

Theoretical prediction of a carrier gas effect under nucleation in thermal diffusion chambers

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Abstract

Analytical dependencies of critical supersaturation S_* and $\partial S_*/\partial P$ on a carrier gas pressure P_0 and temperature T in a diffusion cloud chamber (DCC) are derived on the basis of the microscopic nucleation theory [A.L. Itkin, E.G. Kolesnichenko, *Microscopic Theory of Condensation in Gases and Plasma*, World Scientific, New York, 1997], specially modified for the case of diffusion-limited nucleation [A. Itkin, *Kinetic model of effect of a carrier gas on nucleation in diffusion chamber*, *Aerosol Sci. Technol.*, in press], and a proper treatment of transport processes in a DCC. These dependencies qualitatively reproduce available experimental data. In addition, an effect of nature of both the carrier gas and condensing vapor on the observed phenomenon is discussed. The conclusion is made that the effect of the carrier gas in the experiments in a DCC has no connection to the real rate of chemical reactions of clusterization and, at other conditions (for instance, in expansion chambers), may not occur. Nevertheless, an existence of the carrier gas influence on the total nucleation rate can be of great importance for the control of nucleation. © 2000 Elsevier Science B.V. All rights reserved.

1. Physical processes in a diffusion cloud chamber

Diffusion cloud chambers (DCCs) have frequently been used when investigating homogeneous nucleation. The typical scheme of an experiment on studying nucleation in DCCs is as follows [3]. A DCC usually consists of two horizontal plates – top cold and bottom hot, but an inverse scheme has also been utilized (for instance, by Ref. [4]). Over the bottom plate, there is a liquid whose vapor condensation is a subject of the research. The space between plates is usually

filled in with a background gas. By virtue of the existing distribution of temperature and pressure, the vapor evaporating from the bottom surface moves due to diffusion through a chamber, then cooling and again condensing. As a result of these processes, an appropriate steady-state distribution of supersaturation S over the height of the chamber ξ (usually reckoned from the bottom plate) is established. An occurrence of drops of the condensed vapor is detected by some kind of light-scattering or even visually. With the help of such a system, it is possible to determine a steady-state nucleation rate (i.e. a quantity of drops of the detectable size formed in a unit volume in time units). Other characteristics – temperature, pressure, supersaturation – are usually found solving appropriate equations of diffusion and

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heat conduction under appropriate boundary conditions set on the walls of the chamber. The equipment described was repeatedly applied to research homogeneous nucleation of various substances. The experimental conditions are usually chosen so that outside a narrow zone where S reaches its maximum (zone N), the latter is practically equal to unity, and nucleation is not observed there.

As the vapor concentration in the chamber is low as compared with the concentration of the buffer gas, the processes of condensation do not practically influence the distribution of temperature and pressure over the height of the chamber, which is determined only by the boundary conditions at the walls and by the carrier gas pressure P_0 . Moreover, it is possible to show that gradients of the temperature $d(\ln T)/d\xi \approx 0.1 \text{ cm}^{-1}$ and density realized in the chamber are small as compared with gradients of the clusters' concentrations and, in the first approximation, may be neglected when describing the nucleation kinetics in DCCs.

In the existing theories of homogeneous nucleation, it is accustomed to consider that a concentration of a noncondensable (background) gas does not affect the rate of nucleation. For instance, classical nucleation theory (CNT) originally treats the nucleation process as an isothermal one. So, from the point of view of this theory, a high concentration of the carrier gas just provides such isothermal conditions while at low concentrations, one should probably take care about taking into account nonisothermal effects. That is why when in Refs. [3,5] and some other works, it had been discovered that critical supersaturation of the condensable vapor linearly increases with the increase of the background gas pressure, it stimulated a new and significant interest in this problem. A number of investigators have attempted to model these experimental results that have been published representing the effect of the background gas on nucleation with little or no success.

The author is aware of at least two main approaches exploited to explain the background gas effect: The first one considers an influence of the background gas pressure on thermophoretic forces.

It assumes that the more is this pressure, the more droplets move to the top wall of the chamber and are deposited on it that is reduced the counted number of droplets and measured nucleation rate, respectively. The other one takes into account that the droplet growth rate at continuous regime is inversely proportional to P_0 . Both approaches are not able to predict quantitatively the observed dependence of critical supersaturation of the pressure variation. Moreover, nucleation rate measured in DCC approximately exponentially depends upon P_0 while the discussed theories predict essentially a weaker effect.

One more theoretical approach presented in a recent paper [6] accounts for the influence of high pressure background gases on the vapor-to-liquid nucleation process. The key idea is to treat the carrier gas pressure as a perturbation parameter that modifies the properties of the nucleating substance. Two important mechanisms are identified in this respect. With increasing carrier gas pressure, the saturated vapor density tends to increase (enhancement effect), whereas the surface tension generally decreases. The authors use this approach to explain the results of expansion wave tube experiments. Note that the enhancement effect was already discussed in the literature as applied to nucleation in nozzles and jets (see, for instance, Ref. [7]), but for DCC, it is small, or in other words, P_0 is small to turn such a mechanism on.

In this paper, we propose a new model that allows not only a qualitative but also a quantitative explanation of the observed phenomenon. A first part of this investigation is presented in Ref. [2], and some preliminary results were reported in Refs. [8,9] while here we derive a direct dependence of critical supersaturation on the background gas pressure as well as some other dependencies observed in experiments. Within this model, as diffusion and nucleation are supposed to be main processes influencing behavior of the condensable vapor in DCCs. Despite the dominant role of just these processes being revealed more than 10 years ago, so far in the existing literature, one can discover some attempts to explain the effect of the background gas by making an impact on other processes such as already mentioned thermopho-

retic forces, droplets' growth, etc. That is why we pay special attention briefly discussing in Appendix A the role of other processes as well as under what conditions they can play a significant role in DCCs.

1.1. Main physical idea of the model

First, we have to discuss the main physical idea of our theory, which, in more detail, is given in Ref. [2]. We consider nucleation process when a certain molecule attaches a cluster. In the existing theories, usually rate constant of this process is not supposed to depend on any characteristic (for instance, pressure) of background gas. This is true unless transport of this molecule to the surface of the cluster is regulated by diffusion of the molecule through the background gas, and the rate of chemical reaction (attachment of the molecule to the cluster) is much more than the rate of diffusion. As shown in Ref. [2], typical conditions in DCCs just meet these requirements, and hence, this is the case when nucleation kinetics is a diffusion-limited one.

To give more substantial treatment of this problem, let us consider a usual expression of the nucleation theory for flux I_j in a space of the available cluster's sizes:

$$I_j = K_j^+ n_{j-1} - K_j^- n_j. \quad (1)$$

Here K_j^+ is the rate constant of the formation of j cluster which consists of j molecules, from the $j-1$ one by attaching a monomer, K_j^- is the dissociation rate constant of j cluster, n_j is the concentration of j clusters. In view of low concentration of dimers, trimers, etc. we neglect their contribution to K_j^+ ; therefore, $K_j^+ \propto n_1$, monomer number concentration. Thus, if a certain cluster transits to another sort by attaching a monomer, the rate of this process in the usual nucleation theory is proportional to the free-molecular flux of monomers on the surface of this cluster, and this flux is determined by the numerical concentration of monomers.

Under the conditions of DCC, this assumption stops to be valid because the real concentration of

monomers at the external boundary of the Knudsen layer over the cluster surface differs from the concentration n_1 determined far from the cluster because of the presence of the background gas. This is caused by the existence of a concentration jump in the vicinity of the cluster surface, and the value of this jump becomes considerable when the mean free path of the condensing molecules in the carrier gas is of the order of the cluster radius.

In Fig. 1 borrowed from Ref. [2], an isolated cluster surrounded by a mixture of the condensable vapor and background gas is presented. For DCCs, the number density of the background gas n_0 is a few orders more than the number density of the vapor n_1 . Therefore, the mean free path of the vapor molecule in its own vapor λ_v is about two orders more in length than the mean free path of this molecule in the carrier gas λ_{vg} . We consider pointwise molecules so that at this assumption,

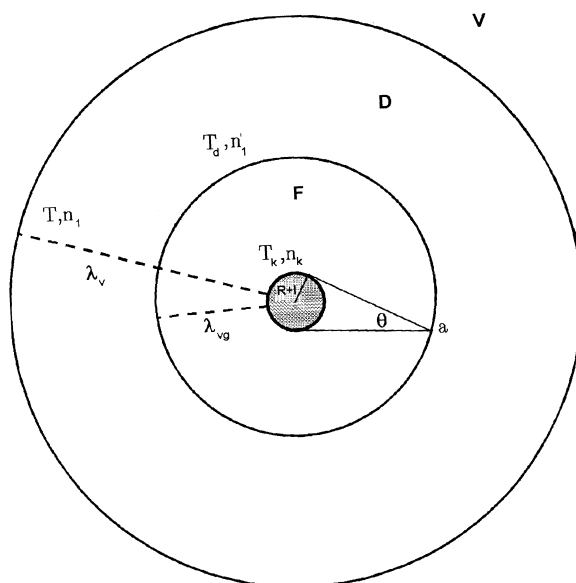


Fig. 1. Areas around a cluster, R is the radius of the cluster, l is the radius of the condensing molecule, λ_v and λ_{vg} are mean free paths of vapor molecules in the vapor and in the carrier gas, T , T_d , T_k and n_1 , n'_1 , n_k are temperatures and numerical densities of the vapor in the respective areas, F is the area of a free-molecular flow, D , the area of diffusion of the vapor through the carrier gas, V , the a fluid dynamic area.

collision between molecule and cluster occurs when this molecule reaches the surface of the absorbing sphere of the radius $R + l$, R is the cluster radius. In Fig. 1, T_k and n_k are the temperature and concentration of the incident molecules at the surface of the droplet, T_d and n'_1 are the corresponding parameters at the internal interface which is located approximately at the distance λ_{vg} from the surface of the absorbing sphere, T and n_1 are the corresponding parameters at the external interface which is located approximately at the distance of λ_v from the surface of the sphere.

In area V , a behavior of both the vapor and the carrier gas is described by usual fluid dynamic models. In area D , vapor molecules collide only with the carrier gas while in area F , vapor molecules move as in vacuum without collisions with the velocity u' . Therefore, the actual flux of the vapor molecules per unit time on j cluster in the simplest approximation could be written in the form,

$$K_j = 4\pi\gamma_c(R + l)^2(u'n'_1 - \Psi_o), \quad (2)$$

where γ_c is a condensation coefficient, R is the droplet radius, Ψ_o is the flux of outgoing molecules (evaporating and reflecting from the cluster surface), n'_1 should be found from the solution of the Knudsen layer problem with boundary conditions established at the external interface and at the surface of the absorbing sphere. As shown in Ref. [2], in a rough approximation,

$$n'_1 = \frac{n_1 + n_{1c}a_j}{1 + a_j},$$

$$a_j = \frac{u'(R + l)^2\lambda_v}{D_1(R + l + \lambda_{vg})(R + l + \lambda_v)\Delta_j}, \quad (3)$$

$$R = R(j),$$

and hence,

$$K_j^+ = 4\pi(R + l)^2u'n_1 \frac{S + a_j}{S(1 + a_j)}, \quad (4)$$

where $S = n_1/n_{1c}$ is supersaturation, n_{1c} is a monomer equilibrium concentration, D_1 is a coefficient of binary diffusion of vapor through the

carrier gas. It is also shown that u' is equal to the free-stream velocity of the carrier gas at the internal interface (Fig. 1), i.e.

$$u' = \left(\frac{8k_B T_d}{\pi m_0} \right)^{1/2} \quad (5)$$

with m_0 being a molecular mass of the background gas and k_B , the Boltzmann constant. As far as Δ_j is concerned, as one can see from Fig. 1, only a certain fraction of the vapor molecules having diffused to point “a” from the external interface can collide with the cluster, namely those that have the direction of the velocity within the angle θ . On the other hand, in point “a”, all directions of the velocity are equiprobable, and hence, as follows from Fig. 1, the fraction of the collided molecules is $\Delta_j = \arcsin[(R + l)/(R + l + \lambda_{vg})]/\pi$. Strictly speaking, to estimate this fraction more precisely, one has to consider a multidimensional diffusion equation, but for a qualitative estimation, our consideration is sufficient. This problem has been explored in more detail in Ref. [10].

From Eq. (4), we see that if $a_j \ll 1$, i.e. if the diffusion rate is much more as compared with the rate of the chemical reaction, this formula gives a commonly used expression of the rate constant of the cluster formation. On the contrary, if $a_j \gg 1$, the rate of the cluster formation is determined by the transfer of the reacting molecules to the surface of the cluster.

In Ref. [2], it is shown that under conditions of DCC, a_j is of the order of unity for monomers and increases as j increases. This gives rise to a new expression of the rate constant of the cluster formation which has never been utilized in the theory of nucleation. Using a general expression of the coefficient of binary diffusion of monoatomic gases given by kinetic theory [11,12] based on the following assumptions made: (i) molecules interact like hard spheres with the Maxwellian distribution of velocities, (ii) the concentration of the carrier gas is much more than the concentration of the vapor, (iii) the attractive part of the potential describing the interaction between vapor molecules is taken into account by introducing the Sutherland correction, we obtained in Ref. [2]

$$\begin{aligned}
K_j^+ &= \mathcal{K}_j^+ \frac{S\Theta_j + 1}{S(1 + \Theta_j)} \approx \mathcal{K}_j^+ \frac{S\Theta_j + 1}{S}, \quad \Theta_j \ll 1, \\
\Theta_j &= \frac{(R + l + \lambda_{\text{vg}})(R + l + \lambda_v)}{(R + l)^2} \frac{3\lambda_{\text{vg}}}{32\lambda_v} \sqrt{1 + \frac{m_1}{m_0}} \arcsin\left(\frac{R + l}{R + l + \lambda_{\text{vg}}}\right) \\
&= \frac{3}{2\pi^2(1 + C/T)} \frac{k_B T}{(R + l)P_0\sigma_{\text{vg}}^2} \equiv \Theta \frac{1}{(j^{1/3} + 1)} \approx \Theta j^{-1/3} \quad \text{at } R < \lambda_v, \\
\Theta &= \frac{3}{2\pi^2(1 + C/T)} \frac{k_B T}{P_0\sigma_{\text{vg}}^2} \left(\frac{4\pi\rho_l}{3m_1}\right)^{1/3}. \tag{6}
\end{aligned}$$

Here C is the Sutherland constant, m_1 is a vapor molecular mass, ρ_l is liquid density, $\pi\sigma_{\text{vg}}^2/4$ is a collision cross-section of the vapor and gas molecules; therefore, σ_{vg} is approximately a half of the sum of effective diameters of the vapor and gas molecules. We also introduced notation \mathcal{K}_j^+ for the traditional (kinetic) rate constant,¹ and Θ_j is our correction for the case of the diffusion-limited kinetics. As follows from analysis of Ref. [2], $\Theta_j < 1$ and is inversely proportional to P_0 , the pressure of the carrier gas because the diffusion coefficient is inversely proportional to P_0 . For the sake of convenience in what follows, we will use the old notation K_j^+ for the traditional rate constant, but, instead in our equations, the product $K_j^+(S\Theta_j + 1)/S$ appears.

As far as for the rate constant of the inverse process K_j^- is concerned, it does not depend on the external environment of the cluster and is determined only by intracluster processes. A convenient approximation of K_j^- derived using the approach of the RRKM theory has been obtained in Refs. [1,13].

1.2. Solution of kinetic equations

Despite the fact that we derived a new representation for the cluster formation rate constant which now depends on the background gas pressure, we cannot proceed just substituting this expression into the nucleation rate, for instance, provided by CNT. Rather, we need to reconsider

¹ It is proportional to R^2 while K_j^+ in Eq. (2) is proportional to $(R + l)^2$, but here we neglect this correction.

kinetic equations describing transport and nucleation of vapor in DCC and try to find their solutions. This program has also been carried out in Ref. [2], and below, we give only the main results of that investigation.

According to our microscopic nucleation theory (MNT) [1], studying mixture of gases and clusters is treated as a mixture of ideal gases each of which is characterized by the size of the identical clusters composing it. Usually, MNT operates with a system of equations describing evolution of mass fraction of clusters which contain j molecules and have an average internal vibrational energy corresponding to a quantum state k (so, actually $\alpha_j(k)$ is a population of this state). We assume that the cluster mass fraction changes due to processes of diffusion, condensation and relaxation of vibrational intracluster states. However, under conditions of DCC, when $n_0 \gg n_1$, relaxation of intracluster vibrations is fast as compared with the rate of nucleation limited by diffusion of the condensing molecules to each other. Thus, in this case, vibrational levels of clusters are in equilibrium. In other words, the main parameter of MNT, r , that just specifies size of cluster for which relaxation rate at high levels is of the same order as condensation rate [1] is equal to unity. That is why from the very beginning, we may simplify the original system of equations given in Refs. [1,14] expressing equilibrium populations $\alpha_j(k)$ through mass fractions α_j according to the Boltzmann equilibrium distribution. If so, the following continuity and diffusion equations for the mixture components obtained in the Navier–Stokes approximation may be considered:

$$\begin{aligned}
\partial(\rho\alpha_i)/\partial t + \nabla(\rho\mathbf{v}\alpha_j) &= \rho\Phi_i - \nabla(\rho\alpha_i\mathbf{V}_i) \\
\nabla X_i &= \sum_j^N \left(\frac{X_i X_j}{D_{ij}} \right) (\mathbf{V}_j - \mathbf{V}_i) + (\alpha_i - X_i) \frac{\nabla p}{\rho} + \frac{\rho\alpha_i}{\rho} \left(\mathbf{f}_i - \sum_{j=0}^N \alpha_j \mathbf{f}_j \right) \\
&+ \frac{\nabla T}{T} \sum_{j=0}^N \frac{X_i X_j}{\rho D_{ij}} \left(\frac{D_{T,j}}{\alpha_j} - \frac{D_{T,i}}{\alpha_i} \right), \quad i = 0, \dots, N, \quad \alpha_i = n_i m_i / \rho.
\end{aligned} \tag{7}$$

Here ρ, P, T are the mass density, pressure and temperature of the mixture, t is the time, \mathbf{v} is the mass-average velocity vector, α_i and \mathbf{V}_i are the mass fraction and diffusion velocity vector of i clusters, X_i is their mole fraction, \mathbf{f}_i is the mass force acting on these clusters, D_{ij} is the coefficient of binary diffusion of the gas composed of i clusters through the gas composed of j clusters, $D_{T,i}$ is the thermal diffusion coefficient, n_i are the corresponding numerical densities (concentrations), index $i = 1, \dots, N$ represents the cluster gases, and $i = 0$, the neutral gas, Φ_i is the kinetic source term associated with condensation. In accordance with Refs. [1,14,15] at $r = 1$, Φ_i can be written as follows:

$$\begin{aligned}
\Phi_j &= I_j - \frac{j}{j+1} I_{j+1} (1 - \delta_{jN}), \quad j > 1, \\
\Phi_1 &= - \sum_{j=2}^N \frac{1}{j} I_j (1 + \delta_{j2}), \quad \Phi_0 = 0, \\
I_j &= K_j^+ \theta_{j-1} \alpha_{j-1} \alpha_1 \frac{\rho j}{m_1(j-1)} - K_j^- \alpha_j, \quad \theta_j \equiv \frac{S\Theta_j + 1}{S(1 + \Theta_j)}; \tag{8}
\end{aligned}$$

however, here in contrast to usual kinetic equations of nucleation, a new term θ_j is presented in the definition of the flux I_j because as described above, under our conditions, the nucleation kinetics is diffusion limited. In Eq. (8), δ_{ij} is Kronecker's symbol.

When deriving Eq. (8), the processes of formation (dissociation) of the cluster by attaching (detaching) dimer, trimer, etc. as well as triple collisions were neglected. But the law of conservation of the total number of molecules in the system has been already taken into account, because Eq. (8) holds the relationship $\sum_j \alpha_j = 1$.

Using a method originally proposed in Refs. [1,14], an explicit asymptotical solution of this

system is obtained in Ref. [2]. In particular, quasi-steady concentrations of the clusters n_j have a form,

$$\begin{aligned}
n_j &= n_{jc} S^j \prod_{i=1}^{j-1} \theta_i \approx n_{jc} S \prod_{i=1}^{j-1} \frac{i^{1/3} + S\Theta}{i^{1/3} + \Theta}, \quad j \leq y, \\
n_j &= n_{ye} S^y \prod_{i=1}^{y-1} \Theta_i \prod_{k=y}^{j-1} \frac{\frac{\partial \ln K_{j+1}^+}{\partial j} + \frac{\partial \ln n_{jc}/n_{j+1,c}}{\partial j}}{\frac{\partial \ln K_{j+1}^+}{\partial j} + \frac{\partial \ln \Theta_j}{\partial j}}, \quad j > y, \tag{9}
\end{aligned}$$

where K_j^+ is a usual rate constant of the monomer attachment to $(j-1)$ th cluster $K_j^+ = \gamma_c K_j^{2/3}$, $K = K_1(3m_1/4\pi\rho_1)^{2/3}$ and $K_1 = (k_B T/2\pi m_1)^{1/2}$ is a free molecular flux per surface of a unit sphere.

In Eq. (9), parameter y is introduced as a cluster size being a boundary between two kinds of solution. In Ref. [2], an equation for y is derived which takes a simple form if S exceeds approximately 1.5 (as usually takes place in a zone N of active nucleation in experiments in DCCs)

$$\frac{2b}{3y^{1/3}} - \ln(S\theta_j) = 0. \tag{10}$$

Two remarks have to be made: First, note that the above formulae can be used for any arbitrary relation between the rates of diffusion and chemical reactions because the term θ_j yields $S\Theta_j + 1$ at small $\Theta_j \ll 1$ (diffusion-limited nucleation), while at high Θ_j (usual nucleation), it yields 1. It is interesting that at high Θ_j , and intermediate S , Eq. (10) yields $y \approx j_{*,cl}$ where $j_{*,cl}$ is critical size, a parameter inherent to all nucleation theories. From the physics standpoint, it is easy to see that an individual droplet with size y is in equilibrium with the surrounding vapor at the diffusion-limited kinetics, and hence, y is an analog of $j_{*,cl}$ in this case.

But at arbitrary S and θ_j , the value of y differs from $j_{*,cl}$.

Concern of the second note is that, as shown in Ref. [2], the quasi-steady distribution of clusters is established within the specific time of evolution of supersaturation. This time could be evaluated by the term,

$$\tau^{-1} \approx n_{y+1,e} S^{y+1} K_{y+2}^- \frac{2b}{9y^{7/3}} \prod_{i=1}^y \theta_i, \quad (11)$$

where $n_{j,e}$ is an equilibrium concentration of j cluster [1], $\beta_j = n_{j,e}/n_{1,e}$, $b = 4\pi\sigma\eta^2/k_B T$, $\eta = (3m_1/4\pi\rho_1)^{1/3}$.

1.3. What is the measured nucleation rate?

In Appendix A, we consider two sorts of clusters. For large clusters (sort 1), gravity prevails thermophoretic forces; therefore, they move to the bottom plate, grow within this movement and, in principle, could be registered by the detecting apparatus. Small clusters, on the contrary, move to the top plate. During this movement, they continue to grow and their further behavior is two-fold. If before they are deposited by the wall some drops manage to reach the so-called “radius of soaring” at which the resulting force vanishes, in what follows, such drops (sort 2) will fall down and can be registered. Otherwise, they will be deposited by the wall and cannot be registered.

As follows from Eq. (9), cluster distribution of sizes monotonously decreases. Therefore, in zone N, the concentration of clusters of sort 1 is much lower than that of clusters of sort 2 (because the size of the clusters of sort 2 is less than that of the clusters of sort 1). The cluster concentration slightly varies far from zone N (because $S \approx 1$) that holds this relationship up to the zone of detection (zone D). Thus, while clusters of sorts 1 and 2 reach zone D in different times after a certain induction period, mainly clusters of sort 2 should be detected in the experiment.

To understand what is the nucleation rate measured in the experiment, we use the following consideration: At the initial stage of the DCC work, a certain quasi-steady distribution of clusters is formed corresponding to the established

distribution of S and T over the height of DCCs. After that, clusters (droplets) start to move due to gravity, the drag and thermophoretic forces that results in a violation of this quasi-steady distribution. A certain amount of clusters reaches zone D and is detected. They could belong to sort 1 or 2, but in any case, all clusters capable of falling down or reaching the top wall leave the zone of active nucleation.

If nucleation stopped, only this falling droplets would be registered during a short period of time while after this period, no droplets should be visible (all of them reach either the bottom or top plates). The flux of droplets per unit square per unit time is $v_g n_j$, where n_j is their concentration. However, experimentalists present another value – the number of droplets per unit volume per unit time. For instance, it could be found by counting the falling drops within a certain (apparently rather long) period of time and then by dividing this number of droplets by the time, the square of the chamber and the width of the laser beam. If the period of detection is more than the time necessary for droplets to reach the bottom plate, but the droplets are still detected, it means that, due to a transport of vapor molecules to clusters (diffusion) and chemical reactions between them (nucleation), the quasi-steady distribution of clusters is restored and new formed droplets fall down following the previous ones. In what follows, the process is frequently repeated.

From the mathematical point of view, S is a slow variable while all n_j are fast variables. This means that at time scale of the S evolution τ variables n_j do not depend on t explicitly but only through the dependence of $S(t)$ and $T(t)$. It is vice versa at time scales of the n_j evolution t_j supersaturation S is practically constant while n_j vary with time. Certainly $t_j \ll \tau$ for all j , and one can consider τ as a period of time necessary to establish a quasi-steady regime over n_j .

Thus, in order to find the necessary average flux, we should find a ratio of the concentration of the falling droplets to the average time of relaxation of the quasi-steady distribution of droplets:

$$J = n_{j,d}/\tau, \quad (12)$$

where J is the number of detected drops per unit volume and time, τ according to its physical sense coincides with that given by Eq. (11), n_{j_d} approximately is the concentration of clusters of a minimum detectable size j_d (the radius of such drops is approximately equal to a half of the wavelength of the detecting laser $\lambda_w/2$), because in view of the exponential decrease of n_j , they give the maximum contribution to the counted number of droplets. Note that the concentrations of these clusters in zone D is practically equal to their concentration in zone N where they have been formed having another size j_0 , i.e. if the clusters of a certain size can be registered they are registered all together.²

Often experimentalists cannot detect directly the number of droplets. For instance, if the presence of the droplets is determined by light-scattering with the help of the Mie theory, the intensity of a scattered light is proportional to the square of the droplet. In this case (12), should be modified a little:

$$J = n_{j_d} q J_d^{2/3} / \tau = n_{j_0} q J_d^{2/3} / \tau, \quad (13)$$

where q is a respective coefficient. Because usually experimentalists represent their results (in particular, J) as a function of S_* , T_* and P_0 where subscript “*” marks the point of the maximum supersaturation or a close point of the maximum nucleation rate, the main goal of this section is to express explicitly J through these parameters. However, for this purpose, a certain kinetic model of nucleation should be introduced. Thus, we should study in more detail processes in the zone of active nucleation because they determine the number of droplets which are then measured in the experiment. But this problem has already been considered above, and we can directly apply all the results obtained. The only unknown parameter yet in Eq. (13) is j_0 .

What is the number j_0 ? From the physical point of view, this is the size of a certain droplet in zone

N which reaches a visible size in zone D. In a general case, in order to restore this number, one should consider (i) a thermophoretic movement of the droplet to the top of the chamber until it reaches the radius of soaring, then (ii) precipitation of this droplet with a constant velocity v_g followed by the further growth of the droplet until it reaches the size j_d , and finally (iii) to invert the time (or more accurately the coordinate ξ) and integrate the corresponding equations of the movement with the following boundary condition: the droplet has the size j_d at the height of detection ξ_d where this drop is detected.

This is a common scheme, but let us consider a typical experiment on nucleation of *n*-butanol in helium [16] with the specific pressure and temperature of the mixture $P_0 = 2\text{--}20$ bar and $T_0 = 300\text{--}350$ K, $S \approx 3$. Direct calculations show that under these conditions, r_s is about of 0.1 μm , λ_v is of the same order, λ_{vg} almost 10 times less. Thus, droplets reach the size λ_{vg} when they are mainly affected by diffusion in zone N, and after that, grow at the transition and continual regimes.

If one neglects gravity, we may find a majorant of the path where a certain droplet grows from λ_{vg} to r_s moving to the top wall. Indeed, the steady velocity of the droplet is determined by equating the drag and thermophoretic forces. Combining this equality with the Maxwell formula (see Appendix A), we obtain

$$\frac{dR}{d\xi} = \Omega_m (1 + 3C_m) \left(1 + 2 \frac{k_g}{k_p} + 2C_t \right) \times \left[\frac{2C_s \mu k_B T}{P_0 m_0} \left(\frac{k_g}{k_p} + C_t \right) \frac{\nabla T}{T} \right]^{-1}. \quad (14)$$

Calculations show that the droplet reaches the radius r_s at the length about 1 μm . If we take gravity into account, this length would be somewhat less. Thus, droplets reach the size r_s immediately in zone N, and therefore, no droplets precipitate on the top wall under the conditions of these experiments despite such a possibility has been discussed above. In other words, while r_s in accordance with Eq. (A.9) depends on the carrier gas pressure, this dependence cannot influence

² A small portion of these clusters certainly is deposited by the side walls, but it does not significantly change the detecting flux.

the experimental results. Hence, in what follows, we do not consider a restricted role of the radius of soaring and assume that the droplet grows at the continual regime everywhere outside of zone N.

Further in order to reveal the dependence of j_d on the parameters in zone N, we should integrate the equation,

$$v_g \frac{dR}{d\xi} = \Omega_m,$$

which, with allowance for the definition of v_g and Ω_m transforms, to the following one:

$$R^4 = R_0^4 + 4 \int \left[\frac{D_1 P_s(T)(S-1)}{\rho_1 (k_B T/m_1)} \frac{9\mu}{2\rho_1 g} \right] d\xi. \quad (15)$$

Here the integral is taken from zone N to zone D and R_0 is the initial radius of the droplet in zone N. In order to determine the integral on the right-hand side, let us assume that T depends linearly on ξ i.e. $dT/d\xi \approx \text{const}$. The results of more precise numerical calculations (see, for instance, Ref. [16]) give some evidence for the assumption made. The dependence of S on ξ can be found if, in the equation describing the variation of the mass fraction of monomers, we neglect the influence of nucleation on the distribution of monomers over the height of the chamber that yields

$$\frac{d}{d\xi} \left(D_1 \frac{d}{d\xi} \frac{\alpha_1}{\alpha_0} \right) = 0. \quad (16)$$

Here α_1 and α_0 are mass fractions of molecules of the condensing vapor and carrier gas, respectively. Eq. (16) should be integrated with allowance for the condition $dT/d\xi = \text{const}$ and with the boundary condition that S_* is treated in the literature as either the maximum supersaturation over ξ or supersaturation in the maximum nucleation rate plane. Having in mind that (i) the nucleation rate is treated by experimentalists as that predicted by the classical theory, and (ii) according to the experimental results, these two planes are very close to each other, we can choose any of this definitions. For instance, we choose supersaturation in the maximum nucleation rate plane as S_* .

In accordance with Ref. [17], the classical nucleation rate is written in the form,

$$J = C(T) S^2 \exp \left(- \frac{4b^3}{27 \ln^2 S} \right),$$

$$C(T) = \gamma_c \frac{2m_1}{\rho_1} \left(\frac{\sigma}{2\pi m_1} \right)^{1/2} n_{1c}^2. \quad (17)$$

Thus, the maximum of J over the vertical coordinate of DCC ξ is determined by the equation,

$$\frac{\partial \ln C(T)}{\partial T} \frac{dT}{d\xi} + \frac{2}{S} \frac{dS}{d\xi} - \frac{4b^3}{27 \ln^2 S} \left[3 \left(\frac{1}{T} + \frac{\sigma_2}{\sigma} \right) \frac{dT}{d\xi} - \frac{2}{S \ln S} \frac{dS}{d\xi} \right] = 0, \quad (18)$$

where a commonly used linear dependence of σ on T is utilized $\sigma = \sigma_1 - \sigma_2 T$. It is easy to show that the first two terms in Eq. (18) are small as compared with the last one; that is, in other words, means that the exponent in Eq. (17) strongly depends on S_* rather than the pre-exponent term. Therefore, Eq. (18) can be reduced to the following one:

$$\left. \frac{dS}{d\xi} \right|_{S=S_*} = - \frac{3}{2} \left(\frac{1}{T_*} + \frac{\sigma_2}{\sigma} \right) \frac{dT}{d\xi} S_* \ln S_*. \quad (19)$$

Using this relation as the boundary condition for Eq. (16) and integrating Eq. (16) at $dT/d\xi = \text{const}$, one gets (see Appendix B)

$$S(\xi) = S_* \frac{T}{T_*} \left[1 + 2 \frac{L}{R_g T_*} \left(1 - \sqrt{\frac{T}{T_*}} \right) \right] \times \exp \left(- \frac{L}{R_g T} \frac{T - T_*}{T_*} \right). \quad (20)$$

Here L is a latent heat of the vapor, R_g is the gas constant. It is seen from Eq. (19) that in the maximum rate plane $dS/d\xi$ has a sign opposite to $dT/d\xi$. As for usual DCC $dT/d\xi < 0$ so $dS/d\xi > 0$ in the maximum rate plane.

Now, substituting Eq. (20) into Eq. (15) and integrating it, we obtain an approximate formula:

$$R^4 \approx R_0^4 + 4 \left[\frac{D_1}{\rho_1} \frac{P_s(T)S}{(k_B T/m_1)} \frac{9\mu}{2\rho_1 g} \right] \Big|_{\xi=0} f(\xi),$$

$$f(\xi) = \left(\frac{T_*}{T} \right)^2 \left\{ \xi \exp \left[-\frac{L}{R_g T} (1 - T/T_*) \right] + \frac{2R_g T_*}{L} \left(1 - \exp \left[-\frac{L}{R_g T} (1 - T/T_*) \right] \right) \right\}$$

$$+ \left\{ \left(\frac{T_*}{T} \right)^2 \left[\frac{1}{2} + \frac{L}{R_g T_*} \left(1 - \frac{4}{3} \sqrt{\frac{T_*}{T}} \right) \right] - \frac{1}{2} + \frac{L}{3R_g T_*} \right\} \frac{T_*}{T}, \quad (21)$$

where $\dot{T} \equiv dT/d\xi = \text{const}$ and $\xi = 0$ is a coordinate of zone N. From here, we finally obtain

$$j_0 \approx \left\{ J_d^{4/3} - 4\eta^{4/3} \frac{D_1 * P_s(T_*) S_*}{\rho_{1*} k_B T_*/m_1} \frac{9\mu_*}{2\rho_{1*} g} f(h_d) \right\}^{3/4} \quad (22)$$

with h_d being a coordinate of zone D and $\eta = (3m_1/4\pi\rho_1)^{1/3}$. Note that $\eta j_d^{1/3}$ may differ from $\lambda_w/2$ if an experimental procedure is designed to detect larger sizes of the droplets in order to provide a certain level of the signal of the detector.

Direct calculations of j_0 , based on Eq. (22), show that under the mentioned experimental conditions, even monomers have the time to grow above λ_w . On the other hand, as it is easy to see from Eq. (10), individual droplets tend to evaporate if $j < y$ and grow if $j > y$. Thus, in this case, y is a certain analog of the classical critical size. As we already mentioned, among all growing clusters, y clusters have the maximum concentration; therefore, it is reasonable to assume $j_0 = y$.

Now, we have all formulae to get a direct theoretical prediction of the nucleation rate supposed to be measured in DCCs. We start from Eq. (12) and substitute into it τ from Eq. (11) and n_{j_d} from Eq. (9) having in mind that as we discussed in the paragraph after Eq. (12) $n_{j_d} \approx n_{j_0}$, but in turn, $j_0 = y$ (see a previous paragraph). Parameter y can be found by solving Eq. (10). Finally, it yields

$$J \approx A(T_*) \left[\exp(-by^{2/3}) \prod_{j=1}^y \frac{S\Theta + j^{1/3}}{\Theta + j^{1/3}} \right]^2$$

$$\times qJ_d^{2/3} S^2 K_{y+2}^- \frac{2b}{9y^{7/3}}, \quad (23)$$

where all variables in Eq. (23) are related to zone N, and now,

$$j_d = \left[y^{4/3} + 4\eta^{4/3} \frac{D_1 * P_s(T_*) S_*}{\rho_{1*} k_B T_*/m_1} \frac{9\mu_*}{2\rho_{1*} g} f(h_d) \right]^{3/4}$$

$$\approx \eta \left[4 \frac{D_1 * P_s(T_*) S_*}{\rho_{1*} k_B T_*/m_1} \frac{9\mu_*}{2\rho_{1*} g} f(h_d) \right]^{3/4}. \quad (24)$$

Note that for experiments of Heist et al. [3,16,18], where the falling droplets were registered visually by a telescope, Eq. (23) should be modified a little because in this case, the term $qJ_d^{2/3}$ has to be removed from this equation.

2. Effect of a carrier gas

As the experimental investigations of the carrier gas effect on the nucleation rate in DDCs became relatively popular, it is possible to note from the literature that there is a trend to present the experimental data in coordinates $S_*(P_0)$ or $S_*(T_*)$ where S_* is supersaturation corresponding to $J = 1$ drop/cm³/s. In order to reduce the expressions of our theory to such a form, we should insert this value into Eq. (23), and take the logarithm of both sides of this equation. It yields

$$\begin{aligned}
0 &\approx -by^{2/3} + \ln \prod_{j=1}^y \frac{S\Theta + j^{1/3}}{\Theta + j^{1/3}} + \frac{1}{2} \ln f(T_*) + \ln S - \frac{5}{6} \ln y + \frac{1}{2} \ln qj_d^{2/3} \\
&\approx -by^{2/3} + \int_1^y \ln S\theta_j dj + \ln S + \frac{1}{2} \ln f(T_*), \quad f(T_*) = \frac{2}{9} A(T_*) W_d(T) \exp(-E_a/k_B T) b.
\end{aligned} \tag{25}$$

Here we took into account that $K_y^- \approx W_d(T)y^{2/3} \exp(-E_a/k_B T)$ [1] where E_a is an activation energy of the molecule capable of dissociating from the cluster, $W_d(T)$ is a certain coefficient determined in Ref. [1]. We also neglected the term proportional to $\ln y$ as compared with $by^{2/3}$ because, under usual experimental conditions, y is of the order of the classical critical size $j_{*,cl}$, i.e. about 200–700. In addition, term qj_d weakly depends on P_0 (see Eq. (24)) or even should be removed at all (see the end of Section 1).

Our next assumption is that we consider the case of the diffusion-limited nucleation, i.e. as was shown above the case when $\Theta_j \leq 1$. This inequality is valid at least for large j while according to the previous analysis for DCCs we might expect it as $j > 2-5$. But for the sake of simplicity, we further suppose that it is valid even for $j = 2$.

The assumptions made allow one to rewrite Eq. (25) in the form,

$$\begin{aligned}
0 &\approx -by^{2/3} + \int_1^y \ln \left(1 + \frac{S\Theta}{j^{1/3}} \right) dj \\
&\quad + \frac{1}{2} \ln f(T_*) + \ln S.
\end{aligned} \tag{26}$$

Here y depends on T_*, P_0 and S_* and is determined by Eq. (10). Thus, generally speaking, solutions of Eq. (25) lie on a surface in a three-dimensional space S_*, T_*, P_0 . Therefore, any dependence such as $S_*(P_0)$ or $S_*(T_*)$ is a certain cross-section of this surface. Further, we consider in more detail an explicit form of such dependen-

cies and try to interpret the available experimental data based on this consideration.

Before we pass onto a further discussion, it is necessary to make an important note. We have already mentioned that, under the conditions of experiments in DCCs, the main parameter of MNT r is about unity everywhere in the chamber. Therefore, the only sources of the dependence of J on P_0 are the dependencies $D_1(P_0)$ and $\Theta(P_0)$. It is clear that these dependencies do not have a kinetic nature but are born by a specificity of the transport processes in DCCs. It should be underlined that such a situation is inherent to experiments in DCCs (or HPCC) while, for instance, in nozzles the opposite relationship usually takes place [1,19,20] i.e. Θ_j is high and $r(T, S, P_0)$ is about few tens, and therefore, there is another – kinetic source of the dependence of S on P_0 . The physical nature of this dependence is that the carrier gas does not explicitly affect the elementary processes of the cluster formation and decay but affects the relaxation of intracluster vibrational states. But as shown in Ref. [1], the rate of the cluster attachment or detachment depends on the vibrational state of the cluster and thus implicitly on the carrier gas pressure. For a more detailed discussion of this problem see Ref. [1].

2.1. Dependence of S_* upon P_0

Differentiating Eq. (26) with respect to P_0 with allowance for Eq. (10) we obtain

$$\begin{aligned}
&\left[-\frac{2b}{3y^{1/3}} + \ln \left(1 + \frac{S\Theta}{y^{1/3}} \right) \right] \frac{\partial y}{\partial P_0} + 3 \frac{\partial S\Theta}{\partial P_0} \left\{ \frac{1}{2} y^{2/3} - S\Theta y^{1/3} + (S\Theta)^2 \ln \left(\frac{y^{1/3} + S\Theta}{1 + S\Theta} \right) \right\} \\
&\quad - 3 \frac{\partial \Theta}{\partial P_0} \left\{ \frac{1}{2} y^{2/3} - \Theta y^{1/3} + (\Theta)^2 \ln \left(\frac{y^{1/3} + \Theta}{1 + \Theta} \right) \right\} + \frac{\partial \ln S}{\partial P_0} = 0.
\end{aligned} \tag{27}$$

Here the term in square brackets vanishes due to the definition of y in Eq. (10) and the last term on the left-hand side is small as compared with the previous one because $y \gg 1$ and $\Theta \leq 1$. For just the same reason, the leading term in braces is $y^{2/3}/2$. Thus, the solution of Eq. (27) is $\Theta(S-1) = \text{const}$ or with allowance for the definition of Θ

$$S_* - S_{*1}(T) = c_1(T) \frac{2\pi^2(1 + C/T)}{3} \times \frac{\sigma_{\text{vg}}^2}{k_{\text{B}}T} \left(\frac{3m_1}{4\pi\rho_1} \right)^{1/3} (P_0 - P_{01}), \quad (28)$$

where S_{*1} and P_{01} are certain initial values of S_* and P_0 at $T_* = \text{const}$. As follows from Eq. (28), S_* linearly increases as P_0 increases, which reproduces the available experimental data of Refs. [3,16,18,21]. Thus, we theoretically derived the well-known experimental fact that in order to provide the constant rate of nucleation J supersaturation in the point “*” should be linearly increased as the pressure of the background gas P_0 increases.

2.2. Dependence of S_* upon T_*

Here we start again from Eq. (26) differentiating it with respect to T_* .

$$\left[-\frac{2b}{3y^{1/3}} + \ln \left(1 + \frac{S\Theta}{y^{1/3}} \right) \right] \frac{\partial y}{\partial T_*} + 3 \frac{\partial S\Theta}{\partial T_*} \left\{ \frac{1}{2} y^{2/3} - S\Theta y^{1/3} + (S\Theta)^2 \ln \left(\frac{y^{1/3} + S\Theta}{1 + S\Theta} \right) \right\} - 3 \frac{\partial \Theta}{\partial T_*} \left\{ \frac{1}{2} y^{2/3} - \Theta y^{1/3} + (\Theta)^2 \ln \left(\frac{y^{1/3} + \Theta}{1 + \Theta} \right) \right\} - y^{2/3} \frac{\partial b}{\partial T_*} + \frac{1}{2} \frac{\partial \ln f(T_*)}{\partial T_*} + \frac{\partial \ln S}{\partial T_*} = 0, \quad (29)$$

where again the term in the square brackets vanishes due to the definition of y in Eq. (10), and the last term is small. As S_* is about 2–3, we also omit the terms in the second braces as compared with the terms in the first ones.

In what follows, in order to simplify the remaining part of Eq. (29), let us introduce a commonly used linear dependence of σ on T : $\sigma = \sigma_1 - \sigma_2 T$, where σ_1 is a certain constant spe-

cific for the given substance, $\sigma_2 = \sigma_1/T_c$ and T_c is the temperature at the critical point. Then,

$$\frac{\partial S_* \Theta}{\partial T_*} = \frac{1}{3} \left(y^{2/3} \frac{db}{dT_*} - \frac{1}{2} \frac{d \ln f(T_*)}{dT_*} \right) \left\{ \frac{y^{2/3}}{2} - S\Theta y^{1/3} + (S\Theta)^2 \ln \left(\frac{y^{1/3} + S\Theta}{1 + S\Theta} \right) \right\}^{-1} \quad (30)$$

or

$$\frac{\partial \ln S_*}{\partial T_*} = -\frac{1}{T} - \frac{1}{3S_*\Theta} \left[b \left(\frac{1}{T_*} + \frac{\sigma_2}{\sigma_*} \right) + \frac{1}{2y^{2/3}} \frac{d \ln f(T_*)}{dT_*} \right] \left\{ \frac{1}{2} - \frac{S_*\Theta}{y^{1/3}} + \left(\frac{S_*\Theta}{y^{1/3}} \right)^2 \ln \left(\frac{y^{1/3} + S\Theta}{1 + S\Theta} \right) \right\}^{-1}. \quad (31)$$

In order to estimate the value of $d \ln f(T_*)/dT_*$, we utilize an explicit form of coefficients $W_{\text{d}}(T_*)$, $A(T_*)$, E_a and b given in Ref. [1]. It yields

$$\frac{\partial \ln f(T_*)}{\partial T_*} \approx -\left(\frac{3}{T} + \frac{\sigma_2}{\sigma_*} \right) + \frac{2l_1 E_b}{k_{\text{B}} T^2},$$

where E_b is the dissociation energy per one bond in cluster ($E_b \approx \varepsilon_0(2)$ where the latter is the depth of the potential well for the linear dimer), l_1 is the

average number of bonds per molecule in a macrocluster. Direct calculations show that, for instance, for water at $T = 350$ K, typical values are $l_1 = 4$, $\varepsilon_0(2)/k_{\text{B}}T = 10$ while y is about 500 and $b \approx 8$. Hence, the term $(1/2y^{2/3})(d \ln f(T_*)/dT_*)$ (the second term in the square brackets in Eq. (31)) is small as compared with the first one at $y \gg 1$ and in what follows, we neglect it. Thus, we may rewrite Eq. (31) in the form,

$$\frac{\partial \ln S_*}{\partial T_*} = -\frac{1}{T} - \frac{1}{3S_*\Theta} b \left(\frac{1}{T_*} + \frac{\sigma_2}{\sigma_*} \right) \left\{ \frac{1}{2} - \frac{S_*\Theta}{y^{1/3}} + \left(\frac{S_*\Theta}{y^{1/3}} \right)^2 \ln \left(\frac{y^{1/3} + S\Theta}{1 + S\Theta} \right) \right\}^{-1}. \quad (32)$$

An analysis of Eq. (32) together with Eq. (10) results in a few interesting conclusions, namely:

(1) If under the conditions of DCCs, $S\Theta \gg 1$, then $S\Theta = c_1(T)$, and y depends only on T and does not depend on P_0 and S . In such a case, function $\partial \ln S_*/\partial T$ does not depend on P_0 . Moreover, as $S_* \propto P_0$, the following dependence takes place $\partial S_*/\partial T \propto P_0$.

(2) Critical supersaturation S_* increases as T_* decreases because, under conditions of the experiments, the expression in the first braces is positive, and hence, $\partial \ln S_*/\partial T_* < 0$.

The last conclusion is well confirmed by the available experimental data.

Here we have to make an interesting remark. It surprisingly turns out that a similar-in-form equation can be obtained independent of this model. Indeed, an analysis of the experimental data shows that at some T_* , the value of $2b/3S_*\Theta$ is about $\ln S_*$ while y is large. But it is easy to see from Eq. (19) that, if the nucleation rate is determined by the classical nucleation theory and we neglect a pre-exponential factor in the nucleation rate, then the following equation at $T_* = \text{const}$ expresses the relationship which is valid at the maximum nucleation rate plane.

$$\frac{\partial \ln S_*}{\partial T_*} = -\frac{3}{2} \left(\frac{1}{T_*} + \frac{\sigma_2}{\sigma_*} \right) \ln S_*. \quad (33)$$

A similar form of Eqs. (33) and (32) in such a case is caused by the circumstance that the concentrations of y clusters in MNT n_y and the nucleation rate in the classical theory are both proportional to $S^y n_{y,c}$. Apparently, this is the reason why classical nucleation theory can be used to treat the experimental dependence of S_* on T_* at the constant carrier gas pressure in a narrow interval of T_* .

Integrating Eq. (33) further, one has

$$\ln S_* = \left(\frac{T_{*0}\sigma_*}{T_*\sigma_0} \right)^{3/2} \ln S_{*0}. \quad (34)$$

Here S_{*0} and T_{*0} are certain initial (already known) values of S_* and T_* at a given pressure P_0 . When varying the total pressure or the nature of the background or condensible gas, S_{*0} and T_{*0} also alter their values.

It is necessary to underline that if we do not neglect the pre-exponential factor in the nucleation rate given by CNT, then CNT fails to predict the available experimental data (see below). But Eq. (34) can be directly derived from Eq. (26) if $\Theta_j \gg 1$. Thus, it is more reasonable to say that Eq. (34) is more inherent to the present theory while it could be obtained from CNT only under certain (non-evident) assumptions made.

Using Eq. (34), it is possible to explore the behavior of S_* as T_* decreases at constant P_0 and J . It is seen that S_* sharply increases as T_* decreases because it results in the increase of σ . In Table 1 and Figs. 2–6 the results of experiments [16] at several total pressures for 1-propanol and 1-butanol in He, H₂ and N₂ are reproduced as the dependence of critical supersaturation S_c on T . Using the value of S_c at the lowest given temperature as S_0 , we substituted it into Eq. (34) and calculated S_m (dashed line in the figures). A similar procedure has been used to get S_* from Eq. (32) (solid lines in the figures). It is seen that Eq. (34) reproduces the experimental data with high accuracy (better than 2%) for a light background gas and with an accuracy of about 10–20% for a more dense background gas.

An emphasis has to be made that at the intermediate pressures when $\Theta_j \gg 1$, Eq. (26) transforms to Eq. (34) while at high pressures, when $\Theta_j \leq 1$, it results in Eq. (32). In other words, Eq. (26) gives the value S_m at low pressures and S_* at high pressures. This is well demonstrated by the data presented in the figures because at the intermediate pressures and temperatures when $\Theta_j \geq 1$, the experimental data lie closer to S_m while at high pressures they approach to S_* .

As the same as pointed out in Ref. [22], the denser background gas can lead to unstable density layering inside the chamber which can then result in buoyancy driven convection.

Table 1

Dependence of critical supersaturation on temperature T_0 at several pressures P_0 of the background gas for 1-propanol and 1-butanol in He, H_2 and N_2 . S_c : experiments [9], S_m : our prediction made on the basis of Eq. (36), S_* : our prediction made on the basis of numerical solving of Eq. (33), the initial point with T_{01} and S_{01} is taken on the experimental curve from Ref. [9], S_c is calculated based on the classical nucleation rate at $J = 1$ droplet/cm³/s (thermophysical properties of substances are taken from Refs. [3,9,11])

Substance	$T(K)$	$P = 5$ bar			$P = 10$ bar			$P = 20$ bar			$P = 30$ bar			CNT S_c
		S_c	S_m	S_*	S_c	S_m	S_*	S_c	S_m	S_*	S_c	S_m	S_*	
1-PROH/ H_2	319.9	2.83	2.83	2.83	2.99	2.99	2.99	–	3.37	–	–	3.73	–	17.8
	334.6	2.42	2.40	2.31	2.54	2.51	2.27	2.78	2.78	2.78	3.03	3.03	3.03	11.1
	362.5	–	1.86	1.63	1.94	1.92	1.38	2.11	2.07	1.94	2.23	2.20	2.24	5.43
	387.9	–	1.56	1.25	–	1.60	–	1.70	1.68	1.42	1.80	1.75	1.70	3.31
1-PROH/ He	321.7				2.91	2.91	2.91	–	3.57	–	–	4.17	–	16.8
	334.2				2.50	2.51	2.35	3.00	3.00	3.00	3.43	3.43	3.43	11.3
	363.1				1.89	1.91	1.49	2.12	2.16	2.20	2.33	2.37	2.43	5.36
	387.6				–	1.60	–	1.70	1.74	1.70	1.82	1.87	1.78	3.33
1-PROH/ N_2														
	334.3				2.94	2.94	2.94	–	3.20	–				11.3
	348.4	2.13	2.24	2.00	2.45	2.48	2.31	–	2.67	–				7.6
	362.8	–	1.96	1.53	1.93	2.14	1.82	2.27	2.27	2.27				5.40
	375.0	–	1.78	1.24	1.57	1.91	1.50	1.93	2.01	1.96				4.19
1-BUOH/ H_2														
	334.4				3.69	3.69	3.69	4.22	4.22	4.22	4.77	4.77	4.77	8.79
	348.7	2.78	2.81	2.60	3.08	3.04	3.08	3.49	3.41	3.53	3.83	3.79	3.83	5.92
	362.8	–	2.41	2.03	2.60	2.58	2.59	2.90	2.84	2.96	3.18	3.10	3.02	4.51
1-BUOH/ N_2														
	334.3				3.90	3.90	3.90	–	4.45	–				8.81
	348.4	2.52	2.75	2.54	3.00	3.20	3.04	3.58	3.58	3.58				5.95
	362.8	–	2.36	1.96	2.30	2.68	2.38	2.80	2.95	2.90				4.51

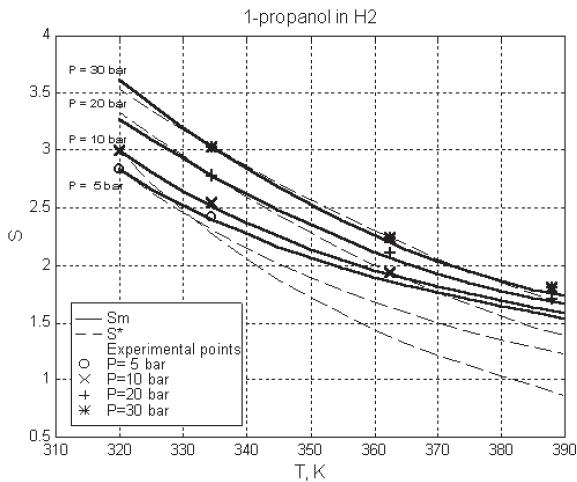


Fig. 2. The plot of S_c vs. T_c at constant P_0 and $J = 1$ drop/cm³/s for 1-propanol in H_2 . S_c : experimental data of Ref. [16], S_* : our prediction according to Eq. (32), S_m : our prediction according to Eq. (34).

Unfortunately, the authors of Ref. [16] do not bring an accuracy of the experiment, but it is reasonable to expect that experimental errors increase for the heavy background gas. Nevertheless, we bring the calculated S_m even for the heavy background gas, and it is seen that the experimental and calculated results do not deviate so much.

What is the sense in comparing the presented experimental results with the classical nucleation rate as is usually done in the literature? The idea of experimentalists was that due to a sharp dependence of supersaturation on ζ in DCCs all droplets are formed in zone N where the nucleation rate reaches its maximum and further their total number is not changed. Thus, if the optic system counts about 1 droplet/cm³/s, it is suspected that at point N, the nucleation rate is also about 1 droplet/cm³/s.

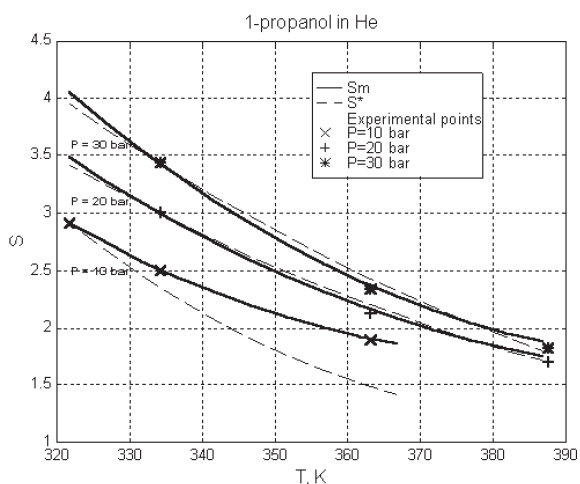


Fig. 3. The plot of S_* vs. T_* at constant P_0 and $J = 1 \text{ drop/cm}^3/\text{s}$ for 1-propanol in He. S_c : experimental data of [16], S_* : our prediction according to Eq. (32), S_m : our prediction according to Eq. (34).

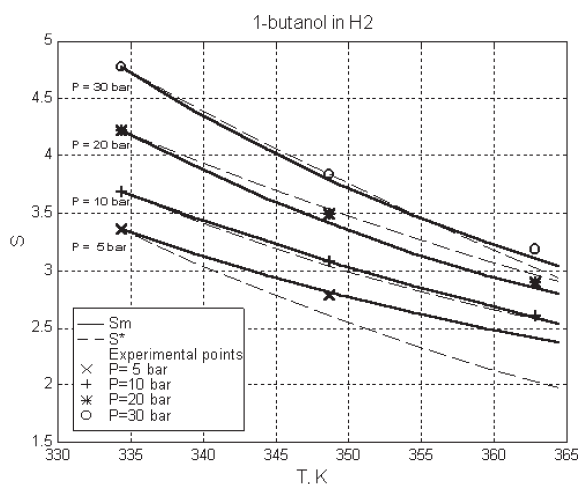


Fig. 5. The plot of S_* vs. T_* at constant P_0 and $J = 1 \text{ drop/cm}^3/\text{s}$ for 1-butanol in H_2 . S_c : experimental data of Ref. [16], S_* : our prediction according to Eq. (32), S_m : our prediction according to Eq. (34).

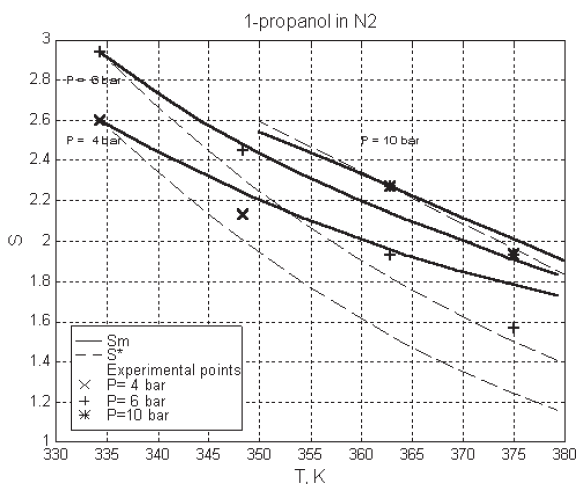


Fig. 4. The plot of S_* vs. T_* at constant P_0 and $J = 1 \text{ drop/cm}^3/\text{s}$ for 1-propanol in N_2 . S_c : experimental data of Ref. [16], S_* : our prediction according to Eq. (32), S_m : our prediction according to Eq. (34).

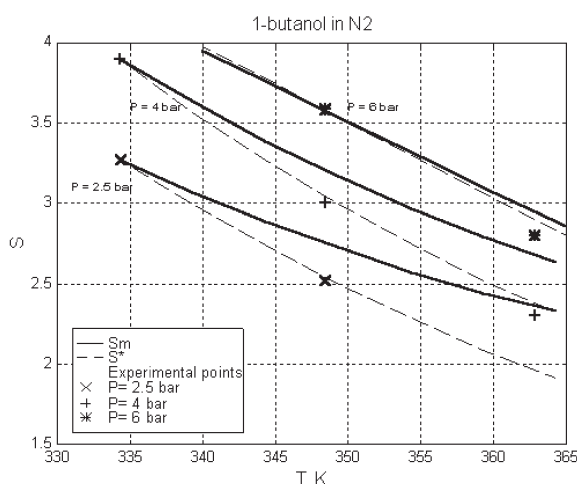


Fig. 6. The plot of S_* vs. T_* at constant P_0 and $J = 1 \text{ drop/cm}^3/\text{s}$ for 1-butanol in N_2 . S_c : experimental data of Ref. [16], S_* : our prediction according to Eq. (32), S_m : our prediction according to Eq. (34).

As it is easy to check this statement, we choose $J = 1 \text{ droplet/cm}^3/\text{s}$ and $\gamma_c = 0.01$ further restoring the dependence of S on T from the usual expression of the classical nucleation rate equation (17). The last lines of Table 1 just contain the

values of S_c found in such a way (obviously S_c does not depend on P_0). From the results obtained one can see a disagreement between CNT and the experimental data. On the other hand, at $J = 1 \text{ droplet/cm}^3/\text{s}$ from Eq. (17), we obtain

$$\ln S_* = \left(\frac{\sigma}{T}\right)^{3/2} \frac{1}{C(T)} \left(\frac{4\pi}{k_B}\right)^{3/2} \frac{2m_1}{4\sqrt{3}\pi\rho_l}. \quad (35)$$

This expression coincides with Eq. (34) if one assumes that $\Theta = 1$ and

$$\ln S_{*0} = \left(\frac{4\pi}{k_B}\right)^{3/2} \frac{2m_1}{4\sqrt{3}\pi\rho_l} \left(\frac{\sigma_0}{T_0}\right)^{3/2} \frac{1}{C(T)}; \quad (36)$$

however, there is no evidence for such an assumption at all, because $C(T)$ depends on T and weakly on S . This dependence explains a deviation observed in Table 1. In other words, despite n_y in our approach and J_c being proportional, the counted flux of droplets is not a nucleation rate in its classical sense.

Finally, in order to verify our theory proposed, we performed direct calculations of S_* as a function of T_* at $P_0 = \text{const}$ solving numerically coupled equations (31) and (10). In doing so, we used the following data. Thermophysical properties of the condensing vapor were taken from Refs. [3,16,18,23]. In particular, for butanol, we used $\rho_l = 0.936331 - 8.775192 \times 10^{-5}t - 1.16705 \times 10^{-6}t^2$, $m_1 = 74.123$. To determine the other parameters, we used some correlations from Refs. [12,23] built on the basis of the critical parameters of the vapor. For butanol, the temperature, pressure in the critical point and the normal boiling temperature (at $P=1$ atm) are, respectively, $P_c = 43.6$ atm, $T_c = 562.9$ K, $T_b = 390.9$ K. Then, coefficients determining the dependence of σ_* on T_* are obtained as follows: $\sigma_1 = P_c^{2/3} T_c^{1/3} [0.1207(1 + T_{br} \ln P_c)/(1 - T_{br}) - 0.281]$, $\sigma_2 = \sigma_1/T_c$, where $T_{br} = T_b/T_c$. The Sutherland constant C is determined according to the formula [12] $C = 1.47\sqrt{T_{bv}T_{b0}}$ with T_{bv} and T_{b0} being the normal boiling temperatures of the vapor and the background gas, respectively. We put the condensation coefficient to be equal to unity and did not vary it in order to fit our prediction to the experimental data.

At low temperatures, to get more precise results, we did not neglect the term proportional to $d \ln f(T_*)/dT_*$ in Eq. (31) that corrects S_* about 3%. For such calculations, we used $E_b = 4.5$ kcal/mol, $l_1 = 4$. These values were chosen to be equal to those for water vapor because, on the one hand,

we did not find this data for butanol and propanol in the literature, but on the other hand, they correctly reproduce the order of magnitude of the energy of the hydrogen bond.

For experiments with butanol, the collision cross-section of the vapor molecules with the background gas was obtained from the data on the binary diffusion coefficient that yields $\sigma_{vH_2} = 7.2$ Å and $\sigma_{vN_2} = 8$ Å.

The results of such calculations are presented in Table 1 as S_* . It is seen that they predict the experimental results at high pressure with the same accuracy as formula (34). At low pressures, the difference is a bit more, but nevertheless, our prediction reproduces the experimental data with an accuracy of about 10%.

Calculations performed for propanol revealed a certain disagreement (about 30% at low pressures and high temperatures) between the experimental data and our prediction while formula (34) better predicts this data. Note that we did not find reliable data on the cross-section σ_{vg} for propanol when hydrogen, helium and nitrogen are used as the background gases. That is why in contrast to experiments with butanol, we considered this value as a parameter further fitting it in order to get the best agreement with the experimental results. These fitted values are $\sigma_{vH_2} = 4.94$ Å, $\sigma_{vHe} = 6.06$ Å, $\sigma_{vN_2} = 6.85$ Å. Note that at $P_0 = 5$ bar and $T_* = 319.9$ K for propanol in hydrogen the value of $\Theta/y^{1/3}$ is of about 3 in contrast to the introduced assumption that this ratio is less than unity. On the other hand, when deriving all our formulae, we actually did not use this assumption except the only point when the dependence $S_*(P_0)$ was obtained. Thus, in the vicinity of these parameters, our theory either does not predict at all or predict a weak dependence of S_* on P_0 . However, at $T_* = \text{const}$ with P_0 growth already at $P_0 = 1$ atm, the above assumption becomes valid again.

2.3. Dependence of $\partial S_*/\partial P$ on T

One more experimental fact is that slopes of the straight lines $S_*(P_0)$ decrease as the temperature T_* increases. In order to reveal this dependence, we can take a derivation of Eq. (31) with respect to P_0 at $T_* = \text{const}$. Direct solving of Eq. (10) shows that

for experiments of Ref. [16] at high pressures $y^{1/3} \gg S\Theta$; therefore,

$$\frac{\partial^2 S_*}{\partial T_* \partial P_0} = -\bar{\Theta}^{-1} \left[c_1(T_*) + \frac{2b}{3} \left(\frac{1}{T_*} + \frac{\sigma_2}{\sigma_*} \right) \right] < 0,$$

$$\bar{\Theta}^{-1} = c_1(T) \frac{2\pi^2(1+C/T)}{3} \frac{\sigma_{\text{vg}}^2}{k_{\text{B}}T} \left(\frac{3m_1}{4\pi\rho_1} \right)^{1/3}, \quad T = \text{const}, \quad P_0 = \text{const}. \quad (37)$$

Hence, the slopes of $\partial S_*/\partial P_0$ decrease as T increases; this is in good agreement with the available experimental data.

At low pressures, we should also take into account the dependence of $S\Theta/y^{1/3}$ on P_0 . The dependence of S_* and Θ on P_0 is already known while an explicit form of $\partial y/\partial P_0$ at $T_* = \text{const}$ can be obtained from Eq. (10). Finally, easy but tedious algebra shows the value of the term that appears by taking a derivative of the terms in braces in the denominator of Eq. (31), to be small as compared with the terms in Eq. (37). Therefore, the allowance for the dependence of $S\Theta/y^{1/3}$ on P_0 does not change the result that $\partial^2 S_*/\partial P_0 \partial T_* < 0$.

2.4. Dependence of S_* on the nature of the carrier gas and condensing vapor

From the viewpoint of the above-developed theory, the main source of the influence of the carrier gas on S_* is the dependence of Θ on P_0 . According to Eq. (28), the only cross-section σ_{vg} is related to the specific properties of the carrier gas. In particular, the heavier the carrier gas, the larger is the efficient diameter of its molecule, and hence, a more pronounced dependence of S_* on P_0 should occur as well as the slopes of the lines $S_*(P_0)$ should increase. This fact is also in good qualitative agreement with the experimental data of Ref. [16].

As far as the nature of the condensing vapor is concerned, it is clear that $\eta \approx \sigma_{1\text{v}}/2$, and hence, in Eq. (28) $\sigma_{\text{vg}}^2 \eta \approx \sigma_{\text{vg}}^3$ where σ_{vg} increases as the molecular mass of the condensing vapor increases. In addition, in a similar way as when deriving Eq. (29), one may obtain

$$\frac{\partial c_1}{\partial \eta} = \frac{\partial S_* \Theta}{\partial \eta} = \frac{1}{3} \frac{\partial b}{\partial \eta} \left\{ \frac{1}{2} - \frac{S_* \Theta}{y^{1/3}} \right. \\ \left. + \left(\frac{S_* \Theta}{y^{1/3}} \right)^2 \ln \left(\frac{y^{1/3} + S\Theta}{1 + S\Theta} \right) \right\}^{-1} > 0. \quad (38)$$

Thus, as the molecular mass of the molecule of the condensing vapor decreases, it usually gives rise to the decrease of the carrier gas effect. Such a situation has also been observed in experiments. For instance, in Ref. [5], it was experimentally discovered that, for all alcohols, the effect of the background gas becomes greater as the formula weight of this gas increases and vice versa, i.e. for methanol, this effect is practically negligible.

3. Conclusions

For the first time, a model of the nucleation process under conditions when a transport of condensing molecules to the cluster surface is determined by their diffusion through a carrier gas is proposed. A qualitative and even quantitative explanation of the dependence of critical supersaturation on the temperature, pressure and nature of the background gas and condensing vapor is presented. The approach in use is strongly based on the microscopic theory of nucleation [1] which allows an analytical representation of the cluster's concentrations through supersaturation, the gas temperature and, that is quite new, the carrier gas pressure. As shown in this paper, usual conditions of experiments in DCCs meet the requirements of the model validity, which means that this model can be adopted to explain a mechanism of the carrier gas pressure influence on the nucleation kinetics observed in experiments.

On the basis of this approach, we have managed to derive analytical dependencies of S_* and $\partial S_*/\partial P$ on P_0 and T_* in DCCs. In particular, these dependencies show that

- S_* linearly increases as P_0 increases at $T_* = \text{const}$ that reproduces the available experimental data of Refs. [3,16,18,21].
- Critical supersaturation S_* increases as T_* decreases at $P_0 = \text{const}$ (also in accordance with the experiments).
- If under the conditions of DCC, $S\Theta \gg 1$ then $S\Theta = c_1(T)$ and y depends only on T and does not depend on P_0 and S . In such a case, the function $\partial \ln S_*/\partial T$ does not depend on P_0 . Moreover, as $S_* \propto P_0$, the following dependence takes place $\partial S_*/\partial T \propto P_0$.
- The slopes of the straight lines $S_*(P_0)$ decrease as the temperature T_* increases.
- The heavier the carrier gas, the more is the efficient diameter of its molecule, and hence, the more pronounced is the dependence of S_* on P_0 which occurs as well as the slopes of the lines $S_*(P_0)$ increase. This fact is also in good qualitative agreement with the experimental data of Ref. [16].
- As the molecular mass of the molecule of the condensing vapor decreases, it usually gives rise to the decrease of the carrier gas effect. Such a situation has also been observed in experiments [5].

The main conclusion which is made here based on the results obtained is that the dependence of S_* on P_0 observed in the experiments in DCCs has no connection with the nucleation kinetics itself and is determined by the peculiarities of the transport processes in DCCs.

Another interesting problem related to this conclusion is why in some experiments in expansion chambers the dependence of the nucleation rate on the carrier gas pressure has not been detected at all, or if detected was comparatively slight [24] while in experiments [16], it was pronounced. We intend to publish a detailed review of this problem elsewhere, but as a preliminary explanation, we suspect that the transport processes in expansion chamber differ from that in DCCs. A similar explanation could be proposed for nozzles where the transport of condensible molecules to

the cluster surface is not determined by diffusion. On the other hand, a slight effect of the carrier gas pressure in nozzles and jets [25] (see also a more extensive description of this problem in Ref. [1]) has to be associated with the dependence of the parameter r , the main parameter of MNT, on P_0 .

The physical meaning of this parameter is rather simple because r is the number of molecules contained in the cluster for which the rate of its dissociation from the top-most level M_r is of the same order as the vibrational relaxation rate at the same level. For clusters with $j > r$, the rate of relaxation of intracluster vibrations is much greater than the rate of the cluster dissociation but at $j < r$ there is an opposite situation. Details of this model are discussed in Ref. [13]. But what we should have in mind is that at $r > 1$, kinetic equations describing nucleation (evolution of the cluster concentrations) as well as their solutions has a different form at $j < r$ as compared with that considered in this paper. The reason why, for instance, in nozzles $r > 1$ is that under the conditions of that experiments $n_0 \sim n_1$ and thus for small clusters their intracluster vibrations are nonequilibrium because of the limited number of collisions with both the carrier gas and vapor molecules. Thus, another kinetic theory is needed to describe this situation, for instance, MNT in its original treatment [1].

The model and formulae derived here permit a consistent explanation of the available experimental results. We also derived a dependence of S_* on T_* at $P_0 = \text{const}$ using the classical nucleation theory under the assumption made that S_* is supersaturation in the maximum nucleation rate plane which predicts the experimental results with accuracy about 2–10%. However, the classical nucleation rate at such supersaturations is not equal to 1 drop/cm³/s as it is counted in the experiments; therefore, the good accuracy of Eq. (34) does not mean the validity of the classical nucleation theory in such a case. In addition, CNT does not predict the dependence of S_* on P_0 at all. That is why at the moment, within the framework of our theory, the only explanation of the good accuracy of Eq. (34) is the following. The counted flux of droplets within CNT is proportional to $S^{*n_{\text{re}}}$, where $x \equiv j_{*,\text{cl}}(T, S)$ is the classical critical size. In MNT,

this flux is also proportional to $S^y n_{ve}$; however, here y is determined by Eq. (10) rather than $j_{*,cl}$, and in addition at low supersaturations about 2–4 strongly depends on P_0 . But at low temperatures and pressures accidentally under the conditions of the discussed experiments in DCCs and high-pressure diffusion chambers, the product $2b/(3S\Theta)$ is of about unity as well as $\ln S$. This results in a similar structure of the equations describing such a dependence for both CNT and our theory.

Direct numerical calculations made on the basis of formula (31) derived in this paper revealed that it predicts the experimental data of Refs. [3,16,18] on the dependence of S_* on T_* at $P_0 = \text{const}$ with an accuracy of 2–10% for butanol in hydrogen. The data on nucleation of butanol in nitrogen are predicted with the same accuracy despite in Ref. [22] the authors suspecting that the denser background gas can lead to unstable density layering inside the chamber which can then result in buoyancy driven convection and a large error in the data obtained. Apparently, it gives a reason to suspect that either the convection does not strongly influence the measured supersaturation or the influence of convection lies within the double accuracy of our prediction, i.e. 5–20%.

As far as the experiments with propanol are concerned, the agreement is worse (up to 30%), but at some temperatures and pressures, it is still good. We might propose two explanations of this fact. The first one is that we used the linear dependence of the surface tension on the vapor temperature while for polar mediums like spirituous this is not valid. In order to examine this point, we used more complicated correlations presented in Refs. [12,23] that take into account the dipole momentum of the condensing molecule and its acentric factor. We have obtained an improvement of about 5% that in our opinion is not very essential.

Another possible effect that was not considered here at all is that the surface tension of liquid in the mixture depends also on the concentration and the nature of molecules over the liquid surface [12]. In particular, in Ref. [12], the work of J. Gielessen and W. Schmatz (in 1961) is cited wherein the authors studied the influence of nitrogen, argon and helium on the surface tension of hydrocarbons of a normal structure. They revealed that σ_v de-

creases as the argon or nitrogen pressure increases while σ_v linearly increases when the helium pressure increases. Unfortunately, at present, there is no appropriate theory to take this effect into account as well as the amount of the available experimental results is not sufficient to fit such a dependence on a self-empirical basis.

We also mentioned that the final results strongly depend on the collision cross-section of the vapor and gas molecules that is presented in the definition of Θ . Fortunately, for butanol mixed with either hydrogen or nitrogen, usage of the same value of the cross-section allows a good prediction of the experimental data, but this is not the case for propanol. That is why for numerical calculations, it is necessary to carefully choose the corresponding data.

It is also important to underline that despite the formulae derived in this paper describing the dependencies of S_* , $\partial S_*/\partial P_0$ and $\partial S_*/\partial T_*$ on P_0 and T_* , they contain an uncertain coefficient (see, for instance, Eq. (28)). It could be specified in two ways: First, if we develop a more consistent theory of the kinetic and transport processes in DCCs, especially with allowance for the peculiarities of the design of the chamber, we could explicitly express this coefficient through the temperature of the system. The idea of the second approach used in this work is to exclude this coefficient from our consideration. It can be done if two values of S_* are already known either at a constant pressure of the background gas but at different temperatures, or at a constant temperature of the mixture but at different pressures of the background gas. Generally speaking, to compare our prediction with the experimental data, the best way is to have not two but many experimental points obtained in such a manner. That is the reason why we used experiments of Heist et al. to verify our theory, because they just meet such requirements. At the same time, these experiments were performed at relatively high pressures of the background gas while there is a lot of experiments at low pressures where the effect of the background gas has also been found. Unfortunately, these experiments were provided at arbitrary temperatures and pressures; therefore, it is difficult to make a consistent comparison between our theory and these

experimental results in view of the above-mentioned problem.

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Appendix A. Role of various processes in a diffusion cloud chamber

Here we consider various processes in DCCs that can affect a distribution of macroparameters in DCCs as well as the nucleation process itself.

A.1. Brownian diffusion

Brownian diffusion is important for small droplets whose radius is of order of 10^{-6} cm or less. The mean square displacement of the particle in a certain volume within the time t under diffusion is [26,27]

$$s^2 = \frac{4}{\pi} D_1 t \quad (\text{A.1})$$

with D_1 being a diffusion coefficient. We use a general expression of the coefficient of the binary diffusion of monoatomic gases given by the kinetic theory [11] under the assumptions made that (i) molecules interact like hard spheres with the Maxwellian distribution over velocities and (ii) the concentration of the carrier gas is much more than the concentration of the vapor. It yields

$$D_1 = \frac{3}{8n_0} \left(\frac{k_B T}{2\pi m_0} \right)^{1/2} R^{-2}, \quad (\text{A.2})$$

where $n_0 = P_0/k_B T$, m_0 are the numerical density and the molecular mass of the background gas, k_B is the Boltzmann constant, R is the radius of the particles. Hence, the average velocity of the particles is

$$v_d = \sqrt{\frac{4D_1}{\pi t}}. \quad (\text{A.3})$$

A.2. Forces affecting the drops

All clusters are affected by three forces – gravity, a drag force and a thermophoretic one, and the value of these forces depends on the cluster size or the Knudsen number specific for droplets of a certain size.

A convenient approximation of the thermophoretic force for an arbitrary Knudsen number is given in [26,28]

$$F_t = -12\pi \frac{\mu^2}{\rho} R C_s \frac{\nabla T}{T} \left(\frac{k_g}{k_p} + C_t \text{Kn} \right) (1 + 3C_m \text{Kn})^{-1} \times \left(1 + 2 \frac{k_g}{k_p} + 2C_t \text{Kn} \right)^{-1}. \quad (\text{A.4})$$

Here C_t , C_m , C_s are certain kinetic coefficients of order unity, $\text{Kn} = \lambda_{vg}/R$, λ_{vg} is the mean free path of the vapor molecule in the carrier gas, μ , ρ are the viscosity and density of the carrier gas, ∇T is the temperature gradient in the vicinity of the droplet, k_g, k_p are coefficients of thermal conductivity for the gas and droplets.

For the drag force, we use the Stokes–Cunningham expression [26,28],

$$F_v = \frac{6\pi\mu u R}{1 + a \text{Kn}}, \quad (\text{A.5})$$

where u is the gas velocity and a is a constant of order unity.

For small droplets, a thermophoretic acceleration prevails the gravitational one while for large droplets, the opposite relationship takes place.

A.3. Nucleation

As the vapor in DCCs is supersaturated, various clusters are formed because of nucleation. The specific feature of this processes is that the vapor molecules are transferred to the clusters by means of diffusion. To describe nucleation in DCCs we use a special modification of our microscopic theory of nucleation (MNT) [1] whose main statements as applied to DCCs are given in the previous sections.

A.4. Droplet growth

Separate droplets formed under nucleation in what follows move to the top or bottom wall of the chamber and grow or evaporate during this movement. As shown in Ref. [2] in whose regime – free molecular or diffusion – the droplet growth is approximately determined by the ratio

$$v = D_1 \sqrt{\frac{2\pi m_1}{k_B T} \left(\frac{R^2 \gamma_c \lambda_v}{(R + \lambda_{vg})(R + \lambda_v)} \right)^{-1}}.$$

If $v > 1$, the growth of the droplet follows the Hertz–Knudsen formula, and the rate of the growth does not depend upon R .

$$\frac{dR}{dt} = \frac{\gamma_c P_s(T)(S-1)}{\rho_l \sqrt{2\pi k_B T/m_1}} \equiv \Omega_n, \quad (\text{A.6})$$

where it is assumed that the temperature of the droplet is equal to the gas temperature, P_s is the saturation vapor pressure, S is supersaturation, ρ_l is the liquid density. Generally speaking, for small droplets, the dependence of P_s on R should be taken into account:

$$P_s = P_\infty(T_s) \exp\left(\frac{2\sigma v_1}{R k_B T_s}\right), \quad (\text{A.7})$$

where P_∞ is the saturation pressure at the plain surface, σ is the surface tension, v_1 is a volume per molecule in liquid. Thus, at $R > r_{*,cl}$, where $r_{*,cl} = 2\sigma v_1/k_B T_s \ln(P/P_\infty)$ is the classical critical radius the droplets are previously growing while at $R < r_{*,cl}$ they tend to evaporate.

If $v < 1$, the Maxwell formula follows from the common expression given in Ref. [2] where the growth of the droplet is determined by the diffusion coefficient D_1 and the rate of the growth is inversely proportional to R .

$$\frac{dR}{dt} = \frac{D_1 P_s(T)(S-1)}{\rho_l (k_B T/m_1) R} \equiv \Omega_m. \quad (\text{A.8})$$

A.5. Stages of the droplet formation and growth

In the vicinity of the zone where active nucleation occurs (or where S or the rate of nucleation

reach their maximum), zone N, it is possible to separate two sorts of clusters (see Refs. [26,29]). For large clusters (sort 1), gravity prevails thermophoretic forces; therefore, they move to the bottom plate, grow within this movement and, in principle, could be registered by the detecting apparatus. Small clusters, on the contrary, move to the top plate. During this movement, they continue to grow and their further behavior is two-fold. If before they are deposited by the wall, some drops manage to reach the so-called “radius of soaring” at which the resulting force vanishes, in what follows such drops (sort 2) will fall down and can be registered. Otherwise, they will be deposited by the wall and cannot be registered.

The radius of soaring can be determined by equating the gravitational and thermophoretic forces because at $v = 0$, the drag force vanishes. It yields [26,29]

$$r_s = \left[\frac{9\mu^2 C_s k_B \nabla T}{P_0 \rho_l g m_0} \left(\frac{k_g}{k_p} + C_t \text{Kn} \right) (1 + 3C_m \text{Kn})^{-1} \times \left(1 + 2 \frac{k_g}{k_p} + 2C_t \text{Kn} \right)^{-1} \right]^{1/2}. \quad (\text{A.9})$$

For precipitating clusters, the thermophoretic force is less than gravity but an equality of gravity and the drag force is reached rather fast that results in a steady velocity of the cluster precipitation. Under the conditions of DCC ($\text{Re} \ll 1$), it yields [27]

$$v_g = \frac{m_1 g j}{6\pi\mu R} \approx \frac{2\rho_l g}{9\mu} R^2, \quad (\text{A.10})$$

where j is the number of molecules in the cluster, g is the gravity acceleration.

Appendix B. Equation for $S(\xi)$

This appendix aims to integrate Eq. (16) at $dT/d\xi = \text{const}$. Integrating Eq. (16) for the first time, we immediately get

$$\frac{d}{d\xi} \frac{\alpha_1}{\alpha_0} = \frac{c_1}{D_1} \quad (\text{B.1})$$

with $c_1 = \text{const}$. As α_1 and α_0 are mass fractions of vapor and background gas, we can rewrite their ratio in the form

$$\frac{\alpha_1}{\alpha_0} = \frac{m_1 n_{1e}}{m_0 n_0} S, \quad (\text{B.2})$$

whence

$$\frac{d}{d\xi} \frac{\alpha_1}{\alpha_0} = \frac{m_1 n_{1e}}{m_0 n_0} S \frac{d \ln n_{1e}}{dT} \frac{dT}{d\xi} + \frac{m_1 n_{1e}}{m_0 n_0} \frac{dS}{d\xi}. \quad (\text{B.3})$$

According to Ref. [1] n_{1e} can be represented as follows:

$$n_{1e} = \frac{\bar{C}}{k_B T} \exp\left(-\frac{L}{R_g T}\right),$$

where L is latent heat of the vapor, R_g is the gas constant and $\bar{C} = \text{const}$. Therefore,

$$\frac{d \ln n_{1e}}{dT} = -\frac{1}{T} + \frac{L}{R_g T^2}. \quad (\text{B.4})$$

Substituting Eq. (B.4) into Eq. (B.3), then into Eq. (B.1) and making some transformations, we arrive at the following equation:

$$\frac{dS}{d\xi} = \frac{c_1 m_0 n_0}{D_1 m_1 n_{1e}} - \frac{S}{T} \left(\frac{L}{R_g T} - 1\right) \frac{dT}{d\xi}. \quad (\text{B.5})$$

This equation is linear on S and can be directly integrated at $dT/d\xi = \text{const}$. In doing so we represent it in the form,

$$\begin{aligned} \frac{dS}{dT} &= a_1(T)S + a_2(T), \\ a_1(T) &= -\frac{1}{T} \left(\frac{L}{R_g T} - 1\right), \\ a_2(T) &= \frac{c_1 m_0 n_{1e}}{D_1 m_1 n_0} \left(\frac{dT}{d\xi}\right)^{-1}, \end{aligned} \quad (\text{B.6})$$

whence an integration yields

$$\begin{aligned} S &= T \exp\left(\frac{L}{R_g T}\right) (\sqrt{T} \mu + c_2), \\ \mu &= \frac{2c_1 m_0 n_0 k_B}{m_1 \bar{C} (dT/d\xi) D_0}, \end{aligned} \quad (\text{B.7})$$

where $D_0 = D_1 \sqrt{T}$ does not depend on T and c_2 and c_1 are integration constants. These could be

found from appropriate boundary conditions. For instance, we assume that $S = S_*$ at $T = T_*$ and that $dS/d\xi$ in the point (T_*, S_*) is given by Eq. (19). Thus, substituting these values into Eq. (B.7), we obtain two equations to determine c_1 and c_2 . Omitting intermediate algebra, we arrive at the expression,

$$\begin{aligned} S(\xi) &= S_* \frac{T}{T_*} \left[1 + 2 \left(\sqrt{\frac{T}{T_*}} - 1 \right) \left(1 - \frac{L}{R_g T_*} - \frac{3}{2} \right. \right. \\ &\quad \left. \left. \times \left(1 + \frac{\sigma_2 T_*}{\sigma} \right) \ln S_* \right) \right] \exp\left(-\frac{L}{R_g T} \frac{T - T_*}{T_*}\right) \\ &\approx S_* \frac{T}{T_*} \left[1 + 2 \frac{L}{R_g T_*} \left(1 - \sqrt{\frac{T}{T_*}} \right) \right] \\ &\quad \times \exp\left(-\frac{L}{R_g T} \frac{T - T_*}{T_*}\right). \end{aligned} \quad (\text{B.8})$$

References

- [1] A.L. Itkin, E.G. Kolesnichenko, *Microscopic Theory of Condensation in Gases and Plasma*, World Scientific, New York, 1997.
- [2] A. Itkin, Kinetic model of effect of a carrier gas on nucleation in diffusion chamber, *Aerosol Sci. Technol.*, in press.
- [3] R. Heist, M. Janjua, J. Ahmed, Effects of background gases on the homogeneous nucleation of vapors. I, *J. Phys. Chem.* 98 (1994) 4443.
- [4] A. Lushnikov, private communication, 1997.
- [5] V.N. Chukanov, A.P. Kuligin, *Teplofizika Visokich Temperatur* 25 (1987) 70 (in Russian).
- [6] C.C.M. Luijten, M.E.H. van Dongen, Nucleation at high pressure. I. Theoretical considerations, *J. Chem. Phys.* 111 (1999) 8524.
- [7] A.L. Itkin, U.G. Pirumov, Y.A. Rijov, Modified homogeneous nucleation model. Comparison of the theoretical and experimental results. *Proc. 14th RGD Symp.*, Tsukuba University, 1984, pp. 937–943.
- [8] A.L. Itkin, Effect of a carrier gas on nucleation in diffusion chambers, *J. Aerosol Sci.* 29 (1) (1998) S359–S360.
- [9] A.L. Itkin, Kinetics of diffusion-limited nucleation in a diffusion cloud chamber, *J. Aerosol Sci.* 29 (1) (1998) S357–S358.
- [10] R.E. Sampson, G.S. Springer, Condensation on and evaporation from droplets by a moment method, *J. Fluid Mech.* 36 (3) (1969) 557.
- [11] J. Ferziger, H. Kaper, *Mathematical Theory of Transport Processes in Gases*, North-Holland, Amsterdam, 1972.

- [12] S. Bretsznajder, *Wlasności gazow i cieczy*. Wydawnictwa naukowo-techniczne, Warszawa, 1966.
- [13] A.L. Itkin, The rate constants of the unimolecular decay and condensation coefficients of neutral clusters and cluster ions. Proc. 19th Symp. Rarefied Gas Dynam., vol. 1, Oxford, pp. 323–330.
- [14] A.L. Itkin, E.G. Kolesnichenko, Y.E. Gorbachev, Toward the theory of the nucleation inside the thermodiffusion chamber. Technical report 1503, A.Ioffe FTI Acad. Sci. USSR, 1991 (in Russian).
- [15] A.L. Itkin, E.G. Kolesnichenko, Calculation of condensing gas flows by means of the monomolecular condensation theory, *Fluid Dynam.* 25 (5) (1990) 765–774.
- [16] A. Bertelsmann, R. Stuczynski, R. Heist, Effects of background gases on the homogeneous nucleation of vapors 3, *J. Phys. Chem.* 100 (1996) 9762.
- [17] J. Frenkel, *Kinetic Theory of Liquids*, RAS, Moscow–Leningrad, 1945.
- [18] R. Heist, M. Janjua, J. Ahmed, Effects of background gases on the homogeneous nucleation of vapors 2, *J. Phys. Chem.* 99 (1995) 375.
- [19] V. Gorbunov, U. Pirumov, Y. Ryzhov, *Nonequilibrium Condensation in High Speed Gas Flows*, Mashinostroenie, Moscow, 1984.
- [20] A. Binnie, M. Woods, The pressure distribution in a convergent–divergent steam nozzle, *Proc. Inst. Mech. Engrs. (London)* 138 (1938) 229.
- [21] D. Kane, M. El-Shall, Condensation of supersaturated vapors of hydrogen bonding molecules. Ethylene glycol, propylene glycol, trimethylene glycol and glycerol, *J. Chem. Phys.* 105 (1996) 7617.
- [22] A. Bertelsmann, R. Heist, Two-dimensional transport and wall effects in the thermal diffusion cloud chamber. II. Stability of operation, *J. Chem. Phys.* 106 (1996) 624.
- [23] R. Reid, J. Prausnitz, T. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, NY, 1977.
- [24] P. Wagner, R. Strey, Homogeneous nucleation rates of water vapor measured in a two piston expansion chamber, *J. Phys. Chem.* 85 (1981) 2694.
- [25] B.E. Wyslouzil, G. Wilemski, M.G. Beals, M.B. Frish, Effect of carrier gas pressure on condensation in a supersonic nozzle, *Phys. Fluids* 6 (1994) 2845.
- [26] N. Fuchs, *Mechanics of aerosols*, Acad. Sci. USSR, Moscow, 1955.
- [27] P. Reist, *Introduction to Aerosol Science*, Macmillan, NY, 1984.
- [28] L. Talbot, R. Cheng, R. Schefer, D. Willis, Thermophoresis of particles in a heated boundary layer, *J. Fluid Mech.* 101 (4) (1980) 737.
- [29] J. Vitovec, N.V. Pavlukevich, I. Smolik, S.P. Fisenko, Motion and growth of new-phase particles formed in a thermodiffusion chamber, *J. Engng. Phys. Thermophys.* 56 (1989) 648.