisteady populations found in the previous section transforms the equations for the slow variables x_1 , y_0 and z_0 into the following ones

$$\begin{aligned} \frac{dy_0}{dt} &= - \sum_{j=1}^N \sum_{i,k=0}^L \sum_{l=0}^M I_j^{0i}(l, k | i) \\ &\approx - \sum_{i,k=0}^L \sum_{l=0}^M I_1^{0i}(l, k | i) = K_1^{i+} x_1 y_{0e} (1 - S_i) - \hat{I}^i, \quad S_i = y_0/y_{0e}, \\ \frac{dz_0}{dt} &= - \sum_{j=1}^N \sum_{i,k=0}^O \sum_{l=0}^M I_j^{0e}(l, k | i) \approx - \sum_{i,k=0}^M \sum_{l=0}^M I_1^{0e}(l, k | i) = -I_1^{e(1)} \\ \frac{dx_1}{dt} &= - \sum_{j=0}^N \sum_{k=0}^{M_1} \left[\sum_{i,l=0}^M I_j^{00}(l, k | i) (1 + \delta_{lk} \delta_{j1}) (1 - \delta_{j0}) \right. \\ &\quad \left. + \sum_{i,l=0}^L I_j^{i0}(l, k | i) + \sum_{i,l=0}^O I_j^{e0}(l, k | i) \right] \\ &= - \sum_{\nu=0,i,e} \left[\sum_{j=2}^{r^\nu} j \frac{dH_j^\nu}{dt} + r^\nu I_{r^\nu+1}^{\nu 0} + \sum_{j=r^\nu+2}^N I_j^{\nu 0} \right] \\ &\quad - K_1^{i+} x_1 y_{0e} (1 - S_i) + \hat{I}^i - I_1^{e(1)} + K_1^{e+} z_{1e} x_1 (\bar{z}_1 - S) + \hat{I}^e \\ &= - \sum_{\nu=0,i,e} \left[\sum_{j=2}^{r^\nu} j \frac{dH_j^\nu}{dt} + r^\nu \hat{I}^\nu + \sum_{j=r^\nu+1}^N I_j^{\nu(1)} \right] \\ &\quad - K_1^{i+} x_1 y_{0e} (1 - S_i) + \hat{I}^i - I_1^{e(1)} + K_1^{e+} z_{1e} x_1 (\bar{z}_1 - S) + \hat{I}^e. \end{aligned} \quad (1.47)$$

Here dH_j^ν/dt denotes the right hand part of the corresponding equation in Eq. (1.43).

To solve Eqs. (1.43)–(1.47) we use our quasisteady-state method already described in chapter ???. Below we take a liberty once again to dwell briefly on the essence of this method. Since Eq. (1.43) can hardly be solved exactly it seems expedient to seek for asymptotic solutions. In doing this one has to divide all the concentrations appearing in Eq. (1.43) into fast and slow ones. As shown earlier this cannot be done with the original variables (concentrations), therefore we should rewrite the initial equations with the help of the following nonlinear substitution of variables $x_0 \rightarrow S_0$, $y_0 \rightarrow S_i$, $z_0 \rightarrow S_e$, $S_0 \equiv S$, $S_e = z_0/z_{0e}$, $x_2, \dots, x_N \rightarrow f_1^0, \dots, f_{N-1}^0$, $y_2, \dots, y_N \rightarrow f_1^i, \dots, f_{N-1}^i$, $z_2, \dots, z_N \rightarrow f_1^e, \dots, f_{N-1}^e$, where

$$f_{j-1}^\nu = \begin{cases} \bar{H}_j^\nu/S_0^j, & k_\nu \leq j \leq r^\nu, \\ \bar{H}_j^\nu/S_0 \bar{H}_{j-1}^\nu & j \geq r^\nu, \end{cases} \quad (1.48)$$

and $k_\nu = 2$, $\nu = 0$, $k_\nu = 1$, $\nu = i, e$. In new variables Eq. (1.43) reads

$$\begin{aligned} \frac{df_j^\nu}{d\tau} &= Y_j^\nu - (j+1)f_j^\nu \frac{d \ln S}{d\tau}, \quad j = 1, \dots, r^\nu - 1 \\ \frac{df_r^\nu}{d\tau} &= Y_r^\nu - \left(f_r^\nu + \frac{H_{re}^\nu}{S H_{r+1,e}^\nu} \right) Y_{r-1}^\nu - f_r^\nu \frac{d \ln S}{d\tau}, \\ \frac{df_j^\nu}{d\tau} &= R(f_j^\nu) - f_j^\nu \frac{d}{d\tau} \ln \left(\frac{S H_{j+1,e}^\nu}{H_{je}^\nu} \right) + \mu_j^\nu \\ &+ \delta_{j,r+1} \frac{H_{re}^\nu}{H_{r+1,e}^\nu S} \frac{f_{r+1}^\nu}{f_r^\nu} \left[Y_{r-1}^\nu + \frac{\bar{\gamma}}{K x_{1e}} \hat{I}_u^\nu \right], \\ & \quad j = r^\nu + 1, \dots, N - 1 \end{aligned} \quad (1.49)$$

Here Y_j^ν are the fluxes that turn to zero at $f_j^\nu = 1$.

$$\begin{aligned} Y_j^\nu &= \frac{\bar{C}_{j+1,0G_\nu}^\nu S}{s_{j+1}^\nu(0)} \left(1 - f_j^\nu + \gamma_3^\nu \frac{f_{r-1}^\nu}{S \theta^\nu \tau_r^\nu} \hat{I}_u^\nu \right), \quad j = 1, \dots, r^\nu - 2 \\ \gamma_3^\nu &= \left[\frac{C_{r-1,G_\nu,G_\nu}^\nu H_{r-1,e}^\nu Z_{r-1}^\nu(G_\nu)}{C_{j+1,G_\nu,G_\nu}^\nu H_{j+1,e}^\nu Z_{j+1}^\nu(G_\nu)} \right] \left[\frac{1 + C_{j+1,G_\nu,G_\nu}^\nu x_1 \alpha_{j+1}^\nu}{1 + C_{r-1,G_\nu,G_\nu}^\nu x_1 \alpha_{r-1}^\nu} \right] S^{r-j-1}, \\ Y_{r-1}^\nu &= -\frac{\bar{\gamma}^\nu}{K x_{1e}} (1 - f_{r-1}^\nu f_r^\nu) + \frac{\gamma_1^\nu}{x_{1e} K} (1 - f_r^\nu) f_{r-1}^\nu, \\ \bar{\gamma}^\nu &= \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu Z_r^\nu(G_\nu)}{\kappa^\nu \theta^\nu \tau_r^\nu}, \\ \gamma_1^\nu &= \frac{1}{\tau_r^\nu} \left[\frac{Z_r^\nu(G_\nu)(1 - \tau_r^\nu \theta^\nu)}{\tau_r^\nu \theta^\nu} - \sum_{k=1}^{G_\nu-1} Z_r^\nu(k) \frac{C_{r,kG_\nu}^\nu x_1}{C_{r,kG_\nu}^\nu x_1 + (\tau_r^\nu)^{-1}} \right], \end{aligned}$$

$$\begin{aligned}
Y_r^\nu &= -\frac{\bar{\gamma}^\nu}{K x_{1e}} \frac{H_{re}^\nu}{S H_{r+1,e}^\nu} \hat{I}_u^\nu - \bar{K}_{r+2}^{\nu+} S f_r^\nu (1 - f_{r+1}^\nu), \\
\hat{I}_u^\nu &= -\theta^\nu \tau_r^\nu \left(1 - \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu}{\kappa^\nu \theta^\nu} \right) \frac{1 - f_r^\nu f_{r-1}^\nu}{f_{r-1}^\nu} + 1 - f_r^\nu
\end{aligned}$$

The bar over parameters means that they are dimensionless. As a unit of time $(x_{1e}K)^{-1}$ is chosen while as the characteristic formation rate K — the value of the free molecular flux per unit of the cluster surface area is used. All the other notations are determined by the relations

$$\begin{aligned}
R(f_j^\nu) &= (a_j^\nu f_j^\nu - c_j^\nu)(f_j^\nu - 1), \\
a_j^\nu &= [\bar{K}_{j+2}^{\nu+}(1 - \delta_{j,N-1}) - \bar{K}_{j+1}^{\nu+}] S, \quad c_j^\nu = \frac{\bar{K}_{j+1}^{\nu-} - K_j^{\nu-}(1 - \delta_{j,r+1})}{x_{1e}} \\
\mu_j^\nu &= \bar{K}_j^{\nu-} (x_{1e})^{-1} \left(1 - \frac{f_j^\nu}{f_{j-1}^\nu} \right) (1 - \delta_{j,r+1}) \\
&\quad - \bar{K}_{j+2}^{\nu+} S (f_j^\nu)^2 \left(1 - \frac{f_{j+1}^\nu}{f_j^\nu} \right) (1 - \delta_{j,N-1}), \quad \nu = 0, i, e. \quad (1.50)
\end{aligned}$$

In new variables an equation for f_0^e has a special form

$$\frac{df_0^e}{d\tau} = -f_0^e \frac{d \ln S}{d\tau} + \bar{K}_1^{e+} \frac{z_{0e}}{z_{1e}} S (S_e - f_0^e) + \bar{K}_2^{e+} S^2 (1 - f_0^e) - \frac{\hat{I}^e}{K x_{1e} z_{1e} S}. \quad (1.51)$$

In order to derive equations for supersaturations S, S_i, S_e in new variables let us present the flux \hat{I}^ν in the form

$$\hat{I}^\nu = \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu Z_r^\nu(G_\nu)}{\kappa^\nu \tau_r^\nu \theta^\nu} H_{re}^\nu S^r f_{r-1}^\nu \left[1 - f_r^\nu - \tau_r^\nu \theta^\nu \left(1 - \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu}{\kappa^\nu \theta^\nu} \right) \frac{1 - f_{r-1}^\nu f_r^\nu}{f_{r-1}^\nu} \right] \quad (1.52)$$

where we took into account that the last term in Eq. (1.46) vanishes for the equilibrium distribution $x_1(k) = x_1 Z_1^0(k)$, $y_0(k) = y_0 Z_0^i(k)$. Using this representation we may rewrite Eq. (1.47) as follows

$$\begin{aligned}
dS_i/d\tau &= \bar{K}_1^{i+} S (1 - S_i) + \frac{y_{re}}{y_{0e}} \frac{\mathcal{E}_{r,L,L}^i Z_r^i(L)}{\kappa_i \tau_r^i \theta^i K x_{1e}} S^r f_{r-1}^i \\
&\quad \cdot \left[1 - f_r^\nu - \tau_r^\nu \theta^\nu \left(1 - \frac{\mathcal{E}_{r,G_\nu,G_\nu}^\nu}{\kappa^\nu \theta^\nu} \right) \frac{1 - f_{r-1}^\nu f_r^\nu}{f_{r-1}^\nu} \right], \quad r \equiv r^i, \\
dS_e/d\tau &= -\bar{K}_1^{e+} S (S_e - f_0^e), \\
dS/d\tau &= - \sum_{j=r^0+2}^N [1 + (r+1)\delta_{j,r+2}] \bar{K}_j^{0+} S^j \beta_{j-1}^0 (1 - f_{j-1}^0) \prod_{i=r^0-1}^{j-1} f_i^0
\end{aligned}$$

$$\begin{aligned}
& - \sum_{j=r^i+2}^N [1 + (r+1)\delta_{j,r+2}] \bar{K}_j^{i+} S^j \beta_{j-1}^i (1 - f_{j-1}^i) \prod_{k=r^i-1}^{j-1} f_k^i \\
& - \sum_{j=r^e+2}^N [1 + (r+1)\delta_{j,r+2}] \bar{K}_j^{e+} S^j \beta_{j-1}^e (1 - f_{j-1}^e) \prod_{k=r^e+1}^{j-1} f_k^e \\
& - \bar{K}_1^{i+} \frac{y_{0e}}{x_{1e}} S(1 - S_i) - \bar{K}_1^{e+} \frac{z_{0e}}{x_{1e}} S(S_e - f_0^e) \\
& - \bar{K}_2^{e+} \frac{z_{1e}}{x_{1e}} S(1 - f_0^e) - \frac{r^0}{Kx_{1e}^2} \hat{f}^0 - \frac{(r^i - 1)}{Kx_{1e}^2} \hat{f}^i - \frac{(r^e - 1)}{Kx_{1e}^2} \hat{f}^e \\
& - \sum_{\nu=0, i, e} \sum_{j=2}^{r^\nu} j \beta_j^\nu S^j f_{j-1}^\nu Y_{j-1}^\nu \\
& - \sum_{\nu} (r+1) \beta_r^\nu S^r f_{r-1}^\nu \left[Y_r^\nu - \frac{H_{r+1, e}^\nu}{H_{r, e}^\nu S} Y_r^\nu \right] \\
\beta_j^\nu & = H_{j, e}^\nu / x_{1e}. \tag{1.53}
\end{aligned}$$

As shown in chapter ?? and section ??? at vapor condensation under adiabatic conditions in nozzles, jets, and thermal diffusion chambers f_j is a smooth function of number j , so that $\mu_j \ll 1$. On the strength of this the equations under consideration in variables f_j split into independent subsets. By full analogy with the case of homogeneous condensation it can be shown that among all the new variables only supersaturation S and f_j , $j > \bar{j} \approx (2/3\varepsilon)^3$, $\varepsilon \ll 1$ are slow, while the rest of f_j including f_N are fast. This feature of Eqs. (1.49)–(1.53) allows us to apply again the asymptotic methods developed for singularly perturbed system of ordinary differential equations. The corresponding solution is

$$\begin{aligned}
f_j^\nu & = \min_j [1, c_j^\nu / a_j^\nu], \quad j = r^\nu + 1, \dots, \bar{j}, \\
f_j^\nu & = 1, \quad j < r^\nu, \quad \nu = 0, i, e, \\
f_0^e & = \frac{\bar{K}_2^{e+} S + \bar{K}_1^{e+} z_{0e} S_e / z_{1e}}{\bar{K}_2^{e+} S + \bar{K}_1^{e+} z_{0e} / z_{1e}}. \tag{1.54}
\end{aligned}$$

In what follows we denote by h^ν the size of a cluster for which $c_j^\nu / a_j^\nu = 1$.

Equations (1.49) and (1.53) for slow f_j are the Riccati equations with the known partial solution $f_j = 1$. Hence, we can write their explicit solution in quadratures⁶. Using relation $\beta_j \equiv n_{j, e} / n_{1e} \ll 1$, $j \geq 2$ proved in section ??? and Eq. (1.53) for supersaturation S we arrive at a closed equation

$$dS/d\tau = - \sum_{j=r^0+2}^N [1 + (r+1)\delta_{j,r+2}] \bar{K}_j^{0+} S^j \beta_{j-1}^0 (1 - f_{j-1}^0) \prod_{i=r^0+1}^{j-1} f_i^0$$

$$\begin{aligned}
& - \sum_{j=r^i+2}^N [1 + (r+1)\delta_{j,r+2}] \bar{K}_j^{i+} S^j \beta_{j-1}^i (1 - f_{j-1}^i) \prod_{k=r^i+1}^{j-1} f_k^i \\
& - \sum_{j=r^e+2}^N [1 + (r+1)\delta_{j,r+2}] \bar{K}_j^{e+} S^j \beta_{j-1}^e (1 - f_{j-1}^e) \prod_{k=r^e+1}^{j-1} f_k^e \\
& - \bar{K}_1^{i+} \frac{y_{0e}}{x_{1e}} S(1 - S_i) - \frac{\bar{K}_1^{e+} K_2^{e+} z_{0e}/x_{1e}}{\bar{K}_2^{e+} S + \bar{K}_1^{e+} z_{0e}/z_{1e}} S(1 - S_e)(1 - S).
\end{aligned} \tag{1.55}$$

In order to decide to which type of variables, fast or slow, S_i and S_e belong, we might estimate the characteristic rates \bar{K}_1^{i+} and \bar{K}_1^{e+} are needed, but their finding is not an easy task. Therefore we retain the differential form of the equations describing evolution of these variables rather than the use of the truncated equations. This does not contradict the general idea of the method of singular perturbations since the truncated equations, that follow from the full differential equations at $\bar{K}_1^{i+} = O(1)$ and $\bar{K}_1^{e+} = O(1)$, are particular cases of the latter. Substituting the values of f_j^ν found in Eq. (1.53) yields

$$\begin{aligned}
dS_i/d\tau &= \bar{K}_1^{i+} S(1 - S_i) \\
dS_e/d\tau &= \frac{\bar{K}_2^{e+} S \bar{K}_1^{e+} z_{0e}/z_{1e}}{\bar{K}_2^{e+} S + \bar{K}_1^{e+} z_{0e}/z_{1e}} S(1 - S_e).
\end{aligned} \tag{1.56}$$

Thus, the set of Eqs. (1.43) reduces to three equations Eqs. (1.55)–(1.56) governing the evolution of supersaturations S , S_i and S_e . The remaining concentrations x_j , y_j and z_j of heterogeneous and homogeneous clusters may be found by means of already known supersaturations and f_j^ν according to analytic formulae given in this section.

The closed set of equations for concentrations of heterogeneous and homogeneous clusters derived here and the equations for supersaturations S_ν , $\nu = 0, i, e$ that follow from this set enable one to qualitatively analyze the kinetics of heterogeneous condensation within the microscopic condensation model. This problem is discussed in the following section.

5. An analysis of specific features of heterogeneous condensation on ions and electrons

In the previous sections we have formulated the basic equations governing evolution of the populations of neutral and charged (both positive and negative) clusters and found their equilibrium and quasisteady solutions. These results substantially simplify the original kinetic equations for populations of

the vibrational states of clusters reducing their number to three equations describing the evolution of the concentrations of monomers and free electrons and ions. The concentrations and populations of the other clusters are evaluated from the known concentrations of monomers and free electrons and ions using the analytical formulae derived. This section is devoted to an analysis of the aforesaid three equations for the concentrations of free molecules, ions, and electrons or for supersaturations $S_0 = x_1/x_{1e}$, $S_i = y_0/y_{0e}$ and $S_e = z_0/z_{0e}$ related to these concentrations. We also discuss the qualitative peculiarities of heterogeneous condensation in expanding flows. It is found that the condensation processes involving ions and electrons differ significantly.

5.1. An analysis of equations for supersaturations

Applying Eqs. (1.55)–(1.56) we may qualitatively analyze and provide physical interpretation of the peculiarities of vapor condensation in the presence of ions and electrons. However, for this purpose one should derive an explicit expression for quantity h^ν , $\nu = 0, i, e$. This can be done using the equations for the equilibrium concentrations of the homogeneous and heterogeneous clusters Eq. (1.24) and definitions of h^ν , a^ν and c^ν provided by Eq. (1.54).

5.1.1. Calculation of h^0

Constants K_j^{0-} and K_j^{0+} appearing in the expressions that define a_j^0 and c_j^0 are related by the detailed balance equation:

$$\begin{aligned} K_j^{0+} &= \sum_{l,i} C_{j-1}^{00}(l, i | M) Z_{j-1}^0 Z_1^0(i) \\ &= \frac{x_{je}}{x_{j-1,e} x_{1e}} \sum_{l,i} E_j^{00}(M | l, i) Z_j^0(M) = \frac{x_{je}}{x_{j-1,e} x_{1e}} K_j^{0-} \end{aligned}$$

therefore it is sufficient to specify only one of these constants. To find K_j^{0-} we use the results of section ?? in which an explicit expression Eq. (??) of this dissociation rate constant has been obtained based on the statistical theory of reactions. Further it is easy to note that the definition of h_0 is exactly equal to the definition of j_* in Eq. (??). Thus, we can utilize the final representation of j_* obtained in section ?? (see also section ??) and put that h_0 is the root of Eq. (??)

$$\frac{1}{S} \exp\left(\frac{2b}{3j^{1/3}}\right) = 1 + \delta_j,$$

that yields

$$j_* = \begin{cases} j_{*,cl}/8, & \text{at low } S \\ j_{*,cl}, & \text{at high } S \end{cases} \quad (1.57)$$

where as usual $j_{*,cl}$ is the classical critical size. We recall that at $j < j_*$ the quasisteady solution takes the form $f_j = 1$ while at $j > j_*$ it looks like $f_j = S^{-1} \exp(2b/3j^{1/3})$.

5.1.2. Calculation of h^ν , $\nu = i, e$

By analogy with the previous paragraph, we find

$$\begin{aligned} c_j^i/a_j^i &\approx y_{je}/y_{j+1,e} = x_{je}K_j^i/x_{j+1,e}K_{j+1}^i \approx \varphi_j^i c_j^0/a_j^0, \\ \varphi_j^i &\equiv K_j^i/K_{j+1}^i \approx \exp\left[\frac{1}{k_B T} \left(\frac{\partial \Delta \Psi_j^i}{\partial j}\right)\right], \\ c_j^e/a_j^e &\approx \varphi_j^e c_j^0/a_j^0, \quad \varphi_j^e \equiv K_j^e/K_{j+1}^e \approx \exp\left[\frac{1}{k_B T} \left(\frac{\partial \Delta \Psi_j^e}{\partial j}\right)\right]. \end{aligned} \quad (1.58)$$

Using representation Eq. (1.22) for $\Delta \Psi_j^e$ and $\Delta \Psi_j^i$ we specify the terms in brackets:

$$\frac{\partial \Delta \Psi_j^e}{\partial j} = -\frac{44\pi B e^2}{9\eta j^{4/3}} - 4\pi e \frac{\partial \mathcal{P}(j)}{\partial j}. \quad (1.59)$$

A similar expression can be written for $\partial \Delta \Psi_j^i/\partial j$ provided $r_a^3 \ll \eta^3 j$. In particular, the last inequality obviously holds for heterogeneous condensation of water vapors.

To find $\partial \mathcal{P}(j)/\partial j$ according to ²¹ we expand polarization $\mathcal{P}(j)$ into a series in terms of charge e retaining only quadratic terms

$$\begin{aligned} \mathcal{P} &= \mathcal{P}_0 + a_1 e + a_2 e^2, \\ a_1 &= 4B\bar{\eta}/r(r + \bar{\eta}), \quad a_2 = k_2(r + \xi)^{-4}. \end{aligned} \quad (1.60)$$

Here $\bar{\eta}$ is the shift of the phase interface from the state with $a_1 = 0$ to the state with $a_1 \neq 0$, k_2 and ξ are parameters of the model and \mathcal{P}_0 is the spontaneous polarization. Quantity k_2 was expressed in ²¹ by the following approximate equation

$$k_2 = -\frac{\mathcal{P}_0}{8\pi^2 \mathcal{P}_\infty^2} \left(1 - \frac{1}{\epsilon_l}\right)^2, \quad (1.61)$$

where $\mathcal{P}_\infty = p\rho_l$ and p is the dipole moment of the molecule. Thence,

$$\frac{\partial \mathcal{P}(j)}{\partial j} = \frac{\partial \mathcal{P}(r)}{\partial r} \frac{\partial r}{\partial j} \approx -\frac{8B\bar{\eta}e}{3\eta^2 j^{5/3}} \left(1 - \frac{8Be\mathcal{P}_0}{\bar{\eta}\eta^2 \mathcal{P}_\infty^2 j}\right). \quad (1.62)$$

Then we have for φ_j^ν , $\nu = i, e$

$$\varphi_j^\nu = \exp \left\{ -\frac{44\pi Be^2}{9\eta j^{4/3} k_B T} \left[1 - \frac{24\bar{\eta}}{11\eta} j^{-1/3} \left(1 - \frac{8Be\mathcal{P}_0}{\bar{\eta}\eta^2 \mathcal{P}_\infty^2 j} \right) \right] \right\}. \quad (1.63)$$

Thus, to find h^ν one should solve the equation that follows from Eqs. (??), (1.57), and (1.63)

$$-\frac{44\pi Be^2}{9\eta j^{4/3} k_B T} \left[1 - \frac{24\bar{\eta}}{11\eta} j^{-1/3} \left(1 - \frac{8Be\mathcal{P}_0}{\bar{\eta}\eta^2 \mathcal{P}_\infty^2 j} \right) \right] + \frac{2b}{3j^{1/3}} - \ln S = 0 \quad (1.64)$$

or

$$-\frac{\delta_1}{j^{4/3}} \left[1 - \frac{\delta_2}{j^{1/3}} \left(1 - \frac{\delta_3}{j} \right) \right] + \frac{\delta_4}{j^{1/3}} - \ln S = 0. \quad (1.65)$$

We estimate the characteristic value of each term of Eq. (1.62) using parameters appearing in them from [?]. For water vapor $\mu = 18$ g/mol and $\rho_l = 1$ g/mol³, therefore $\eta = 2.15\text{\AA}$ and $e^2/\eta k_B = 6 \cdot 10^4$ K. The ϵ_l values depend on the temperature: $\epsilon_l = 78.8$ at $T = 298$ K, $\epsilon_l = 34.6$ at $T = 481$ K, $\epsilon_l = 10.1$ at $T = 637$ K, and $\epsilon_\vartheta = 1$ at any temperature. Thence, $4\pi B = 0.24$ for water vapor at $T = 300$ K. As a result $\delta = 44\pi Be^2/9\eta j^{4/3} = 58.7$. At the same temperature $\sigma = 128 - 0.19T = 71$ dyne/cm and $\delta_4 = 8\pi\sigma/3k_B T = 6.5$. Furthermore, according to the data given in ²¹ $4\pi\mathcal{P}_0 = -0.1$ V and $p = 1.8$ Deby for water molecules and thus $k_2 = 8.6 \cdot 10^{-17}$ CGSE units. The value of $\bar{\eta}$ for a water molecule must be less than 1.3\AA , the value suggested in ²¹ is $\bar{\eta} = 1\text{\AA}$. Then $\delta_3 = \pm 1.3$ and $\delta_2 = 1$. The sign of δ_3 depends on the sign of charge e . For condensation on positive ions $e > 0$ and $\delta_3 < 0$ while for condensation on electrons $\delta_3 > 0$.

Since the solution of Eq. (1.65) cannot be written in an explicit analytical form we perform its qualitative analysis. For this purpose we rewrite Eq. (1.65) as follows

$$1 - \frac{\delta_1}{j\delta_4} \left[1 - \frac{\delta_2}{j^{1/3}} \left(1 - \frac{\delta_3}{j} \right) \right] = \left(\frac{j}{j_{*,cl}} \right)^{1/3}. \quad (1.66)$$

We recall that we have denoted solution of Eq. (1.66) by h . At a fixed temperature $j_{*,cl}$ depends only on supersaturation ($j_{*,cl} = (\delta_4/\ln S)^3$).

The solution of Eq. (1.66) depends essentially on the sign of the heterogeneous cluster charge. For ionic clusters $\delta_3 < 0$, therefore the left hand side of

Fig. 1
Dependencies of h_i (the dash line), h_e (the dash-dot line) and j_* (the solid line) on $\ln S$ at $T = \text{const}$.

Eq. (1.66) is positive at $j \geq 1$. In view of this Eq. (1.66) has a single solution in this range of j values (the other solutions are physically meaningless). As S values close to unity $j_{*,cl} \rightarrow \infty$, therefore $h^i \approx j_{*,cl}$. As S grows the $j_{*,cl}$ value drops (see Fig. 1). The value of h^i also drops due to this. The $h^i(S)$ curve intersects the $j_{*,cl}(S)$ line at j values making the bracketed expression in Eq. (1.66) vanish.

For the electronic clusters the value of δ_3 is positive. This makes the left hand side of Eq. (1.66) vanish at some $j = h_*^e$ and the $h^e(S)$ dependence assumes the form demonstrated in Fig. 1. It is seen that at $S < S_c$ Eq. (1.66) has two roots. The greater root $h_1^e \approx j_{*,cl}$ at S values close to unity and $h_1^e < h^i < j_{*,cl}$. As S rises, h_1^e drops while h_2^e increases until their values become equal at point $S = S_c$. Equation (1.66) has no root at $S > S_c$.

Since the dependence $h^e(S)$ of this type is unusual (e.g., compared to those for h^i and h^0), we have to specify more precisely the c_j^e/a_j^e values appearing in Eqs. (1.55)–(1.56). These values can easily be derived from Eq. (1.66) based on the analysis performed above, because $c_j^e/a_j^e = \varphi_j^e \exp(-\ln S + \delta_4 j^{-1/3})$. At $S < S_c$ the result reads

$$\begin{aligned} c_j^e/a_j^e < 1, \quad h_2^e > j > h_1^e, \\ c_j^e/a_j^e > 1, \quad h_2^e < j < h_1^e. \end{aligned} \quad (1.67)$$

At $S > S_c$ one has $c_j^e/a_j^e < 1$ for any j .

Note that δ_2 and δ_3 are independent of T , whereas the δ_1/δ_4 ratio depends on T only due to the $\delta(T)$ function. As T grows parameters σ and $j_{*,cl}$ fall off, whereas the δ_1/δ_4 ratio grows. For this reason at a fixed S the h^i value drops with increasing T steeper than $j_{*,cl}$ does (Fig. 2). An increase in T raises h_2^e and reduces h_1^e . To derive the S_c and h_c^e dependence on T we should find the explicit solution of the equation $\partial \ln S / \partial h^e = 0$. Differentiating Eq. (1.65) with respect to $\ln S$ and equating $\partial \ln S / \partial h^e$ yields

$$1 = \frac{\delta_1}{\delta_4 h_c} \left(4 - \frac{\delta_2}{h_c^{1/3}} \right) \quad (1.68)$$

whence

$$\frac{\partial h_c}{\partial T} = h_c \frac{\partial \ln \sigma}{\partial T} \left(\frac{\delta_1 \delta_2}{3 \delta_4 h_c^{4/3}} - 1 \right)^{-1}.$$

It is well known that $\partial \ln \sigma / \partial T < 0$. Quantity $\delta_1 \delta_2 / 3 \delta_4$ for water ranges between 3 and ∞ as T varies from 300K to T_c , where T_c is the temperature at the critical point. Therefore, at low T values $\partial h_c / \partial T > 0$, while at high T they are negative.

Fig. 2
Dependencies of h_i and $j_{*,cl}$ on T at $\ln S = \text{const.}$

Note that though the c_j^e/a_j^e ratio is greater than unity for homogeneous and ionic clusters at $S < 1$, this ratio for electronic clusters at $S < 1$ is below unity within some region $j < h_2^e$.

5.1.3. Equations for supersaturations S , S_i and S_e

In this paragraph we show that a closed set of equations for supersaturations S , S_i and S_e can be derived from Eqs. (1.55)–(1.56). We note that the sums appearing in Eq. (1.56) can be transformed into

$$\begin{aligned} \sum_{j=q+2}^N K_j^{0+} S^j \beta_{j-1}^0 (1 - f_{j-1}^0) \prod_{i=q+1}^{j-1} f_i^0 &= \sum_{j=q+2}^{\bar{j}+1} S^{q+1} \left[S - \exp\left(\frac{2b}{3j^{1/3}}\right) \right] \tau_j^{-1} \\ &+ \sum_{j=\bar{j}+2}^N S^{q+j-\bar{j}} (1 - f_{j-1}) \prod_{i=\bar{j}+1}^{j-1} f_i/\bar{\tau}_i, \quad q \equiv \max(r^0, h^0). \\ \tau_j^{-1} &= \bar{K}_j^{0+} \beta_{j-1}^0 (\bar{A}_{q+1}/\bar{A}_{j-1}) \exp\left[\frac{2b}{3} \sum_{i=q+1}^{j-1} i^{-1/3}\right] \approx \bar{K}_j^{0+} \beta_{q+1}, \\ \bar{\tau}_j &= \bar{K}_j^{0+} \beta_j^0 \exp\left[\frac{2b}{3} \sum_{i=q+1}^{\bar{j}} i^{-1/3}\right] \\ &\approx \bar{K}_j^{0+} (\bar{A}_j/x_{1e}) \exp\left[-b(j^{2/3} - \bar{j}^{2/3} + q^{2/3})\right] \ll 1. \end{aligned} \quad (1.69)$$

At $q > \bar{j}$ the first sum in Eq. (1.69) is missing. Since according to estimates of section ???.?? $b_j^0 \ll 1$ at $j > \bar{j}$, we may neglect the second sum in Eq. (1.69). That yields the final expression

$$\begin{aligned} \sum_{j=q+2}^N K_j^{0+} S^j \beta_{j-1}^0 (1 - f_{j-1}^0) \prod_{i=q+1}^{j-1} f_i^0 \\ = \sum_{j=q+2}^{\bar{j}+1} S^{q+1} \left[S - \exp\left(\frac{2b}{3j^{1/3}}\right) \right] \tau_j^{-1} \approx \frac{2\beta_{q+1}^0 S^{q+2} \bar{K}_{q+2}^{0+} b}{9q^{4/3}}. \end{aligned} \quad (1.70)$$

We apply a similar procedure to transform the remaining sums in Eq. (1.62)

$$\begin{aligned} \sum_{j=r^\nu+2}^N K_j^{\nu+} S^{j+1} \beta_{j-1}^\nu (1 - f_{j-1}^\nu) \prod_{i=r^\nu+1}^{j-1} f_i^\nu &= \sum_{j=q+2}^{\bar{j}+1} \bar{K}_j^{\nu+} \beta_{j-1}^\nu S^{q+2} \prod_{i=q+1}^{j-1} \varphi_i^\nu \\ \cdot \left[1 - \varphi_j^\nu S^{-1} \exp(-bj^{2/3}) \right] &= \bar{K}_{q+2}^{\nu+} \beta_{q+1}^\nu S^{q+2} \varphi_q^\nu \varphi_{q+1}^\nu \left[\frac{b}{9q^{4/3}} - \frac{\partial \ln \varphi_j^\nu}{\partial j} \right] \end{aligned}$$

$$\approx 2\bar{K}_{q+2}^{\nu+}\beta_{q+1}^{\nu}S^{q+2}\varphi_q^{\nu}\varphi_{q+1}^{\nu}\frac{b}{9q^{4/3}}, \quad \nu = i, e. \quad (1.71)$$

Note that relation

$$\varphi^{\nu}(q_{\nu}) = S \exp\left(-\frac{2b}{3h_{\nu}^{1/3}}\right)$$

follows from Eqs. (1.63)–(1.64) at $q_{\nu} = h_{\nu}$.

The set of Eqs. (1.55)–(1.56) together with Eqs. (1.70)–(1.71) reduces to

$$\begin{aligned} dS/d\tau &= -\bar{K}_1^{i+}\frac{y_{0e}}{x_{1e}}S(1-S_i) - \frac{\bar{K}_1^{e+}K_2^{e+}z_{0e}/x_{1e}}{\bar{K}_2^{e+}S + \bar{K}_1^{e+}z_{0e}/z_{1e}}S(1-S_e)(1-S) \\ &\quad - 2\bar{K}^{0+}(q_0+2)\beta^0(q_0+1)S^{q_0+2}b/9q_0^{4/3} \\ &\quad - 2\bar{K}^{e+}(q_e+2)\beta^e(q_e+1)S^{q_e+2}b/9q_e^{4/3} \\ &\quad - 2\bar{K}^{i+}(q_i+2)\beta^i(q_i+1)S^{q_i+2}b/9q_i^{4/3}, \\ q_{\nu} &= \max(r^{\nu}, h_{\nu}), \quad K(j) = K_j, \quad \varphi(j) = \varphi_j, \quad \beta^{\nu}(j) = \beta_j^{\nu}, \\ dS_i/d\tau &= \bar{K}_1^{i+}S(1-S_i), \\ dS_e/d\tau &= \frac{\bar{K}_2^{e+}S\bar{K}_1^{e+}z_{0e}/z_{1e}}{\bar{K}_2^{e+}S + \bar{K}_1^{e+}z_{0e}/z_{1e}}S(1-S_e). \end{aligned} \quad (1.72)$$

There are two ranges of the terms appearing in Eqs. (1.55)–(1.56) and containing f_j^e where f_j^e differs from unity: a) $r^e \leq j < h_2^e$; b) $h_1^e < j < \bar{j}$. Since $h_1 > h_2$ the terms corresponding to range “b” can be neglected because $\beta(h_1^e) \ll \beta(h_2^e)$. Thus, as a definition of q_e presented in Eq. (1.72) it is reasonable to take $q_e = \max(r^e, h_2^e)$. At $S = S_c$ we have $h_1^e = h_2^e$ and hence this definition is self-consistent (this case corresponds to a situation in which f_j is other than unity in the $r \leq j < \bar{j}$ range for neutral and ionic clusters). At $S > S_c$ the ratio c_j/a_j is greater than unity therefore $q_e = r^e$.

5.1.4. Fast and slow relaxation of S_e and S_i

By solving Eq. (1.72) we may determine how supersaturations S , S_i and S_e vary with time. Generally, the rate of this evolution depends on the dimensionless rate constants \bar{K}_j^{0+} , \bar{K}_j^{i+} and \bar{K}_j^{e+} and on the dimensionless equilibrium concentrations β_j^{ν} , $\nu = 0, i, e$. In this paragraph we analyze the possible regimes of heterogeneous condensation arising at various ratios between these constants.

A fast change of S_i and S_e . First we consider the case $\bar{K}_j^{i+} \sim O(1)$. Then, $dS_i/d\tau \sim O(1)$. To estimate the order of magnitude of $dS_e/d\tau$ we consider the

ratio z_{0e}/z_{1e} presented on the right hand side of the equation for S_e . According to Eq. (1.24) this ratio is

$$z_{0e}/z_{1e} = [\bar{A}_1 \exp(-h_1) K_1^e]^{-1}.$$

The subscript of b signifies the dependence of the macroscopic surface energy on size j for small clusters. It is reasonable to assume that $b_1 \approx 0$. Using the expression of \bar{A}_j given in Eq. (??) and representation Eq. (??) for K_j^e we can show that $z_{0e}/z_{1e} \ll 1$ in view of the inequality $(6\varepsilon_0 + \Delta\Psi_j^e)/k_B T \gg 1$.

Let us also assume that $\bar{K}_2^{e+} S \leq \bar{K}_1^{e+} z_{0e}/z_{1e}$. Then we find from Eq. (1.72) that

$$dS_e/d\tau \approx \bar{K}_2^{e+} S^2 (1 - S_e).$$

Since \bar{K}_1^{i+} and \bar{K}_2^{e+} are of the same order according to their physical meaning, one has $dS_e/d\tau \sim O(1)$.

Finally, we estimate the right hand side of the equation for S . Quantities $\beta_j^\nu \ll 1$, $\nu = 0, i, e$, $j \geq 2$. This is shown for $\nu = 0$ in section ???. For $\nu = i, e$ this can be shown using the relations reported in section 1. Quantity $\beta(q+1)S^{q+1} \ll 1$, $q \equiv q_\nu$, therefore the first two terms $\bar{K}_1^{i+}(y_{0e}/x_{1e})S(1 - S_i)$ and $\bar{K}_1^{e+} K_2^{e+}(z_{0e}/x_{1e}) [\bar{K}_2^{e+} S + \bar{K}_1^{e+}(z_{0e}/z_{1e})]^{-1} S(1 - S_e)(1 - S)$ are dominant in the right hand side of the equation for S if β_0^i and β_0^e are not too small. Further on two situations are possible.

(a) $\beta_0^e \sim O(\varepsilon)$ and $\beta_0^i \sim O(\varepsilon)$. It is easy to see that under the considered conditions $dS/d\tau \sim O(\varepsilon)$, $dS_i/d\tau \sim O(1)$ and $dS_e/d\tau \sim O(1)$. Thus, S_i and S_e are fast variables whereas S is a slow variable. Then we may again perform an asymptotic integration of Eq. (1.72) (the third stage) and obtain the quasisteady values of the fast variables. The solution of the truncated equations for S_i and S_e is trivial: $S_i = S_e = 1$. Hence, the quasisteady concentrations of free ions and electrons in this case are identical with their equilibrium values.

The equation for S takes the following form after substituting S_i and S_e in it

$$\begin{aligned} dS/d\tau = & - 2\bar{K}^{0+} (q_0 + 2) \beta^0 (q_0 + 1) S^{(q_0+2)} b/9q_0^{4/3} \\ & - 2\bar{K}^{i+} (q_i + 2) \beta^i (q_i + 1) S^{(q_i+2)} \varphi^i(q_i) \varphi^i(q_i + 1) b/9q_i^{4/3} \\ & - 2\bar{K}^{e+} (q_e + 2) \beta^e (q_e + 1) S^{(q_e+2)} \varphi^e(q_e) \varphi^e(q_e + 1) b/9q_e^{4/3}, \\ q_\nu = & \max(r^\nu, h_\nu), \quad K(j) = K_j, \quad \varphi(j) = \varphi_j, \quad \beta^\nu(j) = \beta_j^\nu. \end{aligned} \quad (1.73)$$

It is seen that the terms containing S_i and S_e dropped out from this equation. By virtue of this the conditions $\beta_0^e \sim O(\varepsilon)$ and $\beta_0^i \sim O(\varepsilon)$ seem to

be excessively rigorous. Indeed, as seen from Eq. (1.73) the condition under which this regime of the process is realized should be specified by inequality

$$\max_{\nu} [\bar{K}^{\nu+} (q_{\nu} + 2) \beta^{\nu} (q_{\nu} + 1) S^{q_{\nu}+2}] \sim O(\varepsilon).$$

(b) $\beta_0^e \sim O(1)$ and $\beta_0^i \sim O(1)$. On the strength of the aforesaid the solution is completely identical with that obtained in the previous subparagraph.

Slow relaxation of S_i and S_e . The above analysis demonstrates that the rate of the S variation is low enough $dS/d\tau \ll dS_e/d\tau \sim dS_i/d\tau$. Is it possible that under certain conditions all these derivatives are of the same order? A positive reply would require that the following approximate relation holds

$$\max_{\nu} [\bar{K}^{\nu+} (q_{\nu} + 2) \beta^{\nu} (q_{\nu} + 1) S^{q_{\nu}+2}] \sim \bar{K}_1^{i+} \sim \bar{K}_2^{e+} \sim O(1). \quad (1.74)$$

Since β is small this is possible only when supersaturation S is large. In such a case Eq. (1.74) does not tolerate further simplifications, therefore to find S , S_e and S_i one should solve these equations numerically.

5.2. Heterogeneous condensation in expanding flows

The quasisteady-state method described in chapter ?? was extended in chapter ?? as applied to spatially nonuniform systems. Let us remind that the appropriate kinetic equations written in terms of new variables (mass populations and concentrations) have a structure similar to that reported in chapter ??, and their solutions are obtained in a similar way. It can be easily shown that the method of section ?? is directly applicable to the case of heterogeneous condensation. As a result the set of gasdynamic equations governing an expanding flow without condensation is supplemented only by Eq. (1.72). Other parameters such as the concentrations of homogeneous and heterogeneous clusters and populations of their energetic levels may be restored from the analytical expressions derived in this section. In what follows we discuss this problem in more detail.

5.2.1. The method of the reduced description of flows with condensation

In order to understand the qualitative nature of heterogeneous condensation in expanding flows we consider, for instance, a one-dimensional supersonic flow along a stream tube. The corresponding equations governing this

flow with homogeneous condensation were derived in section ???. Similar manipulations yield in our case

$$\begin{aligned}
(M^2 - 1) \frac{d \ln u}{d\xi} &= \frac{d \ln F}{d\xi} - \nu \Omega, \\
(M^2 - 1) \frac{d \ln \rho}{d\xi} &= -M^2 \frac{d \ln F}{d\xi} + \nu \Omega, \\
(M^2 - 1) \frac{d \ln P}{d\xi} &= \frac{\rho u^2}{P} \left[\frac{d \ln F}{d\xi} - \nu \Omega \right], \\
(M^2 - 1) \frac{d \ln T}{d\xi} &= \frac{u^2}{\sigma} \frac{d \ln F}{d\xi} + \left[\frac{u^2}{\sigma} \left(1 - \frac{L\alpha_1^0}{\sigma} \right) - \frac{L\alpha_1^0 (M^2 - 1)}{\sigma} \right] \Omega \\
\frac{u}{Kx_{1e}} \frac{d \ln \alpha_1^0}{d\xi} &= -2\bar{K}^{0+} (q_0 + 2) \beta^0 (q_0 + 1) S^{q_0+1} \frac{b}{9q_0^{4/3}} \\
&\quad - 2\bar{K}^{i+} (q_i + 2) \beta^i (q_i + 1) S^{q_i+1} \varphi^i (q_i) \varphi^i (q_i + 1) \frac{b}{9q_i^{4/3}} \\
&\quad - 2\bar{K}^{e+} (q_e + 2) \beta^e (q_e + 1) S^{q_e+1} \varphi^e (q_e) \varphi^e (q_e + 1) \frac{b}{9q_e^{4/3}} \\
&\quad - \bar{K}_1^{i+} \beta_0^i (1 - S_i) - \frac{\bar{K}_1^{e+} K_2^{e+} \beta_0^e}{\bar{K}_2^{e+} S + \bar{K}_1^{e+} (z_{0e}/z_{1e})} (1 - S_e)(1 - S), \\
\frac{u}{Kx_{1e}} \frac{d \ln \alpha_0^e}{d\xi} &= \frac{\bar{K}_2^{e+} S \bar{K}_1^{e+} z_{0e}/z_{1e}}{\bar{K}_2^{e+} S + \bar{K}_1^{e+} z_{0e}/z_{1e}} S \frac{(1 - S_e)}{S_e}, \\
\frac{u}{Kx_{1e}} \frac{d \ln \alpha_0^i}{d\xi} &= \bar{K}_1^{i+} S \frac{(1 - S_i)}{S_i}, \tag{1.75}
\end{aligned}$$

where

$$\begin{aligned}
q_\nu &= \max(r^\nu, h_\nu), \quad K(j) = K_j, \quad \varphi(j) = \varphi_j, \quad \beta^\nu(j) = \beta_j^\nu, \\
\Omega &= d \ln \alpha_1 / d\xi, \quad \alpha_1 = m_0 x_{1e} S / \rho, \quad \alpha_0^i = m_i y_{0e} S_i / \rho, \quad \alpha_0^e = m_e z_{0e} S_e / \rho, \\
\nu &= 1 - L\alpha_1 \left(\frac{5P}{2\rho} + \frac{T}{\mu_1} \frac{\partial h_{1,i}}{\partial T} \right), \quad M = \frac{u}{a}, \\
\sigma &= u^2 \left(\frac{\rho u^2}{P} - M^2 \right)^{-1} = \left(\frac{5P}{2\rho} + \frac{T}{\mu_1} \frac{\partial H_{1,i}}{\partial T} \right), \\
a^2 &= \frac{\partial P}{\partial \rho} \Big|_{S,\alpha} = \frac{P}{\rho} \sum_{i=1}^r \alpha_i \frac{\partial h_i}{\partial T} - \left[\sum_{i=1}^r \left(\alpha_i \frac{\partial h_i}{\partial T} - R \frac{\alpha_i}{\mu_i} \right) \right]^{-1}.
\end{aligned}$$

Here ξ is the longitudinal coordinate, F is the area of the stream tube, ρ , u , P , and h are respectively the density, velocity, pressure, and enthalpy of the mixture of molecules, ions, electrons and clusters (for simplicity here

we assume that the translational temperature of all the mixture components is the same), M is the Mach number, a is the frozen speed of the sound, L is the specific evaporation heat, μ_1 is molecular weight of monomers, α_1^0 , α_0^i and α_0^e are the mass fractions of monomers, free ions and electrons in the mixture and $h_{1,i}$ is the enthalpy of the internal degrees of freedom of monomers.

5.2.2. A qualitative analysis of heterogeneous condensation in flows

A qualitative analysis of Eq. (1.75) enable us to reveal the characteristic features of the heterogeneous condensation process. To emphasize the difference of homogeneous condensation and condensation on positive ions from that on electrons we consider these processes one after another.

a) Homogeneous condensation. Let the parameters in the initial section of a supersonic flow correspond to an unsaturated vapor ($S < 1$) and the initial concentration of ions and electrons be so low that formation of heterogeneous clusters can be disregarded. Let also the Mach number at the initial section be not very high. Under these conditions $j_{*,cl} < 0$, i.e. $c_j^0/a_j^0 > 1$ for all j . Then all f_j^0 , $j = 1, \dots, \bar{j}$ are equal to unity and $d\alpha_1^0/dt \approx 0$. Due to this the mass fraction of the monomers remains constant in the flow until the vapor parameters attain the saturation point (dew point). At this point on the phase diagram the adiabatic curve along which we have varied the vapor parameters, crosses the vapor-liquid coexisting curve and S becomes equal to unity.

At the further vapor expansion $S > 1$ and $j_{*,cl} > 0$. Under these conditions there exists a region with $j > q \equiv \max(j_{*,cl}, r)$ in which certain f_j^0 differ from unity. At S close to unity, $j_{*,cl} \rightarrow \infty$, $q_\nu \rightarrow \infty$, and $\Omega \rightarrow 0$, therefore $\alpha_1^0 = const$. Hence, P , ρ , u and T adiabatically vary along the stream tube and S grows until Ω attains a value of the order of $d \ln F / d\xi$. From this instant the latent heat evolved during condensation will appreciably influence the flow parameters and they will substantially differ from the corresponding adiabatic values. In reality, the effect of condensation on the behavior of, say, temperature will be noticeable already at δ values appearing in the relation

$$\delta \frac{d \ln F}{d\xi} = \left[1 - \frac{L\alpha_1^0}{\sigma} - (M^2 - 1) \frac{L\alpha_1^0}{u^2} \right] \Omega \quad (1.76)$$

are of the order of 0.1 or 0.3.

Two mechanisms of relaxation of the flow parameters from the adiabatic values to the equilibrium ones are possible.

1. The effect of the latent heat of condensation on the flow parameters is such that they deviate from their corresponding adiabatic values.
2. During an adiabatic variation of the flow parameters condition Eq. (1.74) is attained and all f_j^0 and α_i^0 change with an identical rate. As shown in ⁴ if we are interested in further looking for the quasisteady solutions within the time scale of the slow variables variation (in ⁴ the flow rate Q , total momentum G and total energy of the system E were selected as the slow variables), we should solve the equations for these variables similar to Eq. (1.75) with the only difference that the differential equation for α_1^0 is replaced by the relation $S = 1$. Thus, upon passing through point “k”, at which condition Eq. (1.74) is met, the supersaturation changes within a short period of time τ_1 from S_k to unity, i.e. a “condensation jump” takes place. Point “k” is called the Wilson point in the literature. Quantity τ_1 is the characteristic time of Q , G or E variation.

If we are interested in evolution of all the parameters within the time scale of the α_1^0 variation, upon reaching the Wilson point we have to solve the whole set of equations Eq. (1.49) for S and f_j^0 . The values of Q , G and E remain invariable and equal to their magnitude at the Wilson point. It is not difficult to find out that this condition leads to relations $T = const$, $u \approx const$, $P \approx 1/F$ and $\rho \approx 1/F$.

Since as S tends to unity the value of $h^0 \approx j_{*,cl}$ grows, this solution holds until h^0 again exceeds r_0 and α_1^0 becomes a slow variable. Note that these processes are scrutinized in the theory of relaxational oscillations ²⁵.

The above analysis gives rise to a more precise definition of the Wilson point. In the first case we may use, for instance, Eq. (1.76) as a basic definition of this point, whereas in the second case the parameters at the Wilson point are found from Eq. (1.74).

b) Heterogeneous condensation on positive ions. How the presence of ions or electrons affects the rate of variation of supersaturation and the position of the Wilson point is one of the most interesting problems. Let all the conditions formulated in the previous paragraph hold again at the initial section of the flow, however now the initial concentration of free ions in the system is high enough that the ionic clusters should be taken into account (here we do not use the condition that the mixture should be necessary quasineutral assuming the electron concentration to be negligibly small as compared to the monomer and ion concentrations). At $S < 1$ Eq. (1.66) which defines h^i has no

roots, therefore all f_j^i , $j = 1, \dots, \bar{j}$ are equal to unity. Then α_1^0 is a slow variable whereas α_0^i (and, hence, S_i) is the fast one (the case of fast S_i relaxation). The quasisteady solutions for this case are $S_i = 1$ and $\alpha_0^i = \text{const}$. Owing to this the mass fraction of monomers in the flow remains constant, whereas the ion concentration is equilibrium and corresponds to a local temperature of the flow T and to the initial concentration of the ions ω .

After the dew point is attained (now its position depends on the value of ω , see section 1) $S > 1$ and $j_{*,cl} > h^i > 0$ during further expansion of the vapor. Since at S values close to unity h^i is large and $q_i = h^i$, condition Eq. (1.74) is not met and relaxation of S_i is fast. Then at $S_i = 1$, $j_{*,cl} > h^i$ the major term in the right hand side of Eq. (1.75) for α_1^0 is that pertaining to the ionic clusters (the term containing q_i).

A further increase in S reduces h^0 and h^i , where first $h^0 > h^i$ and then $h^0 < h^i$ (see Fig. 1). Two situations are possible because $r^i \leq r^0$. If at $h^0 > h^i$ equality $h^i = r^i$ is achieved, with further increase in S the rate of the α_1^0 relaxation depends predominantly on the term in Eq. (1.75) that contains q_i (now $q_i = r^i$). Thus, in this case the rate of the α_1^0 relaxation is controlled by the rate of formation of ionic clusters at all $S > 1$. If, on the contrary, condition $h^0 < h^i$ is achieved earlier than the condition $h^i = r^i$, in what follows the rate of relaxation of α_1^0 is determined by the term containing q_0 (i.e. by the rate of homogeneous condensation) while at the beginning it was controlled by the rate of the ionic clusters formation.

It follows from Eq. (1.74) defining the Wilson point that as q_ν drops so does the S value because $\beta(q_\nu)$ rises steeply. Hence, the maximum supersaturation at the Wilson point in heterogeneous condensation on ions turns out less than that in homogeneous condensation under the same conditions, whereas the condensation rate shows the opposite trend.

c) Heterogeneous condensation on electrons. Now we consider the most general case. Let all the conditions listed in paragraph “a” hold again at the initial section of the flow, however now the initial concentration of free electrons and ions is ample to produce appreciable amounts of ionic and electronic clusters. Situation considered here is unusual because at $S < 1$ Eq. (1.66) defining h^e has positive roots (see Fig. 1). If this root $h_2^e > r^e$ then $d\alpha_1^0/dt \neq 0$. Since at $S < 1$ the value of h_2^e is low, the rate of formation of electronic clusters may be quite high under these conditions and the relaxation of S_i and S_e is fast, i.e. the quasisteady solutions have the following form: $S_i = S_e = 1$. Condensation on electrons can result in a substantial deviation of the flow parameters from their adiabatic values and hence, in a total change of the flow pattern.

If, however, the electron concentration in the flow is low as compared with that of monomers ($\omega/n \ll 1$) or $h_2^e < r^e$ then all $f_j^i, f_j^0, f_j^e, j = 1, \dots, \bar{j}$ are equal to unity. In this case α_1^0 is a slow variable while α_0^i and α_0^e (and hence S_i and S_e) are the fast ones (the case of fast S_i and S_e relaxation). The quasisteady solutions are then $S_i = S_e = 1$ and $\alpha_1^0 = \text{const}$. Owing to this the mass fraction of the monomer molecules remains constant during the gas expansion, while the electron and ion concentrations are equal to their equilibrium values corresponding to the local temperature of the flow T and the initial ion and electron concentration ω .

As the flowing mixture of vapor, ions and electrons expands further under condition $h_2^e < r^e$ the mixture parameters attain the values pertaining to the dew point (now its position also depends on the value of ω , see section 1) and S exceeds unity. At values of S slightly exceeding unity condition $h_2^e < r^e$ is met and therefore $q_e = h_1^e, h^0 \approx j_{*,cl} \rightarrow \infty, h^0 > h^i > h_1^e$ and quantity Ω tends to zero. Thus, neither homogeneous nor heterogeneous condensation takes place within this range of flow parameters.

With a further increase in S the h_2^e value grows (see Fig. 1) and at some value of S it may exceed r^e . This introduces a term in the right hand side of Eq. (1.75) for α_1^0 which is much higher than the other terms (this is the term containing q_e) because of the condition $h_2^e \ll h_1^e < h^i < h^0$. Therefore the rate of variation of the mass fraction of monomer will be determined only by the value of this term, i.e. by the formation rate of the electronic clusters. Actually, the condensation experiences a ‘‘jump’’ at point $h_2^e \approx r^e$ and this point can be identified with the Wilson point.

If, however, because of the very small ω/n ratio the rate of heterogeneous condensation is too low to produce a jump in the flow parameters and provide their fast relaxation to the equilibrium values, quantity S keeps growing as the flow expands further. The growth of S leads to an increase in h_2^e and, hence, to a decrease in $d\alpha_1^0/dt$. As follows from Eq. (1.68) because of the temperature drop due to adiabatic expansion the value of h_c grows at high temperatures and drops at low temperatures. Since at high temperatures the value of δ_4 in Eq. (1.68) is low, the rate of the h_c growth is small. For this reason at $S > S_c$ the h_2^e value becomes greater than h_c and $q_e = r^e$. The second ‘‘condensation jump’’ occurs at this point.

It can be inferred from the aforesaid that in heterogeneous condensation of water vapor on electrons the Wilson point is attained earlier than in condensation on ions or in homogeneous condensation. Thus, the maximum supersaturation at the Wilson point in heterogeneous condensation on electrons is lower than that in condensation on ions or in homogeneous condensation under the

same conditions, whereas the ratio of the condensation rates is reverse. This fact was discovered by Wilson for the first time in experiments performed in a chamber that bears his name ²⁶.

In conclusion we should underline the following. Heterogeneous condensation of water vapor on negative particles is carried out with high rates and is specified by low values of supersaturation in the Wilson point. This preference of water vapor with respect to negative particles is determined by the sign of spontaneous polarization of water molecules. For substances with a positive spontaneous polarization this is not the case because they condense more efficiently on positively charged particles. However, all the above analysis is still valid if we substitute ionic clusters instead of electronic ones and vice versa.

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