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Theory of heterogeneous nucleation for vapor undergoing a gradual metastable state formation

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Contents

Abstract. **Major recent advances in the theoretical study of heterogeneous nucleation on macroscopic wettable centers of different nature are reviewed in the context of the classical scheme which uses the thermodynamics of a new phase nucleation to calculate the key kinetic characteristics of nucleation. The review centers on the kinetics of heterogeneous nucleation under conditions where a metastable state of the initial phase gradually forms — a situation in which the factors supporting the phase transition to the metastable state and then deepening the phase into the metastability region also remain active after the intense phase transition has begun. The formulation and control of the conditions of consistency for applying all the**

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thermodynamic and kinetic elements of the theory are emphasized. The thermodynamics of interfaces are discussed in detail and a careful kinetic analysis is performed for the stage at which the main number of stably growing nuclei of the new phase is formed around wettable nuclei consisting of soluble or insoluble, surface-inactive or surface-active materials. The features common to barrier and barrierless heterogeneous nucleation processes are discussed, which open new possibilities in the experimental study of the phenomenon and offer new practical applications of the theory.

1. Introduction

Various first-order phase transitions, from the commonest (the dropwise condensation in a supersaturated vapor) to latent formation of pores from a supersaturated vacancy solution in a solid, proceed in their development through virtually identical stages, the starting point being the creation of a metastable state of matter.

The transformation of matter to a metastable state, such as the production of a supersaturated vapor, superheated and supercooled liquids or supersaturated solution is possible in different ways. In practice, all of them are categorized into two groups depending on how rapidly the physical parameters of a substance are changed under the action of factors which induce metastable state formation. By the *instantaneous formation of metastability* is meant the transition to a metastable state during a time much smaller than the characteristic time of the subsequent phase transition. The *gradual formation of metastability* occurs in the opposite situation when factors responsible for matter transformation to a metastable state and going further into the metastability region remain active after the intense phase transition has begun.

The knowledge of characteristics of a metastable state immediately after its instantaneous formation, when it is not yet perturbed by the subsequent phase transition, considerably simplifies the theory describing the progress of phase transitions under such conditions. This explains to a large extent why the majority of theoretical and experimental works concerning the kinetics of phase transitions and now recognized as classical proceeded from the assumption of instantaneous formation of the initial metastable state [1 – 7].

Although widespread in nature and extensively employed in technology, phase transitions attending the gradual formation of metastability have long been given little attention by theorists and experimenters. The few theoretical works in this field did not arouse great interest. The main reason for such a situation lies in the difficulty of correctly determining metastable state parameters prior to the onset of intense phase transition.

Considerable progress in the description of phase transitions under conditions of the gradual formation of metastability has been achieved during the last two decades. Theoretical studies have demonstrated that, if certain slack constraints are imposed on the metastability formation rate, two conspicuous stages can be distinguished in the course of a phase transition [8]. The initial one is nucleation giving rise to the bulk number of steadily growing nuclei of the new, stable phase. The nonlinearity of nucleation, manifested as the sharp dependence of the intensity of formation of new phase nuclei (nucleation rate) on the degree of metastability of the initial phase, accounts for the short duration of the nucleation stage compared with the characteristic time of metastable state formation. This stage is induced by metastability-forming factors, while its termination is dictated by a decrease in the degree of metastability (despite the continuing action of the causative factors) due to the transfer of a fraction of the matter occurring in the metastable phase into the stable phase nuclei. In the beginning, this fraction is relatively small. The metastable phase almost entirely transforms to the stable one after the termination of the nucleation stage and the onset of the so-called collapse stage. This stage is characterized by the further growth of new phase nuclei without a substantial change in their number. The intensity of the action of factors creating metastability, the number of new phase nuclei formed at the nucleation stage and their growth rate (the rate of consumption of metastable phase material by the nuclei) are interrelated in the process such that practically all the matter rapidly transforms to the stable state at the collapse stage. In the case of an additional constraint imposed on the metastability formation rate, the collapse stage is followed by the well-known Ostwald ripening stage during which large particles of the new phase grow at the expense of disappearing small ones [9, 10].

Ostwald ripening had been described before the theory of nucleation and collapse stages was developed. Only the most general characteristics of the initial state of a system in which the phase transition takes place are used in this explanation. The description of the collapse stage in the gradual metastability formation process is analogous to the description of its counterpart after the instantaneous formation of metastability. The only difference consists in that the transition of the bulk of matter from the metastable state, reached by the onset of the nucleation stage, to the stable state occurs while the metastability-inducing factors are still active.

The nucleation stage poses a most interesting and difficult problem for researchers studying phase transitions in the course of gradual formation of metastability. In the theory of the nucleation stage, the questions of thermodynamics of small systems are closely intermingled with the descriptions of the process of overcoming the energy barrier (which changes during the nucleation stage) by newly-formed stable phase particles, the growth peculiarities of these particles in a wide range of their size variation, and the correct interpretation of the collective effect of an ensemble of the growing stable phase particles on the state of the initial metastable phase. Taken together with the effects of metastability-forming factors, all this gives rise to a complicated, strongly nonlinear mathematical problem. However, a remarkable feature of the conditions for the gradual formation of metastability, reviewed in this paper, consists in that the efforts to surmount mathematical difficulties are repaid by the discovery of interesting and even unusual nucleation properties. The most important of them is the weak dependence of the principal nucleation stage characteristics on the accuracy of determining the thermodynamic parameters of small stable phase nuclei. It is this universal property that makes predictions of the theory under consideration quantitative and distinguishes it from the theory of nucleation after instantaneous metastable state formation, which makes high demands upon the accuracy of describing small critical nuclei.

In this review, the theory of the nucleation stage is formulated for the heterogeneous mechanism, most widespread in nature, by which stable phase nuclei (droplets) arise on foreign particles present in a supersaturated vapor volume. Such foreign particles or heterogeneous centers can be ions, acid droplets, sea-salt crystals, dust or soot particles, etc. Given the great variety of properties and sizes of similar heterogeneous centers and the diversity of phase transition conditions, all attempts to construct a quantitative theory of heterogeneous nucleation may seem impracticable. For example, are sea-salt crystals completely dissolved in the critical-size droplets of aqueous vapor that condenses on them, allowing for the nucleation rate largely dependent on the thermodynamic parameters of such vapor droplets? Is this solution saturated or, on the contrary, lean? Are insoluble aerosol particles totally or partially wettable? Does the critical size of nuclei depend on thin or thick liquid films in nucleation on wettable dust particles? These beforehand unknown circumstances determine to a large extent such characteristics of the nucleation process as the number and average size of the droplets being formed or the duration of nucleation. In the gradual formation of metastability, the initiation and the length of the nucleation stage depend not only on its rate but also on the internal processes in the nucleation system. Peculiar conditions of metastable state formation are in a certain consistency of the sizes of nuclei whose thermodynamic parameters determine the nucleation rate and characteristics of heterogeneous centers around which these nuclei are formed. Such a consistency for the representative types of heterogeneous centers dealt with in this review considerably simplifies the thermodynamic description of stable phase nuclei and leads to the exhibition of universal rules in the theory of heterogeneous nucleation.

The forthcoming discussion of nucleation will be centered on the commonest phase transition of a supersaturated vapor to the liquid-droplet state. Accordingly, liquid droplets will be considered as new phase nuclei.

2. General notions of the thermodynamics of heterogeneous nucleation

The nucleation theory is based on thermodynamic data and its objective is to construct the kinetics of nucleation.

The thermodynamics of heterogeneous nucleation has rather a long history [5, 11–32]. The central issue is the assessment of work of droplet formation or chemical potential of the condensate in a droplet, i.e. a liquid condensed from the vapor. The knowledge of this work or the chemical potential of the condensate as a function of the number of condensate molecules allows all major thermodynamic characteristics of nucleation kinetics to be calculated. In what follows, we shall confine ourselves to considering wettable condensation nuclei (ions, small macroscopic salt crystals or insoluble particles with a zero wetting angle at the surface). Thermodynamic characteristics of nucleation for wettable nuclei include threshold supersaturation of vapor, the height of the activation barrier to nucleation, positions and half-widths of maxima and minima of droplet formation work on the droplet size axis. We shall define these characteristics below and formulate general notions of the thermodynamics of heterogeneous nucleation on wettable nuclei.

2.1 The work of droplet formation on a nucleus

Let us introduce the vapor supersaturation ζ according to formula

$$\zeta = \frac{n}{n_\infty} - 1\,, \tag{2.1}$$

where n is the number density of vapor molecules, and n_∞ is the number density of saturated vapor molecules. The supersaturation ζ lies within the range $-1 < \zeta < \infty$.

Let us now consider a droplet arising in the vapor–gas medium on one of the wettable condensation nuclei of radius R_{n} (Fig. 1). The droplet radius is R. Let us introduce the quantity ν according to the formula

$$\nu = \frac{4\pi R^3}{3 v_\alpha}\,, \tag{2.2}$$

where v_α is the volume per molecule of the liquid condensed by the droplet from the vapor. The quantity ν is a variable to be used in the description of the droplet. In the subsequent discussion the subscripts α, β, and γ label quantities characterizing liquid, gaseous, and solid phases, respectively.

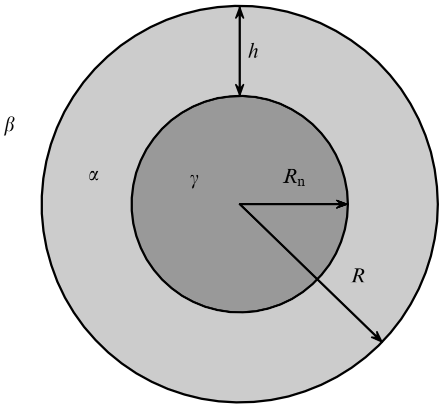

Figure 1. Initial stage of a R-radius droplet formation from a vapor on a wettable nucleus of radius R_{n}. Here, h is the liquid film thickness, phase α is liquid, phase β is gaseous, phase γ is solid.

When condensation nuclei are represented by microscopic heterogeneous condensation centers with $R_{\mathrm{n}} \ll R$, the quantity ν defined by equality (2.2) coincides with the number of condensate molecules.

The quantity ν defined by expression (2.2) has the same sense for soluble macroscopic condensation nuclei because in this case (see Section 4.1) the number of vapor molecules condensed in a droplet is by far greater than the number of molecules of condensation nucleus matter dissolved in the same droplet (it will be shown below that this is true even for droplets close to equilibrium).

In the case of insoluble macroscopic nuclei of condensation, the quantity ν defined by equality (2.2) governs the number of molecules of a liquid which would be contained in a droplet if it had no insoluble condensation nucleus at all. It should be noted that droplet radii begin to grow rapidly after the droplets have overcome, by fluctuation, the activation barrier of nucleation. Then, the quantity ν defined by Eqn (2.2) coincides, with a progressively higher accuracy, with the true number of vapor molecules condensed by a droplet containing the insoluble condensation nucleus. This issue will be discussed at greater length in Section 7.1.

A peculiar feature of heterogeneous nucleation on wettable nuclei, which distinguishes it from homogeneous nucleation, is the limiting threshold value ζ_{th} of vapor supersaturation ζ above which barrierless heterogeneous nucleation occurs. Inequalities $-1 < \zeta < 0$, $0 < \zeta < \zeta_{\mathrm{th}}$ and

$\zeta > \zeta_{\text{th}}$ indicate regions of stable, metastable, and unstable vapor states, respectively.

The work of droplet formation on a condensation nucleus constitutes an important characteristic of heterogeneous nucleation thermodynamics. This work is conveniently expressed in $k_B T$ units, where k_B is the Boltzmann constant, and T is the temperature which is the same for the droplets and the surrounding vapor – gas medium if the former and the latter are in thermal equilibrium. Such an equilibrium may be due to a high concentration of passive gas compared with that of vapor in the vapor – gas medium. The work of droplet formation on a nucleus, expressed in $k_B T$ units, is denoted by F. It is a function of two variables: v and ζ.

Typical of heterogeneous nucleation is a change in the dependence of the work F on the variable v (used in the droplet description) with increasing vapor supersaturation ζ. It is illustrated by Fig. 2. Curves *1*, *2*, *3*, and *4* meet vapor supersaturations at which $-1 < \zeta < 0$, $0 < \zeta < \zeta_{\text{th}}$, $\zeta = \zeta_{\text{th}}$, and $\zeta > \zeta_{\text{th}}$, respectively. In Fig. 2, the origin of the v-axis is fixed at the point corresponding to the zero true number of vapor molecules condensed by the droplet. It is taken into account that the work F at this point goes to zero because the vapor intrinsically contains a condensation nucleus; hence, no work is needed to form it.

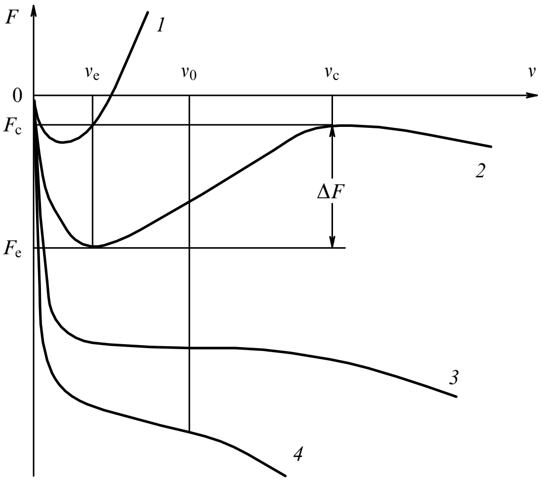

Figure 2. Variation of v-dependence of the work F of droplet formation with increasing vapor supersaturation ζ.

At the values v_e and v_c of variable v, the work F depicted by curve *2* passes a minimum F_e and maximum F_c. The v_e and v_c values correspond to the equilibrium and critical droplets, respectively, which are in stable and unstable chemical equilibrium with the vapor. Obviously, one has

$$\left(\frac{\partial F}{\partial v}\right)_e = 0\,, \qquad \left(\frac{\partial F}{\partial v}\right)_c = 0\,, \tag{2.3}$$

$$\left(\frac{\partial^2 F}{\partial v^2}\right)_e > 0\,, \qquad \left(\frac{\partial^2 F}{\partial v^2}\right)_c < 0\,, \tag{2.4}$$

where the subscripts e and c mark magnitudes taken at values v_e and v_c of variable v. A minimum of work F is also present in curve *1*. Thereafter the work F unboundedly grows with increasing v and therefore has no maximum.

The v_0 value on curves *2*, *3*, and *4* corresponds to the inflection point of a plot of work F versus v. Hence, one obviously obtains

$$\left(\frac{\partial^2 F}{\partial v^2}\right)_0 = 0\,, \tag{2.5}$$

where the subscript 0 indicates magnitudes of quantities at $v = v_0$. Why v_0 does not depend on the supersaturation ζ as shown in Fig. 2 will be explained in Section 2.3.

Further interpretation of Fig. 2 needs invoking additional thermodynamic relations. The known thermodynamic dependence of work F on vapor supersaturation ζ gives rise to the inequality

$$\frac{\partial F(v,\zeta)}{\partial \zeta} < 0\,, \tag{2.6}$$

where the work F is displayed as a function $F(v,\zeta)$ of two variables, v and ζ. The greater v, the stronger inequality (2.6).

Let us first consider a droplet at equilibrium. There is an explicit relation

$$F_e(\zeta) = F(v,\zeta)\Big|_{v=v_e(\zeta)} \tag{2.7}$$

indicating the dependence on ζ of the minimum F_e of work F and the position $v = v_e$ of this minimum on the v-axis. It follows from Eqn (2.7), in compliance with a known rule of differentiation, that

$$\frac{\partial F_e}{\partial \zeta} = \frac{\partial F}{\partial v}\bigg|_{v=v_e} \frac{\partial v_e}{\partial \zeta} + \frac{\partial F}{\partial \zeta}\bigg|_{v=v_e}\,. \tag{2.8}$$

By virtue of formula (2.3), the first term on the right-hand side of Eqn (2.8) vanishes. Then, according to relation (2.8), one arrives at

$$\frac{\partial F_e}{\partial \zeta} = \frac{\partial F}{\partial \zeta}\bigg|_{v=v_e}\,. \tag{2.9}$$

A similar line of reasoning as regards a critical droplet leads to

$$\frac{\partial F_c}{\partial \zeta} = \frac{\partial F}{\partial \zeta}\bigg|_{v=v_c}\,, \tag{2.10}$$

in addition to Eqn (2.9).

Bearing in mind that the greater v, the stronger inequality (2.6) and that $v_c > v_e$, the following chain of inequalities follows from expressions (2.9), (2.10):

$$\frac{\partial F_c}{\partial \zeta} < \frac{\partial F_e}{\partial \zeta} < 0\,. \tag{2.11}$$

Let us further examine Fig. 2. For $-1 < \zeta < 0$ (i.e. in the region of vapor stable state), the work F depicted by curve *1* has a negative minimum after which it starts to grow infinitely with increasing v.

Upon the transition from the region $-1 < \zeta < 0$ to the region $0 < \zeta < \zeta_{\text{th}}$ of vapor metastable state, the work F acquires, in addition, a maximum lying to the right of the minimum on the v-axis. This maximum is positive and rather large at small ζ values.

As the vapor supersaturation ζ continues to grow, both the maximum and the minimum of work F according to inequality (2.11) decrease, the former more rapidly than the latter. The initially positive maximum gradually turns to a negative one. While increasing in absolute value, the minimum naturally remains negative. Curve *2* in Fig. 2 corresponds to the situation in which the maximum has just become negative.

With a further increase of supersaturation ζ, the maximum of work F according to Eqn (2.11) progressively comes close to its minimum. At $\zeta = \zeta_{\mathrm{th}}$, when the vapor supersaturation ζ reaches a threshold value ζ_{th}, the maximum and minimum of the work F coincide giving rise to an inflection point on a plot of work as a function of ν. Both the first and the second derivatives of work with respect to ν vanish at this point. Curve *3* in Fig. 2 is appropriate to the vapor supersaturation $\zeta = \zeta_{\mathrm{th}}$.

Finally, after the transition into the region $\zeta > \zeta_{\mathrm{th}}$ of the vapor unstable state described by curve *4* in Fig. 2, the work F monotonically decreases with increasing ν and shows neither maximum nor minimum, in conformity with inequality (2.6) and its strengthening with a rise in ν. The point of inflection in the curve describing the ν-dependence of F still exists. However, the first ν-derivative of F is smaller than zero at this point, while the second ν-derivative of F remains zero.

Let us introduce the height difference ΔF between the potential hump and potential well in work F, derived from the relation

$$\Delta F = F_{\mathrm{c}} - F_{\mathrm{e}} \qquad (0 < \zeta < \zeta_{\mathrm{th}}) \tag{2.12}$$

(see Fig. 2), in the region $0 < \zeta < \zeta_{\mathrm{th}}$ of vapor metastable state. This difference gives the energy in $k_{\mathrm{B}}T$ units necessary for the fluctuation transition of a droplet from the bottom of the potential well in work F over its potential hump, i.e. for overcoming the activation barrier to heterogeneous nucleation via fluctuation mechanism. Being determined by the equality (2.12), ΔF has the physical sense of the activation energy in heterogeneous nucleation. Kinetic evidence of this meaning of ΔF will be given in Section 3.1.

According to Eqns (2.11) and (2.12), the inequality

$$\frac{\partial \Delta F}{\partial \zeta} < 0 \qquad (0 < \zeta < \zeta_{\mathrm{th}}) \tag{2.13}$$

holds in the vapor metastable state region $0 < \zeta < \zeta_{\mathrm{th}}$. Hence, the activation energy ΔF monotonically decreases with increasing vapor supersaturation ζ. When the supersaturation ζ attains its threshold value ζ_{th}, the maximum and minimum of the work F merge into the point of inflection as above. Then, the ΔF activation energy vanishes and barrierless heterogeneous nucleation in the region $\zeta > \zeta_{\mathrm{th}}$ takes place.

The behavior of the work F of droplet formation on a condensation nucleus illustrated by Fig. 2 and its interpretations will be used in Section 3.1 for the qualitative representation of heterogeneous nucleation under conditions of gradual vapor metastable state formation.

2.2 Near-equilibrium and near-critical droplets

Bearing in mind Eqns (2.3) and (2.4), the following approximations may be written:

$$F = F_{\mathrm{e}} + \frac{(\nu - \nu_{\mathrm{e}})^2}{\Delta\nu_{\mathrm{e}}^2} \qquad \left(|\nu - \nu_{\mathrm{e}}| \lesssim \Delta\nu_{\mathrm{e}}\right), \tag{2.14}$$

$$F = F_{\mathrm{c}} - \frac{(\nu - \nu_{\mathrm{c}})^2}{\Delta\nu_{\mathrm{c}}^2} \qquad \left(|\nu - \nu_{\mathrm{c}}| \lesssim \Delta\nu_{\mathrm{c}}\right), \tag{2.15}$$

where

$$\Delta\nu_{\mathrm{e}} = \left[\frac{2}{\left(\partial^2 F/\partial \nu^2\right)_{\mathrm{e}}}\right]^{1/2}, \qquad \Delta\nu_{\mathrm{c}} = \left|\frac{2}{\left(\partial^2 F/\partial \nu^2\right)_{\mathrm{c}}}\right|^{1/2}. \tag{2.16}$$

It follows from Eqn (2.14) that if the variation of ν from ν_{e} is $\Delta\nu_{\mathrm{e}}$, the work F increases by a thermal unit of energy (recall that the work F is expressed in such units). In contrast, according to Eqn (2.15), the work F decreases by a thermal unit of energy if the difference between ν and ν_{c} equals $\Delta\nu_{\mathrm{c}}$. For this reason, quantities $\Delta\nu_{\mathrm{e}}$ and $\Delta\nu_{\mathrm{c}}$ defined by equalities (2.16) are in fact 'half-widths' of the potential well and potential hump in the work F on the ν-axis. Quantities $\Delta\nu_{\mathrm{e}}$ and $\Delta\nu_{\mathrm{c}}$ play an important role in the kinetics and thermodynamics of heterogeneous nucleation. An equally important part is played by near-equilibrium and near-critical droplets for which the variable ν lies in the vicinities $|\nu - \nu_{\mathrm{e}}| \lesssim \Delta\nu_{\mathrm{e}}$ and $|\nu - \nu_{\mathrm{c}}| \lesssim \Delta\nu_{\mathrm{c}}$ of points $\nu = \nu_{\mathrm{e}}$ and $\nu = \nu_{\mathrm{c}}$, respectively.

The condition that the terms with the third ν-derivative of F at points $\nu = \nu_{\mathrm{e}}$ and $\nu = \nu_{\mathrm{c}}$, neglected in the approximations (2.14) and (2.15), should be smaller than the retained terms with the second ν-derivative of F at the same points is given by the inequalities

$$\frac{\Delta\nu_{\mathrm{e}}}{3(\nu_0 - \nu_{\mathrm{e}})} \ll 1\,, \qquad \frac{\Delta\nu_{\mathrm{c}}}{3(\nu_{\mathrm{c}} - \nu_0)} \ll 1 \tag{2.17}$$

(the factor 3 in the denominators originates from the factorial multipliers in a Taylor series; it is taken into account that $\nu_{\mathrm{e}} < \nu_0 < \nu_{\mathrm{c}}$).

Inequalities (2.17) show that the potential well and hump in work F are fully manifested: they are spaced apart on the ν-axis as is qualitatively represented in Fig. 2.

It will be shown in Sections 4 and 6 that inequalities (2.17) are satisfied if the inequality

$$\exp(\Delta F) \gg 1 \tag{2.18}$$

is fulfilled, thus defining the condition that an effective supercritical droplet formation proceeds when the droplets pass a significant activation barrier to nucleation.

In the thermodynamics and kinetics of heterogeneous nucleation, the essentially discrete quantity ν is understood as a continuous one. If such an understanding is to be acceptable for near-equilibrium and near-critical droplets, the following inequalities need to be fulfilled:

$$\Delta\nu_{\mathrm{e}} \gg 1\,, \qquad \Delta\nu_{\mathrm{c}} \gg 1\,. \tag{2.19}$$

The threshold supersaturation ζ_{th} of vapor and quantities ΔF, ν_{e}, ν_{c}, $\Delta\nu_{\mathrm{e}}$, and $\Delta\nu_{\mathrm{c}}$ as functions of vapor supersaturation are the main thermodynamic characteristics of nucleation. For macroscopic condensation nuclei, these characteristics will be represented in the analytical form in Sections 4 and 6, along with the illustration of the fulfillment of conditions (2.17)–(2.19) in nucleation kinetics.

It is worthwhile to note that analogues of conditions (2.17)–(2.19) in the problem of homogeneous nucleation in a vapor have been found earlier in Ref. [33].

2.3 Relationship between the work of droplet formation and the condensate chemical potential in the droplet

Let us denote as b_ν the chemical potential of the condensate in a droplet, which depends on the droplet description variable ν. We shall further express b_ν in $k_{\mathrm{B}}T$ units and reckon it from a value corresponding to the equilibrium between the condensate and the vapor, with a flat interface between them. The condensate in the droplet is much denser than the vapor, and its chemical potential b_v is practically independent of the vapor supersaturation ζ.

Let us denote the vapor chemical potential as b, express it (similar to b_v) in $k_B T$ units, and reckon from a value corresponding to the equilibrium between the vapor and the liquid which undergoes condensation and has a flat contact surface.

Assuming that vapor by virtue of its supposedly low density is an ideal gas, using a known thermodynamic relation between the chemical potential and density of an ideal gas, and taking into account the definition (2.1) of vapor supersaturation, we obtain

$$b = \ln(1+\zeta)\,. \tag{2.20}$$

In agreement with Eqn (2.20), the threshold value $\zeta_{\rm th}$ of vapor supersaturation ζ corresponds to the threshold value $b_{\rm th}$ of vapor chemical potential b and this linkage is given by the equality

$$b_{\rm th} = \ln(1+\zeta_{\rm th})\,. \tag{2.21}$$

Evidently, there is not only thermal but also mechanical equilibrium between the droplet and the vapor – gas medium. Hence the availability of the thermodynamic relation [34]

$$\frac{\partial F}{\partial v} = b_v - b\,. \tag{2.22}$$

It is taken into consideration in the above expression that the droplet is incapable of exchanging matter with a passive gas. Equation (2.22) also takes into account that the material of soluble condensation nuclei is fully retained in the droplet. This equation will be frequently referred to in the forthcoming discussion.

Let us consider the region $0 < \zeta < \zeta_{\rm th}$ of the vapor metastable state. According to relations (2.20) and (2.21), the vapor chemical potential b in this region satisfies the inequality $0 < b < b_{\rm th}$. The use of relation (2.22) in (2.3) – (2.5) leads to

$$(b_v)_{\rm e} = b\,, \qquad (b_v)_{\rm c} = b\,, \tag{2.23}$$

$$\left(\frac{\partial b_v}{\partial v}\right)_{\rm e} > 0\,, \qquad \left(\frac{\partial b_v}{\partial v}\right)_{\rm c} < 0\,, \tag{2.24}$$

$$\left(\frac{\partial b_v}{\partial v}\right)_0 = 0\,. \tag{2.25}$$

It can be seen from Eqns (2.24), (2.25) and $v_{\rm e} < v_0 < v_{\rm c}$ that b_v has a maximum at the point $v = v_0$. Therefore, the following inequality holds:

$$\left(\frac{\partial^2 b_v}{\partial v^2}\right)_0 < 0\,. \tag{2.26}$$

The point $v = v_0$ (similar to b_v) does not depend on the vapor supersaturation ζ. The work F having the point of inflection at $v = v_0$ [in accordance with equality (2.5)] explains why this inflection point is independent of vapor supersaturation as stated in Section 2.1.

The maximum of b_v at the point $v = v_0$ appears when the points $v = v_{\rm e}$ and $v = v_{\rm c}$ of F-work maximum and minimum merge together. This takes place at the $\zeta_{\rm th}$ value of vapor supersaturation ζ or (which is the same) at the $b_{\rm th}$ value of vapor chemical potential b related to $\zeta_{\rm th}$ by formula (2.21). Hence the validity of the equality

$$b_{\rm th} = \max b_v = (b_v)_0\,. \tag{2.27}$$

The solid line in Fig. 3 depicts the condensate chemical potential b_v in a droplet as a function of the variable v in the droplet description. This relationship, characteristic of heterogeneous nucleation, agrees with Eqns (2.22) – (2.27) and with Fig. 2. The point of reference on the v-axis is chosen in the same way as in Fig. 2. The tending of b_v towards $-\infty$ when the variable v tends to this point ensues, because of Eqn (2.22), from the behavior of the work F shown in Fig. 2. The tendency of b_v towards zero as $v \to \infty$, when the condensate – vapor interface flattens, results from the mode of reckoning adopted in the definition of b_v.

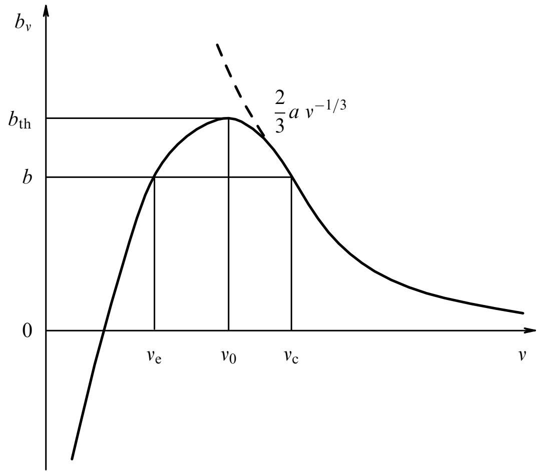

Figure 3. Dependence on v of the condensate chemical potential b_v in a droplet.

The dashed line in Fig. 3 shows the dependence on v of the chemical potential b_v of the condensate in homogeneous nucleation. This potential is given by the Gibbs – Kelvin relation

$$b_v = \frac{2}{3}\,a v^{-1/3}\,, \tag{2.28}$$

which takes into consideration the capillary pressure in a droplet. The quantity a is determined by the equality

$$a = \frac{4\pi\gamma}{k_B T}\left(\frac{3v_\alpha}{4\pi}\right)^{2/3}, \tag{2.29}$$

where γ is the droplet surface tension. The quantity a has the sense of the dimensionless surface tension of the droplet. It will be of importance in the theory of heterogeneous nucleation as well. When the variable v is sufficiently large, the dashed and solid lines in Fig. 3 coalesce. In such a case, the chemical potentials of the condensate in homogeneous and heterogeneous nucleation practically coincide.

At the chemical potential b of vapor, which lies in the region $0 < b < b_{\rm th}$ of the vapor metastable state (see Fig. 3), both equilibrium and critical droplets exist [in agreement with relations (2.23)]. This confirms what was said in Section 2.1 about curve *2* in Fig. 2.

Figure 3 also describes at once the characteristic cases $-1 < \zeta < 0$, $\zeta = \zeta_{\text{th}}$ and $\zeta > \zeta_{\text{th}}$, i.e. $-\infty < b < 0$, $b = b_{\text{th}}$ and $b > b_{\text{th}}$ [in accord with Eqns (2.20), (2.21)], which are represented by curves *1*, *3*, and *4* in Fig. 2. Indeed, if the chemical potential b of vapor in Fig. 3 lay in the stable state region $-\infty < b < 0$, it would indicate the existence of an equilibrium droplet, thus confirming what was said in Section 2.1 about curve *1* of Fig. 2. Experimental examination of such a droplet, i.e. a solvated condensation nucleus, for $-\infty < b < 0$ gives additional evidence that quantity b_v tends to $-\infty$ while the variable v tends to its reference point in Fig. 3.

If the chemical potential b of vapor in Fig. 3 was assumed to be equal to or higher than a threshold value b_{th}, it would be clear from the figure and relation (2.22) that the work F monotonically decreases with increasing v. At $b = b_{\text{th}}$, however, its v-derivative vanishes at the point $v = v_0$. This also confirms what was said in Section 2.1 about curves *3* and *4* in Fig. 2.

The chemical potential b_v of the condensate, given by relation (2.28) and shown by the dashed line in Fig. 3, grows monotonically in homogeneous nucleation with decreasing v and has no maximum. No matter how large is the chemical potential b of vapor, the inequality $b_v - b > 0$ will hold at a sufficiently small v; the same refers to the inequality $\partial F/\partial v > 0$, owing to relation (2.22). This indicates that homogeneous nucleation cannot be a barrierless process.

Being independent of vapor supersaturation ζ, the chemical potential b_v is a simpler theoretical object in the thermodynamics of heterogeneous nucleation than the work F which depends not only on v but also on ζ. For all that, the knowledge of chemical potential b_v as a function of v is sufficient for determining all the most important thermodynamic characteristics of nucleation. Indeed, the threshold supersaturation ζ_{th} of vapor is deduced from formulas (2.21) and (2.27). Points $v = v_{\text{e}}$ and $v = v_{\text{c}}$ of the maximum and minimum of work F are found as the roots of equations given by equalities (2.23). Furthermore, the half-widths Δv_{e} and Δv_{c} are found from the formulas ensuing from Eqns (2.16) and (2.22):

$$\Delta v_{\text{e}} = \left[\frac{2}{(\partial b_v/\partial v)_{\text{e}}} \right]^{1/2}, \qquad \Delta v_{\text{c}} = \left| \frac{2}{(\partial b_v/\partial v)_{\text{c}}} \right|^{1/2}. \tag{2.30}$$

Finally, the activation energy ΔF follows from relations (2.12) and (2.22):

$$\Delta F = \int_{v_{\text{e}}}^{v_{\text{c}}} (b_v - b)\,\mathrm{d}v\,. \tag{2.31}$$

As a result, when the chemical potential b_v is given as a function of v, the thermodynamic characteristics v_{e}, v_{c}, Δv_{e}, Δv_{c}, and ΔF of heterogeneous nucleation can be determined as functions of vapor supersaturation.

The construction of heterogeneous nucleation thermodynamics by analyzing the dependence of the condensate chemical potential b_v in a droplet on variable v of the droplet description will be employed in Sections 4 and 6. Also, these sections will be concerned with more complicated details, having important practical implications, of the general concepts that touch upon the thermodynamics of heterogeneous nucleation considered in Sections 2.1 – 2.3.

3. Fundamentals of the kinetic theory of heterogeneous nucleation

The activation barrier to nucleation is overcome owing to an increase of the droplet size through the fluctuation mechanism associated with vapor adsorption from the surrounding vapor – gas medium. In the course of this process, the droplet becomes supercritical, i.e. it steadily grows until overcondensation begins [9, 10]. Just such supercritical droplets are of special interest in the context of this review.

Although droplets overcome the barrier via the fluctuation mechanism throughout the entire period of the effective supercritical droplet formation (nucleation stage), this is only an initial event with respect to this stage. The nucleation stage is of special interest because it gives rise to all important kinetic characteristics of the nucleation process open for experimental examination, such as the total number of newly-formed supercritical droplets, the time of onset and duration of supercritical droplet formation or the width of the supercritical droplet size spectrum.

The nucleation kinetics are nontrivial in their theoretical description and susceptible to nucleation system parameters when the activation barrier is sufficiently but not extremely high. Otherwise, the intensity of the process may prove negligibly low. The situation with the sufficient activation barrier will be considered below.

In the case of gradual formation of a vapor metastable state, neither the magnitude of vapor supersaturation nor the concentration of condensation nuclei is known in advance. Both are determined by nucleation kinetics. Papers [35 – 39] report a study of these kinetics which correlates the supersaturated vapor intake and consumption of condensation nuclei by droplets with the rate of external gradual vapor metastable state formation.

3.1 Ideal vapor supersaturation and its reference value

Let us consider in greater detail the results of the above-mentioned kinetic studies [35 – 39] of a nucleation stage under conditions of gradual vapor metastable state formation.

Following paper [8], let us first define an ideal vapor supersaturation Φ by the equality

$$\Phi = \frac{n_{\text{tot}}}{n_\infty} - 1\,, \tag{3.1}$$

where n_{tot} is the total number of molecules of the condensing matter per unit volume of vapor – gas medium including molecules condensed on the droplets. Evidently, the ideal supersaturation depends on the external conditions alone. The time-course of nucleation is governed from the outside by a given increment of ideal supersaturation in time. The ideal supersaturation Φ cannot be lower than the true one, ζ, determined by equality (2.1) in which n is the current number of vapor molecules per unit volume of the vapor – gas medium.

In laboratory and technical devices (as well as in nature at large), an external increase of ideal supersaturation with time may be due to adiabatic expansion of the vapor – gas medium. There is a one-to-one correspondence between the ideal supersaturation and the temperature of the vapor – gas medium undergoing adiabatic expansion [8, 35]. This relationship accounts for a rise in ideal vapor supersaturation with decreasing vapor – gas temperature, which initiates the process of nucleation. Moreover, the relationship makes it possible to follow, based on the given increment of ideal supersaturation, the time-course of vapor – gas temperature and the equivalent (under thermal equilibrium) temperature of the droplets.

Under certain conditions, chemical (e.g. photochemical) reactions in the vapor – gas medium can proceed and be accompanied by the production of vapor molecules. In such cases, a time-dependent rise in the ideal supersaturation will be due to the bulk 'pumping' of a vapor into the vapor – gas medium by chemical reactions occurred in the latter. If the amount of pumped vapor is relatively small, the temperature of the vapor – gas medium during phase transition remains practically unaltered.

Here is a brief description of a supercritical droplet formation process running as the ideal supersaturation Φ increases in time.

The intensity j of supercritical droplet formation (the number of supercritical droplets formed per unit volume of vapor – gas medium per unit time as a result of overcoming the activation barrier to nucleation by droplets via fluctuation mechanism) is proportional (as shown in Ref. [40]) to $\eta \exp(-\Delta F)$, where η denotes the concentration of condensation nuclei (their number per unit volume of the vapor – gas medium) and ΔF is determined by equality (2.12). Here, we mean by condensation nuclei only those which are not yet taken up by the supercritical droplets arising from them. In other words, these nuclei continue to give rise to new supercritical droplets. The dependence of the intensity j on vapor supersaturation, largely expressed in the form of an exponent $\exp(-\Delta F)$, provides a kinetic proof of the fact that ΔF has the sense of an activation energy (expressed in $k_{\mathrm{B}}T$ units) as was stated in Section 2.1.

With a rise in the ideal supersaturation Φ in time, starting from $\Phi = 0$ (which corresponds to the onset of vapor metastable state formation), the work of droplet formation on a nucleus is characterized not only by a potential well (which also existed at $\Phi < 0$) but also by a potential hump. It follows from inequalities (2.11) that the potential well sinks as the ideal supersaturation increases. Simultaneously, there is an even more rapid lowering of the potential hump. As a result, the activation energy ΔF falls but remains fairly high. Practically, each condensation nucleus takes up as many vapor molecules as is sufficient for the newly-formed droplet to sink to the bottom of the potential well. It is the concentration of condensation nuclei η introduced in the previous paragraph that stands for the concentration of such droplets. Droplets on the bottom of the potential well seek to overcome the activation barrier to nucleation by fluctuation. As the activation energy ΔF decreases, the intensity j of supercritical droplet formation increases in proportion to the exponent $\exp(-\Delta F)$ but remains rather low. In this situation, practically no new supercritical droplets develop. Hence, there is no vapor absorption by the droplets, and the vapor supersaturation ζ is almost identical to the ideal supersaturation Φ. The two supersaturations increase at equal rates. The above scenario constitutes the preliminary stage of supercritical droplet formation.

As the ideal supersaturation Φ grows further with time, the activation energy ΔF decreases so as to enable the droplets 'accumulated' at the bottom of the potential well to overcome, with a high probability, the activation barrier to nucleation via fluctuation mechanism. This gives an impetus to the nucleation stage which is the subject-matter of this discussion.

The supercritical droplets that have passed the activation barrier take up progressively more vapor as they grow. This results in vapor supersaturation ζ getting lower than the ideal supersaturation Φ. The earlier a supercritical droplet forms, the greater is its size and the more vapor it absorbed. Moreover, the newly-formed supercritical droplets cause the concentration η of condensation nuclei to decrease. Each supercritical droplet 'takes away' one condensation nucleus.

A fall in vapor supersaturation ζ relative to the ideal supersaturation Φ and a decrease of condensation nuclei concentration η compared with its initial value at the onset of the nucleation stage tend to slow down a time-dependent rise in the intensity j of new supercritical droplet formation. Nevertheless, this rise continues until approximately the middle of the nucleation stage. As soon as the intensity j passes its peak, it starts to decrease and eventually becomes so low that the effective supercritical droplet formation stops despite the continuing increase of ideal supersaturation Φ in time. This brings the nucleation stage to an end. If the time-dependent growth of the ideal supersaturation Φ is rather slow [as permitted by the constraint (3.39) introduced below in Section 3.4], this stage has time to reach the end while the activation barrier to nucleation is still sufficiently high.

It is clear from what is said about the supercritical droplet formation on condensation nuclei that its termination may be due to vapor absorption by the growing droplets, which accounts for the maximum of vapor supersaturation ζ (with a continuous external rise in the ideal supersaturation Φ) and its subsequent fall. However, the droplet formation can just as well discontinue if the stock of condensation nuclei is depleted by supercritical droplets formed on them, while the vapor supersaturation ζ continues to increase for a certain period as a result of enhanced ideal supersaturation Φ. Which of the two feasible mechanisms prevails will be elucidated in Section 3.2.

After the nucleation stage is completed (even though the ideal supersaturation continues to grow with time), subsequent stages of vapor – liquid phase transformation follow at which no new supercritical droplets form. These stages were investigated in Refs [37 – 39].

A principal kinetic characteristic of the nucleation process is the total number of newly-formed supercritical droplets. This characteristic is determined from the reference value Φ_* of ideal supersaturation Φ at which half of the total number of new droplets develop. For an externally given growth rate of ideal supersaturation Φ in time, the Φ_* value is not known in advance. The accuracy with which it is found determines how correctly the kinetic theory predicts the total number of newly-formed supercritical droplets.

For a given t-time dependence of the ideal supersaturation (Φ) growth rate, the reference value Φ_* unambiguously determines the corresponding time moment t_*. It is by approximately this moment that the intensity j of supercritical droplet formation passes its maximum.

The power-like approximation to the growth rate of ideal supersaturation Φ with time t is representative for the description of gradual external metastable vapor state formation:

$$\Phi = \left(\frac{t}{t_\infty}\right)^m . \tag{3.2}$$

We adopt this approximation following Refs [8, 35, 36]. It contains two independent positive parameters: the characteristic scale time t_∞, and the exponent m. Time t is reckoned from the moment at which, in the power-like approximation, $\Phi = 0$. According to formula (3.2), the time moment t_* is related to Φ_* by the equation

$$t_* = t_\infty \Phi_*^{1/m} . \tag{3.3}$$

In fact, the power-like approximation (3.2) is needed only at the stage of effective supercritical droplet formation. It will be shown in Section 3.2 that the relative change of ideal supersaturation Φ at this stage is very small. Therefore, the power-like approximation (3.2) will be extremely accurate for any time-dependent growth law of ideal supersaturation Φ, given from the outside. In this case, however, the parameters t_∞ and m are no longer given straightforwardly. It will be clarified in Section 3.5 how the parameters t_∞ and m can be found based on the given growth law of ideal supersaturation Φ in time. The same section will elucidate an approach to determining the time moment at which $\Phi = 0$ in reality and not according to the power-like approximation (3.2).

It is clear from the aforesaid that a study of the effective supercritical droplet formation stage requires the solution of a difficult, essentially nonlinear and nonlocal in time kinetic problem of correlation between the absorption of supersaturated vapor as well as the consumption of condensation nuclei by supercritical droplets and the rate of external amplification of ideal supersaturation Φ in time, i.e. the rate of the external gradual vapor metastable state formation. This problem is nonlinear because the dependence of the intensity of supercritical droplet formation on the vapor supersaturation ζ is expressed in the form of $\exp(-\Delta F)$. The problem is nonlocal in time since both the vapor supersaturation ζ and the condensation nuclei concentration η, which determine the supercritical droplet formation intensity at each current moment, are themselves dependent on the number and size of all previously formed supercritical droplets.

The nucleation kinetics problem under consideration has been resolved without regard to the specific nature of condensation nuclei in the kinetic theory of nucleation developed in Refs [35, 36, 38, 39]. The central issue of this theory is the iterative method of contracting approximations which allows all important kinetic characteristics of the nucleation process to be found and compared with those examined in experiment. This method is based on a physical idea [8] that, because the intensity of vapor absorption by supercritical droplets rapidly increases with their size, those droplets which were formed when it was virtually absent, i.e. when the vapor supersaturation was largely due to its external increase, are primarily involved in the absorption.

3.2 Key parameters of the kinetic theory of nucleation and kinetic characteristics of nucleation

An important dimensionless parameter Γ of nucleation kinetics is defined by the equality

$$\Gamma = -\Phi_* \left. \frac{\partial \Delta F}{\partial \zeta} \right|_{\zeta = \Phi_*} . \tag{3.4}$$

This parameter characterizes the sharpness of the dependence of the activation energy ΔF on the vapor supersaturation ζ in the neighborhood of $\zeta = \Phi_*$. In the situation of interest in which droplets have to surmount an appreciable activation barrier to nucleation, the parameter Γ is very large, namely

$$\Gamma \gg 1 . \tag{3.5}$$

Let R_c be the radius of a critical droplet. For essentially supercritical droplets [for which $R > (3-4)R_c$], it is always possible (regardless of the regime of matter exchange between the droplets and the vapor) to pass from the variable ν defined by equality (2.2) to such a variable ρ which grows with time t at a rate $\dot{\rho}$ independent of ρ (and ν) and is determined only by the vapor supersaturation ζ. In what follows, we shall use this convenient variable ρ. Then one has

$$\dot{\rho} = \dot{\rho}(\zeta) . \tag{3.6}$$

We shall refer to the variable ρ as the droplet 'size'. The inequality $R > (3-4)R_c$ is guaranteed at the nucleation stage by meeting the condition (3.46) introduced in Section 3.4.

The radius R_c of a critical droplet is usually much smaller than the mean free path traveled by a vapor molecule in the vapor–gas medium. For this reason, droplets almost invariably overcome the activation barrier to nucleation by fluctuation mechanism in a free-molecule regime of matter exchange between the droplets and the vapor.

However, as soon as the droplets have overcome the activation barrier to nucleation, their size at the nucleation stage is likely to be so large that the free-molecule regime will gradually make room for the diffusion mode. This new regime may even prevail if the passive gas concentration in the vapor–gas medium is sufficiently high while the coefficient of condensation of vapor molecules by a droplet is not too low.

Let us first consider a typical case when the free-molecule regime still predominates at the nucleation stage. Just such a case was examined in Refs [35, 36, 38, 39].

It follows from definition (2.2) that a convenient variable ρ of the supercritical droplet description owing to which the equality (3.6) is fulfilled is

$$\rho = \nu^{1/3} . \tag{3.7}$$

The rate $\dot{\rho}$ of the free-molecule growth of this variable with time is given by

$$\dot{\rho} = \frac{\alpha \zeta}{\tau} . \tag{3.8}$$

Here, α is the coefficient of vapor molecule condensation on a droplet and τ is a characteristic time. This time is defined by the equality

$$\tau = \frac{12}{(36\pi)^{1/3} v_\alpha^{2/3} n_\infty v_T} , \tag{3.9}$$

where v_T is the mean thermal velocity of vapor molecules. Evidently, the characteristic time τ is an estimate of the mean free time of the vapor molecules in a saturated vapor. As required, the velocity $\dot{\rho}$ is independent of ρ, in compliance with Eqn (3.8).

Other important parameters of nucleation kinetics, besides Γ, are c and h which, in the case of the free-molecule growth of supercritical droplets, are given by the equalities

$$c = \frac{m \tau \Gamma}{\alpha t_\infty \Phi_*^{(m+1)/m}} , \tag{3.10}$$

$$h = 6 \, \frac{\eta(-\infty)}{n_\infty} \, \frac{\Gamma}{\Phi_*} \, \frac{1}{c^3} , \tag{3.11}$$

where $\eta(-\infty)$ stands for the initial concentration of condensation nuclei, i.e. their number per unit volume of vapor–gas medium at the beginning of the nucleation stage. It has been shown in Refs [35, 38, 39] how, at a given growth rate of ideal supersaturation Φ with time, the concentration $\eta(-\infty)$ is expressed in terms of nuclei concentration at the onset of vapor metastable state formation when this state is induced by adiabatic expansion of the vapor–gas mixture and the nuclei concentration is time-dependent.

Parameter h is important because it allows us, using the formula

$$N = \eta(-\infty)\left[1 - \exp\left(-\frac{1}{h}\right)\right] \tag{3.12}$$

given by the kinetic theory of nucleation (see formula (28) in Ref. [36]), to find the total number N of supercritical droplets formed anew per unit volume of the vapor–gas medium. For $h \gg 1$ and $h \ll 1$, it follows from Eqn (3.12) that

$$N = \frac{\eta(-\infty)}{h} \quad (h \gg 1)\,, \tag{3.13}$$

$$N = \eta(-\infty) \quad (h \ll 1)\,. \tag{3.14}$$

According to Eqn (3.13), the droplets consume only a very small fraction of the initially available condensation nuclei for $h \gg 1$ (each droplet takes up one nucleus). In contrast, it follows from Eqn (3.14) that for $h \ll 1$ the droplets consume all the initially available condensation nuclei. Therefore, the value of h provides a quantitative criterion for the cause of the termination of the droplet formation stage. The cause can be either vapor absorption by the droplets or depletion of the stock of condensation nuclei by supercritical droplets to which they have given birth.

The inequality (37) in Ref. [36] suggests the validity of the inequality

$$\frac{|\zeta_* - \Phi_*|}{\Phi_*} < \frac{\ln 2}{\Gamma} \quad (h \gg 1 \quad \text{or} \quad h \ll 1)\,. \tag{3.15}$$

The subscript $*$ refers to the values of quantities at the moment t_*. It follows from Eqns (3.5) and (3.15) that

$$\frac{|\zeta_* - \Phi_*|}{\Phi_*} \ll 1 \quad (h \gg 1 \quad \text{or} \quad h \ll 1)\,. \tag{3.16}$$

Parameter c may be used to determine the width $\Delta\rho$ of the supercritical droplet size spectrum on the ρ-axis by the formula

$$\Delta\rho \approx \frac{3}{c} \quad (h \gg 1 \quad \text{or} \quad h \ll 1) \tag{3.17}$$

ensuing from formulas (45) and (48) in Ref. [36]. Only on this axis on which, in agreement with Eqn (3.6), all the supercritical droplets 'travel' with the same speed at each current value of the vapor supersaturation ζ, the spectrum of supercritical droplet sizes (or, to be precise, each part of the spectrum formed by a given moment) transfers as a whole without changing its shape. Therefore, only on this axis the width of the supercritical droplet size spectrum can be regarded as a time-independent quantity.

According to formulas (45)–(50) in Ref. [36], the following relation holds at the nucleation stage:

$$\frac{|\Phi - \Phi_*|}{\Phi_*} \approx \frac{3}{\Gamma} \quad (h \gg 1 \quad \text{or} \quad h \ll 1)\,, \tag{3.18}$$

while the period Δt of this stage satisfies the approximate relation

$$\frac{\Delta t}{t_*} \approx \frac{3}{m\Gamma} \quad (h \gg 1 \quad \text{or} \quad h \ll 1)\,. \tag{3.19}$$

It follows from Eqns (3.5), (3.18) that

$$\frac{|\Phi - \Phi_*|}{\Phi_*} \ll 1 \quad (h \gg 1 \quad \text{or} \quad h \ll 1)\,. \tag{3.20}$$

When the parameter m from relation (3.19) is not too small, it also follows from Eqn (3.19) that

$$\frac{\Delta t}{t_*} \ll 1 \quad (h \gg 1 \quad \text{or} \quad h \ll 1)\,. \tag{3.21}$$

By using equation (3.3) in (3.19) and taking into account (3.10), we arrive at

$$\Delta t \approx \frac{3\tau}{\alpha \Phi_* c} \quad (h \gg 1 \quad \text{or} \quad h \ll 1)\,. \tag{3.22}$$

Therefore, the parameter c is also important for determining the time period Δt.

The moments of time t_{on} and t_{off} corresponding to the initiation and termination of supercritical droplet formation can be found from formula (3.22) with the help of the approximate equalities

$$t_{\text{on}} \approx t_* - \frac{\Delta t}{2}\,, \qquad t_{\text{off}} \approx t_* + \frac{\Delta t}{2}\,, \tag{3.23}$$

which take into account that the moment t_* lies roughly in the middle of the time interval during which the effective supercritical droplet formation occurs. The inequality (3.21) warrants that $t_{\text{on}} > 0$, as it should be.

Figure 4 illustrates the density of distribution of supercritical droplets, $p(\rho, t)$, over size ρ at three characteristic time moments. This density, also understood as the supercritical droplet size spectrum, is defined in such a way that $p(\rho, t)\,\mathrm{d}\rho$ gives the number of supercritical droplets at moment t within the interval $\mathrm{d}\rho$. The origin of the ρ-axis corresponds to a size which is several-fold bigger than the supercritical droplet size. The possibility to consider this size to be formally equal to zero is ensured by the fulfillment of condition (3.46) from Section 3.4. Curve *1* in Fig. 4 corresponds to the time moment t_1 satisfying the inequality $t_{\text{on}} < t_1 < t_{\text{off}}$. The process of

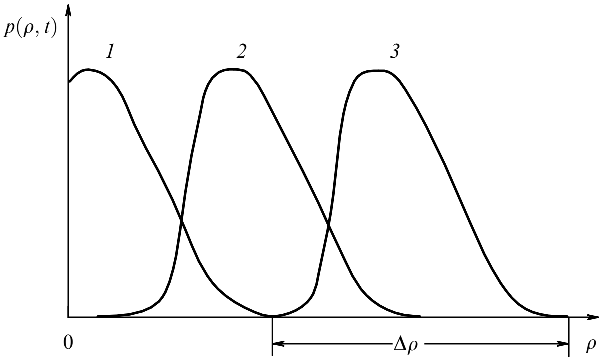

Figure 4. Changes of the density of distribution of supercritical droplets, $p(\rho, t)$, over their size ρ with growing time t.

effective supercritical droplet formation is already in progress by this moment, and the relation $p(\rho, t_1)\big|_{\rho=0} > 0$ is valid. Curve *2* corresponds to the time moment t_2 satisfying the equality $t_2 = t_{\text{off}}$. At this moment, the effective formation of supercritical droplets is discontinued. Then $p(\rho, t_2)\big|_{\rho=0} = 0$. Curve *3* corresponds to the time moment t_3 satisfying the inequality $t_3 > t_{\text{off}}$. The effective formation of supercritical droplets is completed before this moment. The relation $p(\rho, t_3)\big|_{\rho=0} = 0$ is valid as in the case of curve *2*. Starting from the time moment t_2, the spectrum of supercritical droplet sizes is fully developed. The spectral width $\Delta\rho$ is shown in Fig. 4. The shift of the supercritical droplet size spectrum (or, to be precise, each part of the spectrum formed by a given moment) as a whole in the course of time along the ρ-axis without changing its shape is sketched in Fig. 4 as a simple displacement of the curves in time parallel to the ρ-axis. The picture in Fig. 4 agrees with the analytical dependence of the density of distribution $p(\rho, t)$ on ρ and t, found earlier in Refs [35, 36, 38, 39].

It follows from Eqns (3.11), (3.13), and (3.17) that

$$N(\Delta\rho)^3 \approx \frac{9}{2}\,\frac{n_\infty \Phi_*}{\Gamma} \qquad (h \gg 1)\,. \tag{3.24}$$

In agreement with relation (3.7), the quantity $N(\Delta\rho)^3$ in the left-hand side of Eqn (3.24) estimates the total number of vapor molecules (per unit volume of the vapor – gas medium) contained in the supercritical droplets by the end of their effective formation. It is clear from definition (3.4) that the activation energy ΔF increases by unity for a relative decrease of vapor supersaturation ζ by $1/\Gamma$. Hence, there is a significant (e-fold) reduction in the intensity of supercritical droplet formation. In agreement with this circumstance and with the fact that the termination of the effective supercritical droplet formation for $h \gg 1$ is caused by their vapor absorption, the quantity $n_\infty \Phi_*/\Gamma$ on the right-hand side of relation (3.24) estimates the total number of vapor molecules absorbed by supercritical droplets at the nucleation stage. Thus, relation (3.24) has the meaning of the vapor molecule balance equation. The fact that the kinetic theory ensure the fulfillment of this balance equation supports the validity of this theory.

Let us now consider an opposite typical case in which the diffusion mode of material exchange between supercritical droplets and vapor predominates at the nucleation stage. This case was examined in Ref. [41].

It follows from Eqn (2.2) that in this situation the variable

$$\rho = \nu^{2/3} \tag{3.25}$$

is a convenient variable for the description of supercritical droplets satisfying equation (3.6). The rate $\dot{\rho}$ of the diffusive growth of this variable with time is written as

$$\dot{\rho} = \frac{\zeta}{\tau_D}\,. \tag{3.26}$$

Here, τ_D is a characteristic time given by the equality

$$\tau_D = \frac{3}{8\pi}\,\frac{\left[4\pi/(3v_\alpha)\right]^{1/3}}{D n_\infty}\,, \tag{3.27}$$

where D is the diffusion coefficient of vapor molecules in the vapor – gas medium. As required, the velocity $\dot{\rho}$ is independent of ρ, in compliance with Eqn (3.26).

It is easy to see that the relations (3.12) – (3.21), (3.23) also hold in the case of diffusive growth of supercritical droplets. In this case, however, the dimensionless parameters c and h of the theory are determined by the equalities

$$c = \frac{m\tau_D \Gamma}{t_\infty \Phi_*^{(m+1)/m}}\,, \tag{3.28}$$

$$h = \frac{3\pi^{1/2}}{4}\,\frac{\eta(-\infty)}{n_\infty}\,\frac{\Gamma}{\Phi_*}\,\frac{1}{c^{3/2}} \tag{3.29}$$

[the former definition (3.4) of the parameter Γ remains valid].

Therefore, we shall have

$$\Delta t \approx \frac{3\tau_D}{\Phi_* c} \qquad (h \gg 1 \;\text{ or }\; h \ll 1)\,, \tag{3.30}$$

$$N(\Delta\rho)^{3/2} \approx 3^{1/2}\,\frac{4}{\pi^{1/2}}\,\frac{n_\infty \Phi_*}{\Gamma} \qquad (h \gg 1) \tag{3.31}$$

instead of Eqns (3.22), (3.24). Similar to (3.24) and in agreement with (3.35), relation (3.31) has the sense of a balance equation for the number of vapor molecules.

As before, the magnitude of the parameter h remains a quantitative criterion for the completion of the effective supercritical droplet formation.

For the linear dependence of h on the initial concentration $\eta(-\infty)$ of condensation nuclei suggested by the equalities (3.11) and (3.29), the limiting situations $h \gg 1$ and $h \ll 1$ (interesting because of their relative simplicity and physical clarity) are easier to realize than the situation where $h \sim 1$. Therefore, we shall confine ourselves to the discussion of the situations with $h \gg 1$ and $h \ll 1$.

3.3 Equation for the reference value of ideal vapor supersaturation

The key parameters Γ, c, and h of the kinetic theory of nucleation, introduced in the preceding section, depend on the reference value Φ_* of ideal vapor supersaturation. This value also determines the kinetic characteristics of the nucleation process, defined by formulas (3.12), (3.17), (3.22), (3.23), and (3.30), such as the total number of newly-formed supercritical droplets, the width of the supercritical droplet size spectrum, the total duration and times of initiation and termination of supercritical droplet formation, respectively.

There is a relation

$$f_{\text{s}} = \begin{cases} \dfrac{c}{h}\ln 2 & (h \gg 1) \\[2mm] c\ln 2 & (h \ll 1) \end{cases} \tag{3.32}$$

for the reference value Φ_* of ideal vapor supersaturation (relation (36) in Ref. [36]), where the quantity f_{s} in the case of free-molecule growth of supercritical droplets is found from the equation

$$f_{\text{s}} = \frac{3}{\pi}\left(\frac{\nu_{\text{c}}^{2/3}}{\Delta\nu_{\text{e}}\,\Delta\nu_{\text{c}}}\,\frac{1+\zeta}{\zeta}\exp(-\Delta F)\right)\Bigg|_{\zeta=\Phi_*} \tag{3.33}$$

(relations (16) and (27) in Ref. [35]). In the case of diffusive growth of supercritical droplets, the same quantity can be found from

$$f_{\text{s}} = \frac{3}{\pi}\,\frac{\alpha\tau_D}{\tau}\left(\frac{\nu_{\text{c}}^{2/3}}{\Delta\nu_{\text{e}}\,\Delta\nu_{\text{c}}}\,\frac{1+\zeta}{\zeta}\exp(-\Delta F)\right)\Bigg|_{\zeta=\Phi_*} \tag{3.34}$$

(relation (3.3) in Ref. [41]). Here, it is taken into consideration that for the former intensity of droplet formation, there is a

$\tau/(\alpha\tau_D)$-fold change in the characteristic growth rate $\dot{\rho}$ of supercritical droplets at the stage of their effective formation, in agreement with Eqns (3.8) and (3.26). It is worthwhile to note that the concentration of condensation nuclei (the multiplier in the expression for the intensity of supercritical droplet formation) does not enter Eqns (3.32) – (3.34).

Taken together, relations (3.32) – (3.34) give rise to a closed equation for the reference value Φ_* of the ideal supersaturation Φ. This equation is responsible for the coordination among supersaturated vapor absorption as well as consumption of condensation nuclei by supercritical droplets and a rate of external enhancement of the ideal supersaturation Φ with time. Parameters c and h in formula (3.32) are determined by equalities (3.10), (3.11) in the case of the free-molecule growth of supercritical droplets and by equalities (3.28), (3.29) in the case of diffusive growth. A high sensitivity of the exponent $\exp(-\Delta F)$ in Eqns (3.33), (3.34) to the value $\zeta = \Phi_*$ makes it possible to find, by iteration, the reference value Φ_* of the ideal supersaturation Φ.

Let us represent the closed equation for Φ_*, given by relations (3.32) – (3.34), in a form important for further discussion. We will first introduce the time t_s with the help of expression

$$t_s \approx \left.\frac{(\Delta\nu_c)^2}{2W_c}\right|_{\zeta=\Phi_*}, \tag{3.35}$$

where

$$W_c = \pi\alpha v_T n R_c^2 . \tag{3.36}$$

Because the exchange of material between a critical droplet and vapor occurs via a free-molecule mechanism (see above), W_c is the number of molecules absorbed by a critical droplet from the vapor per unit time [in agreement with (3.36)]. Then, the time t_s introduced with the aid of expression (3.35) characterizes the time necessary for the quasi-stationary regime in which droplets overcome the activation barrier to nucleation by fluctuation to set in [40, 32]. This is, however, a rough characteristic because in Eqn (3.35) the vapor supersaturation ζ is assumed to be equal to the reference value Φ_* of the ideal supersaturation Φ. In what follows, the time t_s will be important only in condition (3.39) significant for the applicability of the kinetic theory of nucleation. Due to this, the approximate interpretation of time t_s will be of no practical importance.

Using definitions (2.1), (2.2), and (3.9), we may write (3.36) as

$$W_c = 3\alpha\tau^{-1}(1+\zeta)v_c^{2/3} . \tag{3.37}$$

Expressions (3.32), (3.35), and (3.37), taking into account (3.22), (3.33) in the case of free-molecule supercritical droplet growth and (3.30), (3.34) in the case of diffusive supercritical droplet growth, yield an equation for the reference value of ideal vapor supersaturation

$$\left.\left(\frac{\Delta\nu_e}{\Delta\nu_c}\exp(\Delta F)\right)\right|_{\zeta=\Phi_*} \approx \begin{cases} \dfrac{h}{6\pi\ln 2}\,\dfrac{\Delta t}{t_s} & (h \gg 1)\,, \\[2ex] \dfrac{1}{6\pi\ln 2}\,\dfrac{\Delta t}{t_s} & (h \ll 1)\,. \end{cases} \tag{3.38}$$

Presented in an identical form for the free-molecule and diffusive growth of supercritical droplets, this equation will be important for the following discussion.

3.4 Applicability conditions for the kinetic theory of nucleation

Let us formulate conditions for the applicability of the nucleation kinetic theory [35, 36, 38, 39, 41]. The kinetic theory postulates that droplets overcome the activation barrier to nucleation in a quasi-stationary fluctuation process that continues throughout the entire stage of effective supercritical droplet formation. Evidently, for such a process to proceed the following condition must be fulfilled:

$$\frac{\Delta t}{t_s} \gg 1 . \tag{3.39}$$

Because of relation (3.38), the strong fulfillment of the condition (3.39) ensures that the condition

$$\exp\left(\Delta F\Big|_{\zeta=\Phi_*}\right) \gg 1 \tag{3.40}$$

is also satisfied. This latter condition guarantees that the nucleation stage is completed while the nucleation activation barrier is still of significance. The greater the time t_∞ of the ideal supersaturation (Φ) growth, the greater the time period Δt, in accordance with formulas (3.22) and (3.30) and definitions (3.10) and (3.28) of the parameter c in these formulas. This ensures the better fulfillment of condition (3.39) and also of condition (3.40), by virtue of Eqn (3.38).

In a characteristic case when the free-molecule growth of supercritical droplets prevails during nucleation, the inequality $R \ll \lambda/\alpha$ is satisfied throughout the entire nucleation stage. In this inequality, λ is the mean free path traveled by vapor molecules in a vapor – gas medium, estimated through the kinetic relationship for gases:

$$\lambda \sim (n_\infty + n_g)^{-1} v_\alpha^{-2/3} , \tag{3.41}$$

in which n_g is the number of passive gas molecules per unit volume of the vapor – gas medium ($v_\alpha^{2/3}$ stands for the cross section of collisions between a vapor molecule and molecules of the vapor – gas medium, on the assumption that $n \approx n_\infty$). Passing from the radius R to the variable ρ defined by equalities (2.2) and (3.7), bearing in mind that characteristic values of the variable ρ at the nucleation stage are of the same order of magnitude as the width $\Delta\rho$ of the supercritical droplet size spectrum on the axis of this variable, and taking into consideration estimate (3.41), the inequality $R \ll \lambda/\alpha$ can be presented as

$$\frac{\Delta\rho}{\rho_\lambda} \ll 1 , \tag{3.42}$$

where

$$\rho_\lambda \sim \alpha^{-1}(n_\infty + n_g)^{-1} v_\alpha^{-1} . \tag{3.43}$$

In an opposite characteristic case when the diffusive growth of supercritical droplets prevails during nucleation, the inequality $R \gg \lambda/\alpha$ is satisfied throughout the entire nucleation stage. Passing from the radius R to the variable ρ defined by equalities (2.2) and (3.25), bearing in mind that characteristic values of variable ρ at the nucleation stage are of the same order of magnitude as the width $\Delta\rho$ of the supercritical droplet size spectrum on the axis of this variable, and taking into consideration Eqn (3.41), the inequality $R \gg \lambda/\alpha$ can be presented as

$$\frac{\Delta\rho}{\rho_\lambda} \gg 1\,, \tag{3.44}$$

where ρ_λ is estimated by

$$\rho_\lambda \sim \alpha^{-2}(n_\infty + n_{\rm g})^{-2} v_\alpha^{-2} \tag{3.45}$$

instead of Eqn (3.43).

The kinetic theory suggested the fulfilment of the condition

$$\frac{\Delta\rho}{\rho_{\rm c}} \gg 1\,, \tag{3.46}$$

where $\rho_{\rm c}$ is the critical droplet size on the ρ-axis. In case of the free-molecule growth of supercritical droplets in agreement with Eqns (3.17), (3.22), (3.35), (3.37), and $\rho_{\rm c} = \nu_{\rm c}^{1/3}$, one finds an expression

$$\frac{\Delta\rho}{\rho_{\rm c}} \approx \frac{1}{6}\left[\frac{(\Delta\nu_{\rm c})^2}{\nu_{\rm c}}\,\frac{\zeta}{1+\zeta}\right]\Bigg|_{\zeta=\Phi_*}\frac{\Delta t}{t_{\rm s}} \qquad (h \gg 1 \quad \text{or} \quad h \ll 1)\,. \tag{3.47}$$

It follows from Eqn (3.47) that in this case condition (3.46) is satisfied if condition (3.39) is strongly fulfilled [the coefficient of factor $\Delta t/t_{\rm s}$ in Eqn (3.47) will be estimated in Sections 5.1 and 7.1]. In the case of diffusive growth of supercritical droplets, the fulfilment of condition (3.46) ensues, with ample reserve, directly from inequalities (3.44) and $\rho_{\rm c}/\rho_\lambda \ll 1$, the latter showing (as in Section 3.2) that the critical droplet radius is always much smaller than λ/α.

It was implied in the kinetic theory that in a volume V occupied by the vapor – gas medium under consideration, the relation

$$\int_V n(\mathbf{r}, t)\,\mathrm{d}\mathbf{r} \approx nV \tag{3.48}$$

holds throughout the entire nucleation stage. Here, $\mathbf{r}$ is the spatial point inside volume V, and $n(\mathbf{r}, t)$ is the local number density of vapor molecules perturbed by the supercritical droplet growth. The quantity n denotes, in agreement with definition (2.1), the uniform number density of vapor molecules far from supercritical droplets.

Relation (3.48) allows the approximation for a homogeneous vapor with a molecular number density n to be employed for the description of vapor consumption by supercritical droplets. Because the intensity of supercritical droplet formation varies significantly (e-fold) when the vapor supersaturation ζ changes by $1/\Gamma$, a small relative change of vapor supersaturation ζ by $1/\Gamma$ [in accordance with inequality (3.5)] at the nucleation stage becomes important. Therefore, relation (3.48) must be very accurate. The relative error in relation (3.48) must be much smaller than the small quantity $1/\Gamma$. The fulfilment of relation (3.48) with such a high accuracy was substantiated in Ref. [42] for the case of the strongly fulfilled inequality $n_\infty v_\alpha \ll 1$ typical of the nucleation process.

Finally, it was suggested in the kinetic theory that the effects of condensation heat release in the course of the nucleation process are negligibly small. It was noted in Ref. [8] that these effects are manifested as a deviation of droplet temperature from the vapor – gas temperature and a decrease of the vapor supersaturation by heating of the medium. The assumption of the smallness of condensation heat release effects is true at a high passive gas concentration in the vapor – gas medium, implied in the present review. Generalization of the kinetic theory to the case where the passive gas concentration may be low was undertaken in Refs [37, 43].

Conditions (3.39), (3.40), (3.42), (3.44), and (3.46) are very sensitive to parameters determining the properties of vapor, liquid condensed from the vapor, and condensation nuclei matter. They are equally susceptible to the size of the condensation nuclei and their initial content in vapor – gas medium, the passive gas concentration in the vapor – gas medium, and the external gradual vapor metastable state formation rate. These conditions restrict the scope of applicability of the kinetic theory of nucleation.

3.5 Generalization of the theory to an arbitrary law of gradual formation of a vapor metastable state

The foregoing discussion was concerned with the power-like approximation (3.2) to the law of enhancement of the ideal supersaturation Φ with time. This approximation was used from the moment at which the ideal supersaturation Φ was zero. This moment was taken as the initial moment $t = 0$. By reckoning time t from this moment and using formula (3.3), we found the moment of time t_*, important for nucleation, by which half of the total number of supercritical droplets was formed in the process of nucleation. Parameters t_∞ and m of the approximation (3.2) were regarded as the given ones.

Approximation (3.2) was actually important only at the nucleation stage. At this stage, the relative change of the ideal supersaturation Φ is very small, in agreement with inequality (3.20). Therefore, the power-like approximation (3.2) is rather accurate. However, in the general case of an arbitrary law of gradual vapor metastable state formation, the parameters t_∞ and m of approximation (3.2) are no longer known in advance and have to be found based on an externally given enhancement rate of ideal supersaturation Φ in time. Moreover, the moment of time at which the ideal supersaturation Φ was really equal to zero (we denote this moment as t_0) no longer coincides with the moment $t = 0$ at which the ideal supersaturation Φ vanished according to approximation (3.2). Therefore, the moment t_0 on the time axis convenient for the theory [on which $\Phi\big|_{t=0} = 0$ in terms of approximation (3.2)] must be found together with parameters t_∞ and m. Only after the moment t_0 is found it is possible to pass to the convenient (for the purpose of experiment) time axis on which reckoning is performed from the onset of the vapor metastable state formation under experimental conditions. Thereafter, the location of approximation (3.2) on this axis can be determined.

It will be shown below how the quantities t_∞, m, t_0, and also t_* are found in the case of gradual vapor metastable state formation arbitrary in time. We shall base our reasoning on that adopted in Refs [44, 45].

Let us use, as above, the time axis convenient for the theory, on which $\Phi\big|_{t=0} = 0$ in accord with the power-like approximation (3.2) (it is now used only during the nucleation stage).

In what follows, by $\Phi(t)$ is understood the externally given ideal vapor supersaturation arbitrarily growing with time t. From the definition of the moment t_0 one obtains that

$$\Phi\Big|_{t=t_0} = 0\,. \tag{3.49}$$

Let us represent the ideal supersaturation $\Phi(t)$ as

$$\Phi(t) = \varphi(t - t_0)\,, \tag{3.50}$$

where the function $\varphi(t - t_0)$ describes 'switching on' the ideal supersaturation $\Phi(t)$, i.e. its true increase with time $t - t_0$ reckoned from the moment t_0 at which the ideal supersaturation Φ was really zero [in agreement with the result (3.49)]. The function $\varphi(t - t_0)$ serves to externally govern the progress of supercritical droplet formation in time.

Below, we shall consider the function $\varphi(t - t_0)$ as being known, e.g. given by experimental conditions, and monotonically growing, i.e. satisfying the condition

$$\dot{\varphi}(t - t_0) > 0 \tag{3.51}$$

(the dot over denotes the time-derivative). According to Eqn (3.50) and $\Phi_* = \Phi\big|_{t=t_*}$, the following equality is valid:

$$\varphi(t_* - t_0) = \Phi_*\,. \tag{3.52}$$

Let us choose parameters t_∞ and m of the approximation (3.2) such that at $t = t_*$ (i.e. at the moment of time t_* important for the formation of supercritical droplets) this approximation ensured true values of ideal supersaturation $\Phi(t)$ and its first, $\dot{\Phi}(t)$, and second, $\ddot{\Phi}(t)$, time-derivatives. Taking into account relations (3.50) and (3.52), we arrive at

$$\left(\frac{t_*}{t_\infty}\right)^m = \Phi_*\,, \tag{3.53}$$

$$m\,\frac{t_*^{m-1}}{t_\infty^m} = \dot{\varphi}(t_* - t_0)\,, \tag{3.54}$$

$$m(m-1)\,\frac{t_*^{m-2}}{t_\infty^m} = \ddot{\varphi}(t_* - t_0)\,. \tag{3.55}$$

Evidently, Eqn (3.53) is equivalent to Eqn (3.3).

If the equalities (3.52)–(3.55) are satisfied, the approximation (3.2) is highly accurate at the nucleation stage. Accordingly, the kinetic theory of nucleation set forth in Sections 3.2 and 3.3 will be just as accurate. At the preliminary stage of the process, when the vapor metastable state is already being formed while supercritical droplets are still absent, approximation (3.2) tends to poorly describe the true growth of ideal supersaturation with time (as having a purely formal meaning). This, however, will be apparent only in that the moment of time $t = 0$ (initial for the theory), at which $\Phi = 0$ is satisfied [as a result of approximation (3.2)], is likely to fail to coincide with the moment t_0 at which really $\Phi = 0$ in accordance with Eqn (3.49).

Thus, parameters t_∞ and m are not given in advance but determined (together with t_0 and t_*) by a system of four equations (3.52)–(3.55). The reference value Φ_* of ideal vapor supersaturation in these equations is expressed through parameters t_∞ and m by means of the equation derived for it in Section 3.3.

Let us examine Eqns (3.52)–(3.55), taking into account that Φ_* is a function of t_∞ and m. Owing to inequality (3.51), Eqn (3.52) admits solution in terms of the difference $t_* - t_0$ which is revealed as a function of Φ_* alone:

$$t_* - t_0 = k(\Phi_*)\,. \tag{3.56}$$

The introduced function k is the inverse of function φ and positive. It is easy to find using a given φ function.

According to relation (3.56), the right-hand sides of Eqns (3.54) and (3.55) are functions of Φ_* too. Let us divide these equations by Eqn (3.53) and introduce the functions $k_1(\Phi_*)$ and $k_2(\Phi_*)$:

$$k_1(\Phi_*) = \Phi_*^{-1}\dot{\varphi}\big(k(\Phi_*)\big)\,, \qquad k_2(\Phi_*) = \Phi_*^{-1}\ddot{\varphi}\big(k(\Phi_*)\big) \tag{3.57}$$

[the function φ being known, its derivatives $\dot{\varphi}$, $\ddot{\varphi}$ and functions $k_1(\Phi_*)$ and $k_2(\Phi_*)$ are also known]. As a result, one can write down:

$$m = k_1(\Phi_*)\,t_*\,, \tag{3.58}$$

$$m(m-1) = k_2(\Phi_*)\,t_*^2\,. \tag{3.59}$$

Division of Eqn (3.59) by the square of equation (3.58) yields

$$m = \frac{k_1^2(\Phi_*)}{k_1^2(\Phi_*) - k_2(\Phi_*)}\,. \tag{3.60}$$

Then with the help of Eqn (3.58), the relationship

$$t_* = \frac{k_1(\Phi_*)}{k_1^2(\Phi_*) - k_2(\Phi_*)} \tag{3.61}$$

is obtained. At last, using expression (3.53) and taking into consideration Eqns (3.60) and (3.61), we find that

$$t_\infty = \frac{k_1(\Phi_*)}{k_1^2(\Phi_*) - k_2(\Phi_*)}\,\Phi_*^{[k_2(\Phi_*) - k_1^2(\Phi_*)]/k_1^2(\Phi_*)}\,. \tag{3.62}$$

Formulas (3.56), (3.60)–(3.62) taken together with the equation for the reference value Φ_* of ideal vapor supersaturation, obtained in Section 3.3, give rise to a closed system of equations with which to find the quantities t_∞, m, t_0, and t_* from the experimentally found growth rate of ideal supersaturation in time. We did not solve equation (3.56) for t_0 because it is the difference $t_* - t_0$ that permits us to locate the moment t_0 on the time axis convenient for the theory (used above) from the time moment t_* on this axis.

It can be seen from Eqns (3.50), (3.57) and (3.60) that the values of $m < 1$ and $m > 1$ depend on whether the growth of ideal supersaturation Φ with time in the vicinity of the moment $t = t_*$ is slow or accelerated. It is also clear that in the case of an accelerated growth, when $k_2(\Phi_*) > 0$, the acceleration cannot be too high, to avoid violation of the condition

$$k_1^2(\Phi_*) - k_2(\Phi_*) > 0 \tag{3.63}$$

which guarantees, in accordance with Eqn (3.60), that $m > 0$. Before this condition is broken, m as well as t_∞ and t_* passes to infinity. The growth of the ideal supersaturation Φ with time should not be too rapid (as was noted many times before); otherwise, the process of nucleation will not be completed till its activation barrier is essential.

According to Eqns (3.51) and (3.57), the inequality $k_1(\Phi_*) > 0$ is valid and, together with the condition (3.63) and formulas (3.61), (3.62), warrants that natural inequalities $t_* > 0$, $t_\infty > 0$ are fulfilled. Although the relation $t_* - t_0 > 0$ ensues from Eqn (3.56) and inequality $k(\Phi_*) > 0$, the sign of time t_0 in the general case remains unknown. If the ideal supersaturation rapidly increases with time at the preliminary stage, it is clear that $t_0 > 0$. Conversely, $t_0 < 0$ if the ideal supersaturation grows slowly at this stage.

The solid line in Fig. 5 depicts the true ideal supersaturation $\Phi(t)$ on the time axis on which $\Phi|_{t=0} = 0$ according to the power-like approximation (3.2). The power-like approximation (3.2) is shown by the dashed line which only deviates from the solid one at the preliminary stage, i.e. at $t \lesssim t_* - \Delta t/2$. Throughout the entire nucleation stage, i.e. for $t_* - \Delta t/2 \lesssim t \lesssim t_* + \Delta t/2$, the dashed line practically merges into the solid one, which suggests that the power-like approximation (3.2) is very accurate. Figure 5 illustrates the case in which $m < 1$ and $t_0 > 0$.

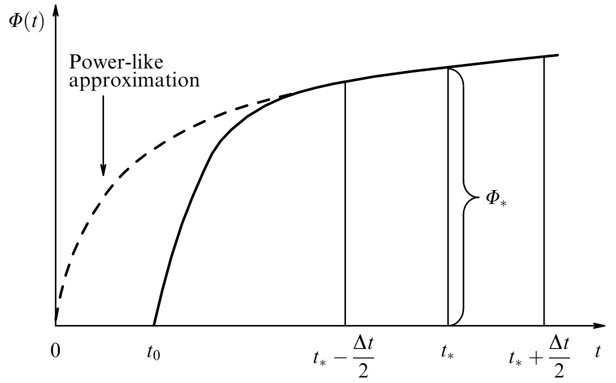

Figure 5. Behavior of ideal supersaturation $\Phi(t)$ on the t-time axis convenient for the theory.

Let us examine the transition to a situation in which the power-like approximation (3.2) holds throughout the entire period of vapor metastable state formation, i.e. when the equality $\varphi(t - t_0) = (t/t_\infty)^m$ takes place according to representation (3.50). Then, the definitions formulated in Eqns (3.56), (3.57) give rise to

$$k(\Phi_*) = t_\infty \Phi_*^{1/m}, \qquad k_1(\Phi_*) = \frac{m}{t_\infty}\,\Phi_*^{-1/m},$$

$$k_2(\Phi_*) = \frac{m(m-1)}{t_\infty^2}\,\Phi_*^{-2/m}. \tag{3.64}$$

As expected, the substitution of relations (3.64) into formulas (3.56), (3.60)–(3.62) leads to equalities (3.3) and $t_0 = 0$ and also confirms that parameters t_∞ and m actually coincide with the parameters of approximation (3.2) [the equality $t_0 = 0$ is readily apparent directly from Eqn (3.49)].

4. Thermodynamics of nucleation on soluble nuclei

Soluble nuclei are the most widespread natural wettable condensation nuclei. In the Earth's atmosphere, the overwhelming majority of active condensation nuclei are sea-salt particles readily soluble in water. For this reason, we begin the discussion of explicit expressions for thermodynamic characteristics of heterogeneous nucleation from the condensation on soluble nuclei.

4.1 Chemical potential of the condensate in a droplet

Let us consider a droplet in a vapor, which is in fact a solution of nuclear matter in the condensate. The number of condensate molecules in the droplet is chosen as the variable ν of the droplet description. The total number of nuclear molecules dissolved in the droplet (or the total number of ions of nuclear matter if it dissociates on solution) is designated as ν_{n}. If the nuclear matter is an electrolyte, it is assumed to be completely dissociated.

Let us further suppose that the condensation nuclei consist of a surface-inactive material and are completely dissolved in the droplet (i.e. the original condensation nucleus shown in Fig. 1 has disappeared). Condensation nuclei consisting of surface-active materials (surfactants) will be considered in Section 4.4, and generalization of the theory to the case of partially soluble nuclei and nuclei of mixed composition in Section 8.

It will be shown below that the inequality

$$\frac{\nu}{\nu_{\mathrm{n}}} \gg 1 \tag{4.1}$$

is satisfied in the case of complete dissolution of a macroscopic condensation nucleus in a droplet over the entire range of variable ν important for the theory. Whenever this inequality is satisfied, the nuclear matter solution in the droplet is dilute, that is the relative concentration of the solution x is equivalent to a small quantity ν_{n}/ν. The surface tension of the droplet and the specific molecular volume of the condensate may be regarded as identical to those in the absence of dissolved matter.

The condensation around soluble nuclei exemplifies the situation in which a study on nucleation thermodynamics may conveniently be begun from finding the expression for the condensate chemical potential in a droplet. The chemical potential of the condensate in a droplet containing dissolved nuclear matter is determined by the difference between the contributions of capillary and osmotic pressures [13, 46, 47]. Taking into consideration the definition of the dimensionless chemical potential b_ν offered in Section 2.3, relation (2.28) for the contribution of capillary pressure, and the expression for the osmotic pressure contribution in the case of a dilute solution, we have

$$b_\nu = -\frac{\nu_{\mathrm{n}}}{\nu} + \frac{2}{3}\,a\nu^{-1/3}. \tag{4.2}$$

It is easy to notice that the ν-dependence of b_ν given by relation (4.2) corresponds to the typical dependence of the chemical potential of the condensate in the case of heterogeneous condensation, depicted in Fig. 3. Specifically, at $\nu = \nu_0$, where

$$\nu_0 = \left(\frac{9\nu_{\mathrm{n}}}{2a}\right)^{3/2}, \tag{4.3}$$

b_ν attains its maximum value of

$$(b_\nu)_{\max} = \frac{4a}{9\nu_0^{1/3}}. \tag{4.4}$$

In the region of relatively small ν, where the droplet may contain an undiluted solution and relation (4.2) is not fulfilled, the chemical potential of the condensate does have to monotonically decrease with decreasing ν as a result of thermodynamic instability of the solution. For this reason, the above maximum of b_ν is unique in the region of complete nucleus dissolution in the droplet. Accordingly, this maximum determines the threshold value b_{th} of the vapor chemical potential during condensation on soluble nuclei. It follows from Eqn (4.4), taking into account Eqn (4.3), that

$$b_{\mathrm{th}} = \frac{2\,(2a)^{3/2}}{27 v_{\mathrm{n}}^{1/2}}\,. \tag{4.5}$$

This equation expresses b_{th} directly through the number of molecules or ions of the condensation nucleus.

According to Eqn (4.3), inequality (4.1) holds in the vicinity of the point $v = v_0$ and to the right of it if the condition

$$v_{\mathrm{n}}^{1/3} \gg 1\,, \tag{4.6}$$

having the sense of the condition of macroscopicity of soluble nuclei, is satisfied. On account of inequality (4.6), Eqn (4.5) yields $b_{\mathrm{th}} \ll 1$. Then, if equality (2.21) is taken into consideration and in agreement with Eqn (4.5), the vapor threshold supersaturation is given by

$$\zeta_{\mathrm{th}} = \frac{2\,(2a)^{3/2}}{27 v_{\mathrm{n}}^{1/2}}\,, \tag{4.7}$$

$$\zeta_{\mathrm{th}} \ll 1\,. \tag{4.8}$$

Equation (4.7) is called *the Kohler formula* [46].

4.2 Thermodynamic characteristics of nucleation on soluble nuclei

Let us represent the vapor chemical potential b in the form

$$b \equiv b_{\mathrm{th}}(1-\varepsilon)\,, \tag{4.9}$$

where ε is its relative deviation from the threshold value b_{th}. Bearing in mind Eqns (2.20), (2.21), and (4.8), we can write down, along with Eqn (4.9), the relation

$$\zeta \equiv \zeta_{\mathrm{th}}(1-\varepsilon)\,. \tag{4.10}$$

Therefore, ε has the sense of relative deviation of vapor supersaturation from the threshold value.

In the subthreshold region of vapor metastability, $0 < \zeta < \zeta_{\mathrm{th}}$, one also has the inequality $0 < \varepsilon < 1$. It has been noted in Sections 2.2 and 2.3 that nucleation kinetics can be described on condition that the dependence of the activation energy ΔF on vapor supersaturation, the locations of v_{e} and v_{c} and the half-widths Δv_{e} and Δv_{c} of the minimum and maximum on the axis of variable v of the droplet formation work F are known. Let us find these thermodynamic characteristics of nucleation as functions of ε in the subthreshold region of vapor metastability.

By expanding b_v in a Taylor series in the neighborhood of the point $v = v_0$ and taking equality (2.27) into account, it is possible to write the parabolic approximation

$$b_v = b_{\mathrm{th}} + \frac{1}{2}\left(\frac{\partial^2 b_v}{\partial v^2}\right)_0 (v - v_0)^2 \tag{4.11}$$

(the subscript 0 marks the values of quantities at $v = v_0$). The condition of smallness of the discarded term containing the third v-derivative of b_v at the point $v = v_0$ assumes the form

$$\frac{1}{3}\left|(v - v_0)\left(\frac{\partial^3 b_v}{\partial v^3}\right)_0 \Big/ \left(\frac{\partial^2 b_v}{\partial v^2}\right)_0\right| \ll 1\,, \tag{4.12}$$

which defines the region in which approximation (4.11) is valid.

Using Eqns (2.23), (4.9), (4.11), we have

$$\begin{aligned} v_{\mathrm{e}} &= v_0 - \left(\frac{2\varepsilon b_{\mathrm{th}}}{\left|\partial^2 b_v/\partial v^2\right|_0}\right)^{1/2}, \\ v_{\mathrm{c}} &= v_0 + \left(\frac{2\varepsilon b_{\mathrm{th}}}{\left|\partial^2 b_v/\partial v^2\right|_0}\right)^{1/2}. \end{aligned} \tag{4.13}$$

Furthermore, the use of Eqns (4.11) and (4.13) in Eqn (2.30) gives

$$\Delta v_{\mathrm{e}} = \Delta v_{\mathrm{c}} = \left(\frac{2}{\varepsilon\, b_{\mathrm{th}}\left|\partial^2 b_v/\partial v^2\right|_0}\right)^{1/4}. \tag{4.14}$$

Finally, the substitution of relations (4.11) and (4.9) into (2.31), taking into consideration formula (4.13), yields

$$\Delta F = \frac{4}{3}\,\varepsilon^{3/2} b_{\mathrm{th}}^{3/2}\left(\frac{2}{\left|\partial^2 b_v/\partial v^2\right|_0}\right)^{1/2}. \tag{4.15}$$

In the case of totally dissolved nuclei consisting of surface-inactive materials, the following equation is valid, in agreement with Eqns (4.2) and (4.3):

$$\left(\frac{\partial^2 b_v}{\partial v^2}\right)_0 = -\frac{2^{11/2} a^{9/2}}{3^{10} v_{\mathrm{n}}^{7/2}}\,. \tag{4.16}$$

Accordingly, it follows from formulas (4.13) – (4.16) that

$$v_{\mathrm{e}} = v_0\left[1 - (6\varepsilon)^{1/2}\right], \qquad v_{\mathrm{c}} = v_0\left[1 + (6\varepsilon)^{1/2}\right], \tag{4.17}$$

$$\Delta v_{\mathrm{e}} = \Delta v_{\mathrm{c}} = 27\left(\frac{3}{2}\right)^{1/4}(2a)^{-3/2} v_{\mathrm{n}}\varepsilon^{-1/4}\,, \tag{4.18}$$

$$\Delta F = \frac{16}{6^{1/2}}\, v_{\mathrm{n}}\varepsilon^{3/2}\,. \tag{4.19}$$

It is clear from Eqns (4.2), (4.17) that condition (4.12) is met over the entire range $v_{\mathrm{e}} \leqslant v \leqslant v_{\mathrm{c}}$ if the following inequality is satisfied:

$$\frac{13}{9}(6\varepsilon)^{1/2} \ll 1\,. \tag{4.20}$$

In conformity with this inequality, the deviation ε from the threshold chemical potential of vapor in formulas (4.17) – (4.19) must be rather small.

An opposite restriction on the deviation ε ensues from the applicability conditions (2.17) for quadratic approximations (2.14) and (2.15) to the work F of formation of near-equilibrium and near-critical droplets. The use of relations (4.13) – (4.15) leads to

$$\frac{\Delta v_{\mathrm{e}}}{v_0 - v_{\mathrm{e}}} = \frac{\Delta v_{\mathrm{c}}}{v_{\mathrm{c}} - v_0} = \frac{2}{(3\Delta F)^{1/2}}\,. \tag{4.21}$$

Hence, and from conditions (2.7), we have the inequality

$$\frac{2}{3(3\Delta F)^{1/2}} \ll 1\,. \tag{4.22}$$

According to formulas (4.22) and (4.19), the quantities ΔF and ε must be fairly large.

It should be emphasized that the equality (4.21) and the equalities $v_0 - v_{\mathrm{e}} = v_{\mathrm{c}} - v_0$, $\Delta v_{\mathrm{e}} = \Delta v_{\mathrm{c}}$ ensuing from formulas

(4.13), (4.14) are corollaries of the parabolic approximation (4.11) alone and unrelated to the specific nature of a macroscopic condensation nucleus.

4.3 Prethreshold region of vapor metastability

It has been mentioned in Section 3.1 that the intensity of supercritical droplet formation is proportional to $\eta\exp(-\Delta F)$. The exponent $\exp(-\Delta F)$ shows a fairly sharp dependence on ΔF while the concentration of condensation nuclei η does not normally exceed 10^5 cm^{-3}. Therefore, only that vapor metastability region appears interesting for the present study in which an approximate double inequality

$$2 \lesssim \Delta F \lesssim 15 \qquad (4.23)$$

is satisfied. Indeed, the activation energy to the left of the lower bound of this inequality, i.e. at $\Delta F \lesssim 2$, is so small that nucleation proceeds in a virtually barrierless way. To the right of the upper bound of the same inequality, i.e. at $\Delta F \gtrsim 15$, the activation energy is already so high that nucleation is practically absent.

According to Eqns (4.19) and (4.23), one obtains

$$\varepsilon^{1/2} \approx \nu_{\mathrm{n}}^{-1/3}\,, \qquad (4.24)$$

where it is taken into consideration that the range of $(\Delta F)^{1/3}$ variations is significantly narrower than that of ΔF variations; therefore, it is roughly assumed that $(6^{1/2}\Delta F/16)^{1/3} \approx 1$. Relation (4.24) will be considered at greater length in Section 5.1.

It follows from Eqns (4.6) and (4.24) that

$$\varepsilon^{1/2} \ll 1\,. \qquad (4.25)$$

The vapor metastability region in which inequality (4.23) is satisfied will be referred to as the *prethreshold* region. The approximate relation (4.24) defines the quantity $\varepsilon^{1/2}$ characteristic of this region. According to inequality (4.25), if condensation nuclei are macroscopic, the prethreshold region of vapor metastability occupies within the entire subthreshold region $0 < \varepsilon < 1$ only a very narrow gap with a width of the order of the distance between the gap and the lower limit $\varepsilon = 0$ of the subthreshold region.

The fulfillment of inequality (4.20) follows from inequality (4.25). Likewise, expression (4.23) accounts for the fulfillment of inequalities (2.18) and (4.22). The latter inequality, in conjunction with expression (4.21), ensures that the conditions (2.17) are met. Opposite limitations on ε and ΔF specified in the preceding section are therefore satisfied in the prethreshold region of vapor metastability in the event of macroscopic condensation nuclei.

According to Eqns (4.17), (4,25), and (4.3), one obtains

$$\nu_{\mathrm{e}} \approx \nu_{\mathrm{c}} \approx \left(\frac{9\nu_{\mathrm{n}}}{2a}\right)^{3/2}. \qquad (4.26)$$

According to relations (4.18) and (4.24), we find that

$$\Delta\nu_{\mathrm{e}} = \Delta\nu_{\mathrm{c}} = 27\left(\frac{3}{2}\right)^{1/4}(2a)^{-3/2}\nu_{\mathrm{n}}^{7/6}\,. \qquad (4.27)$$

Expressions (4.27) and (4.6) account for the fulfilment of conditions (2.19).

4.4 Generalization to the case of nuclei consisting of soluble surfactants

In Sections 4.1 – 4.3, we disregarded nuclear matter adsorption at the droplet surface. In conditions of practical interest, the condensation on soluble nuclei occurs at low vapor saturation. It has been shown earlier that, in this situation, droplets with a low concentration of nuclear matter in the solution play a definitive role. Therefore, the above assumption of the smallness of absolute adsorption is quite acceptable for nuclei consisting of inorganic acid salts. Such nuclei are always present in the Earth's atmosphere, and their role as centers of condensation has been extensively discussed in the scientific literature [13, 17, 30, 48].

Nuclei consisting of soluble surface-active substances (surfactants) are as widespread as those of inorganic acid salts [49 – 52]. Surfactant adsorption at the surface of newly-formed droplets is noticeable even for a very low concentration of the solution. We shall present below a generalization of the thermodynamic theory to fully soluble nuclei, taking into account adsorption of nuclear matter at the droplet surface. In the first place, it will concern soluble surfactant nuclei. But thereafter, it will be shown that the approach being developed allows us to elaborate this theory for nuclei consisting of surface-inactive substances too. We shall base our approach on the results reported in Refs [53 – 60].

Taking into consideration nuclear matter adsorption at the droplet surface, expression (4.2) for the condensate chemical potential in a droplet is written as

$$b_{\nu} = -x + \frac{2}{3}\,a(s)\nu^{-1/3}\,, \qquad (4.28)$$

where the relative concentration x of the dissolved nuclear matter depends on the balance between its content in the bulk of the droplet and at its surface:

$$x = \nu_{\mathrm{n}}\nu^{-1} - s\nu^{-1/3}\,, \qquad (4.29)$$

where $s \equiv (36\pi v_{\alpha}^2)^{1/3}\Gamma_n$ is the dimensionless adsorption, Γ_n is the Gibbs adsorption of the dissolved nuclear matter at the droplet surface, and $a(s)$ is the surface tension of the solution in the droplet, dependent on adsorption s. It should be noted that the quantity $s\nu^{2/3}$ gives the total number of molecules or ions of nuclear matter adsorbed at the droplet surface.

The existence of two-dimensional phase transitions in the adsorbed layers of soluble surfactants having been definitively proved [61], it is reasonable to assume that the adsorption s is not, in the general case, a single-valued function of concentration x. At the same time, the concentration x is invariably a single-valued function of the adsorption s. This accounts for the choice of adsorption s as a variable in the description of the droplet state.

It follows from the Gibbs adsorption equation at a fixed temperature and small x that

$$\frac{\partial a(s)}{\partial s} = -\frac{\partial \ln x}{\partial \ln s}\,. \qquad (4.30)$$

This defines $a(s)$ as a single-valued function of s for a given adsorption isotherm $x(s)$ and, vice versa, defines x as a single-valued function of s for a given equation for $a(s)$ characterizing the state of the droplet surface layer.

The differentiation of expression (4.28) with respect to v and the use of Eqn (4.30) bring about

$$\frac{\partial b_v}{\partial v} = \frac{\partial a}{\partial s}\,\frac{\partial s}{\partial v}\left(\frac{2}{3}\,v^{-1/3} + \frac{x}{s}\right) - \frac{2}{9}\,a(s)v^{-4/3}\,, \tag{4.31}$$

where the derivative $\partial s/\partial v$ is given by differentiating relation (4.29) with respect to v and taking into consideration Eqn (4.30):

$$\frac{\partial s}{\partial v} = -\frac{v_{\mathrm{n}}v^{-2} - (1/3)sv^{-4/3}}{v^{-1/3} - (x/s)\,\partial a/\partial s}\,. \tag{4.32}$$

Also, we shall need an expression for the second v-derivative of b_v. Differentiation of Eqn (4.31) with respect to v and the use of Eqn (4.30) give

$$\begin{aligned}\frac{\partial^2 b_v}{\partial v^2} &= \left(\frac{2}{3}\,v^{-1/3} + \frac{x}{s}\right)\left[\frac{\partial^2 a}{\partial s^2}\left(\frac{\partial s}{\partial v}\right)^2 + \frac{\partial a}{\partial s}\,\frac{\partial^2 s}{\partial v^2}\right] \\ &\quad - \frac{\partial a}{\partial s}\,\frac{\partial s}{\partial v}\left[\frac{4}{9}\,v^{-4/3} + \frac{x}{s^2}\left(1 + \frac{\partial a}{\partial s}\right)\frac{\partial s}{\partial v}\right] + \frac{8}{27}\,a(s)v^{-7/3},\end{aligned} \tag{4.33}$$

where the derivative $\partial^2 s/\partial v^2$ is obtained by differentiating Eqn (4.32) with respect to v and taking into account (4.30) as

$$\begin{aligned}\frac{\partial^2 s}{\partial v^2} &= \frac{1}{v^{-1/3} - (x/s)\,\partial a/\partial s} \\ &\quad\times\left\{\frac{2}{3}\,v_{\mathrm{n}}v^{-3} - \frac{2}{3}\,v^{-4/3}\left(1 - 2\,\frac{x}{s}\,\frac{\partial a}{\partial s}\,v^{1/3}\right)\frac{\partial s}{\partial v}\right. \\ &\quad\left. + \frac{x}{s}\left[\frac{\partial^2 a}{\partial s^2} - \frac{1}{s}\left(1 + \frac{\partial a}{\partial s}\right)\frac{\partial a}{\partial s}\right]\left(\frac{\partial s}{\partial v}\right)^2\right\}.\end{aligned} \tag{4.34}$$

In order to find the threshold value b_{th} of the vapor chemical potential, it is necessary to know the extreme values of b_v corresponding to the roots of equation (2.25), taking into consideration Eqns (4.31) and (4.32). The largest of such extrema corresponds to the threshold b_{th} value. The quantities v_{e}, v_{c}, Δv_{e}, Δv_{c}, and ΔF in the prethreshold region of vapor metastability defined by Eqn (4.23) can then be obtained [as follows from Eqns (4.13)–(4.15)] knowing only the derivative $\partial^2 b_v/\partial v^2$, with v corresponding to the highest b_v maximum.

As this section is concerned with the droplet state associated with an extreme value of the condensate chemical potential, i.e. at $v = v_0$, the quantity

$$z \equiv \frac{sv_0^{2/3}}{v_{\mathrm{n}}} \qquad (0 \leqslant z \leqslant 1)\,, \tag{4.35}$$

needs to be introduced, being the fraction of the total amount of the nuclear matter in the droplet accounted for by the adsorbed matter of condensation nucleus for the extreme value of chemical potential of the condensate. For simplicity, we do not use the index 0 to emphasize that the adsorption s as well as surface tension, its derivatives with respect to s, and concentration x mentioned below are also taken at the extrema of the condensate chemical potential.

Equation (2.25) defining the extrema of the chemical potential of the condensate may be written, with regard for Eqns (4.31), (4.32), (4.29), and (4.35), as

$$\left[2\,\frac{a(s)}{s}\,z(1-z) - (3-z)^2\right]\frac{\partial a}{\partial s} = 2\,\frac{a(s)}{s}\,z^2\,. \tag{4.36}$$

From Eqns (4.28), (4.29), and (4.35), it directly follows that

$$(b_v)_0 = \left(\frac{s}{z}\right)^{3/2} v_{\mathrm{n}}^{-1/2}\left(2\,\frac{a(s)}{3s}\,z + z - 1\right), \tag{4.37}$$

$$v_{\mathrm{n}}^{1/2} = \frac{s^{3/2}}{x}\,\frac{1-z}{z^{3/2}}\,. \tag{4.38}$$

If the derivative $\partial a/\partial s$ is expressed by z with the aid of Eqn (4.36) and Eqns (4.29) and (4.35) are taken into account, then Eqns (4.32)–(4.34) lead to

$$\begin{aligned}\left(\frac{\partial^2 b_v}{\partial v^2}\right)_0 &= \left(\frac{s}{z}\right)^{9/2}\frac{v_{\mathrm{n}}^{-7/2}}{27(3-z)^3}\left\{8\left(\frac{a(s)}{s}\right)^3 z^2(1-z)\right. \\ &\quad - 4\left(\frac{a(s)}{s}\right)^2 z(1-z)(3-z)(6+z) \\ &\quad - 6\,\frac{a(s)}{s}(3-z)^2(z^2+4z-3) \\ &\quad\left. - \left[2\,\frac{a(s)}{s}\,z(1-z) - (3-z)^2\right]^3\frac{s}{z^2}\,\frac{\partial^2 a}{\partial s^2}\right\}.\end{aligned} \tag{4.39}$$

Collectively, the relations (4.35)–(4.39), (4.30), and (4.13)–(4.15) may be used to realize the following algorithm for obtaining b_{th}, ζ_{th}, v_0, $(\partial^2 b_v/\partial v^2)_0$, v_{e}, v_{c}, Δv_{e}, Δv_{c}, and ΔF when taking into consideration the adsorption of condensation nucleus matter. First, from a given adsorption isotherm $x(s)$ or the equation of state for $a(s)$, the functions $a(s)$ and $x(s)$, respectively, are found by integrating Eqn (4.30). The function $a(s)$ is then substituted into Eqn (4.36) which is solved as a quadratic equation for z. This gives the multivalued function $z(s)$. Furthermore, using the functions $x(s)$ and $z(s)$ in Eqn (4.38), an equation relating v_{n} to s is obtained. The solution of this equation with respect to s brings about the multivalued function $s(v_{\mathrm{n}})$. Finally, all the aforementioned thermodynamic characteristics depending on the external data of the condensation problem are found using the functions $a(s)$, $z(s)$, $s(v_{\mathrm{n}})$ in rigorous thermodynamic relations (4.37), (4.35), (4.39), and (4.13)–(4.15) and distinguishing each time the largest of the $(b_v)_0$ values. The results of the calculation of these characteristics using the model Langmuir and Frumkin adsorption isotherms are reported in Refs [54, 57, 59, 60].

In two extreme situations, $z \ll 1$ and $1 - z \ll 1$, pertaining to weak adsorption and the adsorption of almost all nuclear matter at the droplet surface, respectively, relations (4.35)–(4.39) along with (4.30) may be used to find asymptotic expressions for thermodynamic characteristics of nucleation [53]. These extreme situations are realized in the presence of large and small condensation nuclei; they are characterized by a unique extremum of the condensate chemical potential. A situation with $z \ll 1$ is realized if the strong inequality

$$\left(\frac{2a}{9}\right)^{1/2}\frac{|H|}{v_{\mathrm{n}}^{1/2}} \ll 1 \tag{4.40}$$

is fulfilled, where a is the dimensionless surface tension of a pure condensate, and H is the dimensionless Henry constant for a given solution. In this situation, in the first approximation with respect to the small parameter given by relation (4.40), one obtains

$$b_{\mathrm{th}} = 2\left(\frac{2a}{9}\right)^{3/2} \nu_{\mathrm{n}}^{-1/2}\left[1 + (2a)^{1/2}\frac{H}{18\nu_{\mathrm{n}}^{1/2}}\right], \tag{4.41}$$

$$\nu_0 = \left(\frac{9\nu_{\mathrm{n}}}{2a}\right)^{3/2}\left[1 - 2(2a)^{1/2}\frac{H}{9\nu_{\mathrm{n}}^{1/2}}\right], \tag{4.42}$$

$$\begin{gathered}\nu_{\mathrm{e}} = \left(\frac{9\nu_{\mathrm{n}}}{2a}\right)^{3/2}\left[1 - 2(2a)^{1/2}\frac{H}{9\nu_{\mathrm{n}}^{1/2}} - (6\varepsilon)^{1/2}\left(1 - 7(2a)^{1/2}\frac{H}{36\nu_{\mathrm{n}}^{1/2}}\right)\right], \\ \nu_{\mathrm{c}} = \left(\frac{9\nu_{\mathrm{n}}}{2a}\right)^{3/2}\left[1 - 2(2a)^{1/2}\frac{H}{9\nu_{\mathrm{n}}^{1/2}} + (6\varepsilon)^{1/2}\left(1 - 7(2a)^{1/2}\frac{H}{36\nu_{\mathrm{n}}^{1/2}}\right)\right],\end{gathered} \tag{4.43}$$

$$\Delta\nu_{\mathrm{e}} = \Delta\nu_{\mathrm{c}} = 27\left(\frac{3}{2}\right)^{1/4}(2a)^{-3/2}\nu_{\mathrm{n}}\varepsilon^{-1/4}\left[1 - (2a)^{1/2}\frac{H}{8\nu_{\mathrm{n}}^{1/2}}\right], \tag{4.44}$$

$$\Delta F = \frac{16}{6^{1/2}}\,\nu_{\mathrm{n}}\varepsilon^{3/2}\left[1 - 5(2a)^{1/2}\frac{H}{36\nu_{\mathrm{n}}^{1/2}}\right]. \tag{4.45}$$

In the case of soluble nuclei consisting of a surface-inactive material, the Henry constant H in asymptotics (4.41) – (4.45) is negative. It is positive in the presence of nuclei consisting of surfactants.

The other extreme situation, $1 - z \ll 1$, is realized only for the condensation on the nuclei of soluble surfactants, provided the strong inequality

$$\frac{x_1\nu_{\mathrm{n}}^{1/2}}{s_1^{3/2}} \ll 1 \tag{4.46}$$

is satisfied, where the subscript 1 characterizes quantities at $z = 1$. To the leading order in the small parameter given by Eqn (4.46), one finds

$$b_{\mathrm{th}} = \frac{2s_1^{1/2}a_1}{3\nu_{\mathrm{n}}^{1/2}}, \tag{4.47}$$

$$\nu_0 = \left(\frac{\nu_{\mathrm{n}}}{s_1}\right)^{3/2}, \tag{4.48}$$

$$\nu_{\mathrm{e}} = \left(\frac{\nu_{\mathrm{n}}}{s_1}\right)^{3/2}\left\{1 - (6\varepsilon)^{1/2}\left[1 - \frac{4s_1^2}{3a_1}\left(\frac{\partial^2 a}{\partial s^2}\right)_1\right]^{-1/2}\right\}, \tag{4.49}$$

$$\begin{gathered}\nu_{\mathrm{c}} = \left(\frac{\nu_{\mathrm{n}}}{s_1}\right)^{3/2}\left\{1 + (6\varepsilon)^{1/2}\left[1 - \frac{4s_1^2}{3a_1}\left(\frac{\partial^2 a}{\partial s^2}\right)_1\right]^{-1/2}\right\}, \\ \Delta\nu_{\mathrm{e}} = \Delta\nu_{\mathrm{c}} = \left(\frac{3}{2}\right)^{1/4}\frac{3^{1/2}\nu_{\mathrm{n}}}{a_1^{1/2}\varepsilon^{1/4}s_1}\left[1 - \frac{4s_1^2}{3a_1}\left(\frac{\partial^2 a}{\partial s^2}\right)_1\right]^{-1/4},\end{gathered} \tag{4.50}$$

$$\Delta F = \frac{16a_1\varepsilon^{3/2}\nu_{\mathrm{n}}}{6^{1/2}3s_1}\left[1 - \frac{4s_1^2}{3a_1}\left(\frac{\partial^2 a}{\partial s^2}\right)_1\right]^{-1/2}. \tag{4.51}$$

The comparison of formulas (4.41) and (4.47) and also (4.45) and (4.51) leads to several interesting conclusions. When practically all nuclear matter is adsorbed at the droplet surface, the quantity s_1 is by definition equal to the number of surfactant molecules over an area as large as the effective area of one solvent molecule. The size of the solvent molecules (e.g. water molecule) being usually smaller than the transverse diameter of surfactant molecules, it may be expected that $s_1 < 1$. Because in the case of surfactant adsorption $a_1 < a$, it follows from Eqns (4.41) and (4.47) that the threshold values of the vapor chemical potential during condensation on relatively small nuclei consisting of soluble surfactants may be significantly smaller than the threshold values in condensation on similarly sized nuclei consisting of soluble surface-inactive materials. At the same time, it follows from expressions (4.45) and (4.51) that, at given ε and ν_{n}, the activation energy in the case of surfactant nuclei may be significantly higher than that for the condensation at nuclei consisting of surface-inactive materials. This means that in the presence of soluble surfactants in the nuclei, the prethreshold vapor metastability region is narrowed. These inferences are confirmed by the results of a numerical study on the dependence of the threshold value of condensate chemical potential in a droplet and the activation energy on the nuclear size in the case of condensation on the nuclei consisting of soluble surfactants [54].

5. Kinetics of nucleation on soluble nuclei

Based on what has been said in the previous sections, it is now time to turn to an in-depth kinetic analysis of nucleation on soluble nuclei. For definiteness, we confine ourselves to the practically important case of completely soluble nuclei consisting of a surface inactive substance. The kinetics of the initial stage of droplet formation on such nuclei has been described in Ref. [62], and the nucleation stage itself in Refs [63 – 66, 45]. The principle of generalization to the case of soluble nuclei consisting of a surface-active material will be described at the end of Section 7.5.

5.1 Kinetic characteristics of nucleation on soluble nuclei

In conformity with relations (4.10) and (4.25), the current vapor supersaturation in the prethreshold metastability region is, with high accuracy, given by

$$\zeta \approx \zeta_{\mathrm{th}}\,. \tag{5.1}$$

Because the relation mentioned immediately above is valid at $\zeta = \zeta_*$ too, it follows from this relation and Eqn (3.16), also with high accuracy, that

$$\varPhi_* \approx \zeta_{\mathrm{th}}\,. \tag{5.2}$$

The kinetic theory of nucleation is considerably simplified by virtue of expression (5.2) obtained, in the presence of macroscopic condensation nuclei, for the reference value $\varPhi_*$ of ideal vapor supersaturation, which has in its right-hand side the quantity ζ_{th} known from the thermodynamic relation (4.7). In particular, this expression simplifies the method for the consistent determination of parameters t_∞ and m entering the power-like approximation (3.2) described in Section 3.5, which allows $\varPhi_*$ to be taken as equivalent to the known value ζ_{th}.

Expression (5.2) is sufficiently accurate to find quantities weakly depending on $\varPhi_*$ and behaving as a power series in $\varPhi_*$. Also important in the kinetic theory of nucleation are quantities strongly dependent on $\varPhi_*$ through a small deviation $\zeta_{\text{th}} - \varPhi_*$. Our immediate objective is to define expression (5.2) more precisely as well as (4.24), necessary for finding such quantities.

According to Eqn (3.38) and the equality $\Delta\nu_{\text{e}} = \Delta\nu_{\text{c}}$ ensuing from Eqns (4.14) and (4.18), one obtains

$$\exp\left(\Delta F\Big|_{\zeta=\varPhi_*}\right) \approx \begin{cases} \dfrac{h}{6\pi\ln 2}\,\dfrac{\Delta t}{t_{\text{s}}} & (h \gg 1)\,, \\ \dfrac{1}{6\pi\ln 2}\,\dfrac{\Delta t}{t_{\text{s}}} & (h \ll 1)\,. \end{cases} \tag{5.3}$$

Taking the logarithm of the last expression, we obtain with an even higher accuracy:

$$\Delta F\Big|_{\zeta=\varPhi_*} \approx \begin{cases} \ln\left(\dfrac{\varkappa h}{6\pi\ln 2}\right) & (h \gg 1)\,, \\ \ln\left(\dfrac{\varkappa}{6\pi\ln 2}\right) & (h \ll 1)\,, \end{cases} \tag{5.4}$$

where we put

$$\varkappa \equiv \frac{\Delta t}{t_{\text{s}}}\,. \tag{5.5}$$

Similar to Eqn (3.38), the activation energy $\Delta F\big|_{\zeta=\varPhi_*}$ expressed according to Eqn (5.4) through parameters $\varkappa$ and h does not depend on the growth regime of supercritical droplets. It will be shown in Section 7.1 that this expression also retains its universal form for the nucleation on macroscopic nuclei of arbitrary nature.

Let us denote as $\tilde{\varepsilon}$ the value of ε determined from Eqn (4.10) at $\zeta = \varPhi_*$. Then, one has

$$\tilde{\varepsilon} \equiv \frac{\zeta_{\text{th}} - \varPhi_*}{\zeta_{\text{th}}}\,. \tag{5.6}$$

Using the thermodynamic relation (4.19) in (5.4) and taking into account definition (5.6), we obtain

$$\tilde{\varepsilon}^{\,1/2} \approx q\nu_{\text{n}}^{-1/3}\,, \tag{5.7}$$

where

$$q = \begin{cases} \left[\dfrac{6^{1/2}}{16}\ln\left(\dfrac{\varkappa h}{6\pi\ln 2}\right)\right]^{1/3} & (h \gg 1)\,, \\ \left[\dfrac{6^{1/2}}{16}\ln\left(\dfrac{\varkappa}{6\pi\ln 2}\right)\right]^{1/3} & (h \ll 1)\,. \end{cases} \tag{5.8}$$

According to the last formula, the quantity q (same as $\Delta F\big|_{\zeta=\varPhi_*}$) is a function of the dimensionless parameters $\varkappa$ and h. It will be shown in Section 5.2 that these parameters are a convenient choice in the construction of a kinetic theory of nucleation as independent, free parameters compatible, naturally, with the applicability conditions and limitations $h \gg 1$ and $h \ll 1$ used in the theory. In order to simplify the notation, we shall omit the limitations $h \gg 1$ and $h \ll 1$ in the formulas (unless they are important).

Although the parameters $\varkappa$ and h are not initial ones with respect to the theory, it will be shown in Section 5.2 that they allow us to easily determine the characteristic time t_∞ of vapor metastable state formation and the initial concentration $\eta(-\infty)$ of condensation nuclei, both being initial parameters of the theory.

The quantity $\tilde{\varepsilon}$ derived using formula (5.6) is important because it serves to express the parameter $\varGamma$ by means of the relation

$$\varGamma \approx \frac{\partial\Delta F}{\partial\varepsilon}\bigg|_{\varepsilon=\tilde{\varepsilon}} \tag{5.9}$$

ensuing from Eqns (3.4), (4.10), and (5.2). The quantity $\tilde{\varepsilon}$ is also important because it may be employed to express the time t_{s} with the aid of relations (3.35) and (4.18). Both the parameter $\varGamma$ and the time t_{s} exemplify quantities which strongly depend on $\varPhi_*$ through a small deviation $\zeta_{\text{th}} - \varPhi_*$.

Relation (5.7) is a more explicit variant of formula (4.24) which defines the quantity $\varepsilon^{1/2}$ characteristic of the interval (4.23), i.e. the prethreshold vapor metastability region. This refinement can be presented in the form

$$\tilde{\varepsilon}^{\,1/2} \approx q\varepsilon^{1/2}\,. \tag{5.10}$$

Sections 5.3 and 5.4 will illustrate the validity of the approximate equality

$$q \approx 1\,. \tag{5.11}$$

It follows from formulas (5.10) and (5.11) that there is, besides inequality (4.25), a new constraint

$$\tilde{\varepsilon}^{\,1/2} \ll 1\,. \tag{5.12}$$

The use of relation (5.7) in conjunction with Eqn (5.6) allows us to easily give a more precise definition to expression (5.2) for the reference value $\varPhi_*$ of ideal vapor supersaturation. This correction is, however, very small because of inequality (5.12). It is unimportant when the $\varPhi_*$-dependence is weak and power-like in $\varPhi_*$. We therefore forbear from presenting a more elaborate version of the expression (5.2).

Let us now turn to the principal objective of this section. The substitution of Eqn (4.19) into (5.9) and the use of Eqn (5.7) results in

$$\varGamma \approx \frac{24}{6^{1/2}}\,q\nu_{\text{n}}^{2/3}\,. \tag{5.13}$$

Expressions (3.35), (3.37) give [taking into account Eqns (4.8), (4.18), (4.26), (5.2), and (5.7)] the time

$$t_{\text{s}} \approx \left(\frac{3}{2}\right)^{7/2}\frac{\tau}{q\alpha}\,\frac{\nu_{\text{n}}^{4/3}}{a^2}\,. \tag{5.14}$$

Expressions (3.3), (5.2), and (4.7) are used to find

$$t_* \approx \left(\frac{2^{5/2}}{27}\right)^{1/m} t_\infty\,\frac{a^{3/(2m)}}{\nu_{\text{n}}^{1/(2m)}} \tag{5.15}$$

[it is adopted in the theory that time is reckoned from the moment at which $\varPhi = 0$ according to the power-like approximation (3.2)].

A line of further reasoning depends on whether free-molecule or diffusive growth of supercritical droplets predominates at the nucleation stage.

Let us first consider the case of free-molecule growth of supercritical droplets. The use of Eqns (5.2), (5.13), and (4.7) in (3.10), (3.11) brings about

$$c \approx 3^{7/2}\left(\frac{27}{2^{5/2}}\right)^{1/m}\frac{qm\tau}{\alpha t_\infty}\,\frac{\nu_{\text{n}}^{(7m+3)/(6m)}}{a^{3(m+1)/(2m)}}\,, \tag{5.16}$$

$$h \approx \frac{2}{3^6}\left(\frac{2^{5/2}}{27}\right)^{3/m}\frac{\eta(-\infty)}{q^2 n_\infty}\left(\frac{\alpha t_\infty}{m\tau}\right)^3\frac{a^{(6m+9)/(2m)}}{\nu_{\text{n}}^{(14m+9)/(6m)}}\,. \tag{5.17}$$

It follows from Eqn (3.47), taking into account Eqns (4.7), (4.8), (4.18), (4.26), (5.2), and (5.7), that

$$\frac{\Delta\rho}{\rho_{\mathrm{c}}} \approx \frac{v_{\mathrm{n}}^{1/3}}{6^{1/2} q} \frac{\Delta t}{t_{\mathrm{s}}} . \qquad (5.18)$$

Owing to Eqns (4.6) and (5.11), relation (5.18) indicates that condition (3.46) is satisfied with ample reserve provided condition (3.39) is fulfilled too.

Formulas (3.12)–(3.14), (3.17), (3.22), (3.23), and (5.15) taken together with expressions (4.7), (5.2), (5.16), and (5.17) give all the most important kinetic characteristics of nucleation on soluble nuclei under the free-molecule growth of supercritical droplets.

Let us now consider the case of the diffusive supercritical droplet growth. Based on Eqns (5.2), (5.13), and (4.7) in (3.28), (3.29), we find

$$c \approx 3^{7/2} \left(\frac{27}{2^{5/2}}\right)^{1/m} \frac{q m \tau_D}{t_\infty} \frac{v_{\mathrm{n}}^{(7m+3)/(6m)}}{a^{3(m+1)/(2m)}} , \qquad (5.19)$$

$$h \approx \frac{\pi^{1/2}}{2^2\, 3^{3/4}} \left(\frac{2^{5/2}}{27}\right)^{3/(2m)} \frac{\eta(-\infty)}{q^{1/2} n_\infty} \left(\frac{t_\infty}{m\tau_D}\right)^{3/2} \frac{a^{(3m+9)/(4m)}}{v_{\mathrm{n}}^{(7m+9)/(12m)}} . \qquad (5.20)$$

It was shown in Section 3.4 that condition (3.46) is satisfied with ample reserve for the diffusive growth of supercritical droplets.

Formulas (3.12)–(3.14), (3.17), (3.23), (3.30) and (5.15) taken together with expressions (4.7), (5.2), (5.19), and (5.20) give all the most important kinetic characteristics of nucleation on soluble nuclei under the diffusive growth of supercritical droplets.

Comparison of Eqns (3.22) and (5.16) with (3.30) and (5.19), respectively, indicates that the expressions for time Δt have a similar form for free-molecule and diffusive growth of supercritical droplets.

5.2 Parametrization of the characteristic time of vapor metastable state formation

It has been stated in the previous section that the expression for time Δt ensuing from Eqns (3.22) and (5.16) and, respectively, from (3.30) and (5.19) is identical for the free-molecule and diffusive growth of supercritical droplets. Using this expression and taking into account relations (4.7), (5.2), and (5.14), we shall have in either case

$$\frac{\Delta t}{t_{\mathrm{s}}} \approx \frac{2}{27} \left(\frac{2^{5/2}}{27}\right)^{1/m} \frac{\alpha t_\infty}{m\tau} \frac{a^{(4m+3)/(2m)}}{v_{\mathrm{n}}^{(4m+1)/(2m)}} . \qquad (5.21)$$

By expressing t_∞ from Eqn (5.21) and using definition (5.5), the formula

$$t_\infty \approx \frac{27}{2} \left(\frac{27}{2^{5/2}}\right)^{1/m} \frac{\varkappa m \tau}{\alpha} \frac{v_{\mathrm{n}}^{(4m+1)/(2m)}}{a^{(4m+3)/(2m)}} \qquad (5.22)$$

is obtained which parametrizes the characteristic time t_∞ of vapor metastable state formation, i.e. expresses it through the parameter $\varkappa$.

It follows straightforwardly from the definition (5.5) and relation (5.14) that

$$\Delta t \approx \left(\frac{3}{2}\right)^{7/2} \frac{\varkappa\tau}{q\alpha} \frac{v_{\mathrm{n}}^{4/3}}{a^2} . \qquad (5.23)$$

The further consideration will be first concerned with the free-molecule growth of supercritical droplets. The substitution of Eqn (5.22) into Eqns (5.16) and (5.17) yields

$$c \approx 3^{1/2} 2 \frac{q a^{1/2}}{\varkappa v_{\mathrm{n}}^{5/6}} , \qquad (5.24)$$

$$h \approx \frac{27}{4} \frac{\eta(-\infty)}{q^2 n_\infty} \varkappa^3 \frac{v_{\mathrm{n}}^{11/3}}{a^3} . \qquad (5.25)$$

The use of Eqns (3.13),(3.17), taking into account (5.24) and (5.25), gives

$$N \approx \frac{4}{27} \frac{q^2 n_\infty}{\varkappa^3} \frac{a^3}{v_{\mathrm{n}}^{11/3}} \qquad (h \gg 1) , \qquad (5.26)$$

$$\Delta\rho \approx \frac{3^{1/2}}{2} \frac{\varkappa}{q} \frac{v_{\mathrm{n}}^{5/6}}{a^{1/2}} . \qquad (5.27)$$

By solving expression (5.25) for $\eta(-\infty)$ one arrives at

$$\eta(-\infty) \approx \frac{4}{27} \frac{q^2 n_\infty h}{\varkappa^3} \frac{a^3}{v_{\mathrm{n}}^{11/3}} . \qquad (5.28)$$

The expression

$$N \approx \frac{4}{27} \frac{q^2 n_\infty h}{\varkappa^3} \frac{a^3}{v_{\mathrm{n}}^{11/3}} \qquad (h \ll 1) \qquad (5.29)$$

is found with the aid of Eqns (3.14) and (5.28).

Parameters $\varkappa$ and h on which the quantity q depends, in agreement with Eqn (5.8), are chosen as independent, free parameters of the kinetic theory of nucleation, in conformity with what has been said in Section 5.1. Formulas (5.22) and (5.28) then express the time t_∞ and concentration $\eta(-\infty)$ through the parameters $\varkappa$ and h. In turn, formulas (5.23), (5.26), (5.27), and (5.29) express kinetic characteristics of nucleation Δt, N, and $\Delta\rho$ through the parameters $\varkappa$ and h.

The kinetic picture of nucleation described by expressions (5.22), (5.23), and (5.26)–(5.29) depending on the parameters $\varkappa$ and h is as demonstrative as it were if represented as dependent on the initial parameters of the theory: t_∞ and $\eta(-\infty)$. However, the parameters $\varkappa$ and h were used to construct the kinetic theory of nucleation in the analytical form and are therefore believed to be more convenient than t_∞ and $\eta(-\infty)$.

Let us consider the case of diffusive growth of supercritical droplets. The substitution of Eqn (5.22) into Eqns (5.19) and (5.20) yields

$$c \approx 3^{1/2} 2 \frac{q \alpha \tau_D a^{1/2}}{\varkappa \tau v_{\mathrm{n}}^{5/6}} , \qquad (5.30)$$

$$h \approx \frac{81\pi^{1/2}}{2^{7/2}\, 3^{1/4}} \frac{\eta(-\infty)}{q^{1/2} n_\infty} \left(\frac{\varkappa\tau}{\alpha\tau_D}\right)^{3/2} \frac{v_{\mathrm{n}}^{29/12}}{a^{9/4}} . \qquad (5.31)$$

The use of Eqns (3.13), (3.17), taking into account formulas (5.30) and (5.31), gives

$$N \approx \frac{2^{7/2}\, 3^{1/4}}{81\pi^{1/2}} q^{1/2} n_\infty \left(\frac{\alpha\tau_D}{\varkappa\tau}\right)^{3/2} \frac{a^{9/4}}{v_{\mathrm{n}}^{29/12}} \qquad (h \gg 1) , \qquad (5.32)$$

$$\Delta\rho \approx \frac{3^{1/2}}{2} \frac{\varkappa\tau}{q\alpha\tau_D} \frac{v_{\mathrm{n}}^{5/6}}{a^{1/2}} . \qquad (5.33)$$

By solving expression (5.31) for $\eta(-\infty)$ one finds

$$\eta(-\infty) \approx \frac{2^{7/2}\, 3^{1/4}}{81\pi^{1/2}}\, q^{1/2} n_\infty h \left(\frac{\alpha\tau_D}{\varkappa\tau}\right)^{3/2} \frac{a^{9/4}}{v_{\mathrm{n}}^{29/12}} \,. \tag{5.34}$$

The relation

$$N \approx \frac{2^{7/2}\, 3^{1/4}}{81\pi^{1/2}}\, q^{1/2} n_\infty h \left(\frac{\alpha\tau_D}{\varkappa\tau}\right)^{3/2} \frac{a^{9/4}}{v_{\mathrm{n}}^{29/12}} \qquad (h \ll 1) \tag{5.35}$$

is obtained with the aid of Eqns (3.14) and (5.34).

Formulas (5.22) and (5.34) express the time t_∞ and concentration $\eta(-\infty)$ through the parameters $\varkappa$ and h. In turn, formulas (5.23), (5.32), (5.33), and (5.35) express the kinetic characteristics of nucleation Δt, N, and $\Delta\rho$ through the parameters $\varkappa$ and h. It can be seen that the parameters $\varkappa$ and h allowed the kinetic theory of nucleation to be constructed in an analytical form for the diffusive growth of supercritical droplets and are therefore believed to be more convenient than t_∞ and $\eta(-\infty)$.

Expression (5.5) indicates that the principal applicability condition (3.39) of the kinetic theory responsible, in particular, for the fulfilment of conditions (3.40), (3.46) may be written as

$$\varkappa \gg 1 \,. \tag{5.36}$$

Parameter $\varkappa$ makes it possible to use inequality (5.36) to directly estimate the fulfilment of condition (3.39), while parameter h may be used to directly estimate the fulfilment of the inequalities $h \gg 1$ and $h \ll 1$ employed in the theory. This is another important advantage of the parameters $\varkappa$ and h over t_∞ and $\eta(-\infty)$.

5.3 Method for the calculation of kinetic characteristics of nucleation on soluble nuclei under free-molecule growth of supercritical droplets

Bearing in mind what has been said in Section 5.2, we assume in the proposed method that parameters $\varkappa$ and h are free, but restricted by condition (5.36) and the inequalities $h \gg 1$ or $h \ll 1$. The fact that the method right away covers the entire range of applicability of the theory suggests its high efficiency.

The case of free-molecule supercritical droplet formation considered in the present section is characterized by an additional limitation imposed by condition (3.42). Let us make explicit this limitation. It follows from Eqns (3.43) and (5.27) that

$$\frac{\Delta\rho}{\rho_\lambda} \sim \frac{3^{1/2}}{2q}\, \alpha(n_\infty + n_{\mathrm{g}}) v_\alpha \varkappa \frac{v_{\mathrm{n}}^{5/6}}{a^{1/2}} \tag{5.37}$$

(in estimates, numerical values are not rounded off to make it easier to follow them). The use of Eqn (5.37) in Eqn (3.42), taking into account approximate equality (5.11), yields

$$\varkappa \ll \frac{2}{3^{1/2}} \frac{1}{\alpha(n_\infty + n_{\mathrm{g}}) v_\alpha} \frac{a^{1/2}}{v_{\mathrm{n}}^{5/6}} \,. \tag{5.38}$$

Expressions (5.36) and (5.38) are compatible if

$$\frac{2}{3^{1/2}} \frac{1}{\alpha(n_\infty + n_{\mathrm{g}}) v_\alpha} \frac{a^{1/2}}{v_{\mathrm{n}}^{5/6}} \gg 1 \,. \tag{5.39}$$

If the last inequality containing the initially given parameters of the theory in its left-hand side is satisfied, then formulas (5.22), (5.23), and (5.26)–(5.29) are valid in the ranges of variation of parameters $\varkappa$ and h, permitted by the constraints (5.36), (5.38), and $h \gg 1$ or $h \ll 1$. These formulas provide a basis for further calculations.

Let us choose the following values of the initial parameters of the theory:

$$a = 10\,, \quad \alpha = 10^{-1}\,, \quad n_\infty = 10^{17}\ \mathrm{cm}^{-3}, \quad n_{\mathrm{g}} = 10^{19}\ \mathrm{cm}^{-3},$$
$$v_\alpha = 10^{-23}\ \mathrm{cm}^3, \quad \tau = 5.4 \times 10^{-7}\ \mathrm{s}, \quad v_{\mathrm{n}}^{1/3} = 10\,, \quad m = 1\,. \tag{5.40}$$

These values are realistic for a typical condensable liquid, namely, water and its saturated vapor at ordinary temperatures. They are equally realistic for a passive gas at a pressure close to atmospheric. According to equality (2.29), the value of quantity a corresponds to the surface tension γ of 77 dyn cm^{-1}. The chosen $v_{\mathrm{n}}^{1/3}$ value is sufficiently large to ensure that the condition (4.6) of macroscopicity soluble of a nucleus is satisfied; at the same time, it is so small that the value $\zeta_{\mathrm{th}} \approx 2.1 \times 10^{-1}$ of the vapor threshold supersaturation given by formula (4.7) is still amenable to reliable control in experiment. According to the power-like approximation (3.2), the value of parameter m corresponds to the well-representative linear-in-time growth of ideal supersaturation Φ.

Let us use the method suggested for the calculation based on parameters (5.40). In this case, the inequality (5.39) is satisfied. It follows from Eqns (5.36) and (5.38) that

$$1 \ll \varkappa \ll 10^3\,, \tag{5.41}$$

which determines the admitted region of parameter $\varkappa$ variations.

According to Eqns (5.22), (5.15), and (5.23), one finds

$$t_\infty \approx 6.5\varkappa\ \mathrm{s}\,, \tag{5.42}$$

$$t_* \approx 1.4\varkappa\ \mathrm{s}\,, \tag{5.43}$$

$$\Delta t \approx 4.1 \times 10^{-3} q^{-1} \varkappa\ \mathrm{s}\,. \tag{5.44}$$

Units of measurement of dimensional quantities are specified explicitly. The dependence of q on $\varkappa$ and h is given by equality (5.8). Time moments t_{on} and t_{off} are easy to find using approximate relations (3.23).

Finally, Eqns (5.26)–(5.29) result in

$$N \approx \begin{cases} 1.5 \times 10^8 q^2 \varkappa^{-3}\ \mathrm{cm}^{-3} & (h \gg 1)\,, \\ 1.5 \times 10^8 q^2 h \varkappa^{-3}\ \mathrm{cm}^{-3} & (h \ll 1)\,, \end{cases} \tag{5.45}$$

$$\Delta\rho \approx 8.7 \times 10 q^{-1} \varkappa\,, \tag{5.46}$$

$$\eta(-\infty) \approx 1.5 \times 10^8 q^2 h \varkappa^{-3}\ \mathrm{cm}^{-3}\,. \tag{5.47}$$

The radius R of a droplet is more convenient to use in experiment than its size ρ introduced by equalities (2.2) and (3.7). The radius can be obtained from expressions (2.2), (3.7) as

$$R = \left(\frac{3v_\alpha}{4\pi}\right)^{1/3} \rho\,. \tag{5.48}$$

Taking advantage of the proportionality between R and ρ reflected by this equation, we receive for the width ΔR of the supercritical droplet size spectrum on the R-axis:

$$\Delta R = \left(\frac{3v_\alpha}{4\pi}\right)^{1/3} \Delta\rho\,. \tag{5.49}$$

It follows from relations (5.46), (5.49) that

$$\Delta R \approx 10^{-6} q^{-1} \varkappa \ \mathrm{cm} \,. \tag{5.50}$$

Let us show how conditions (3.40) and (5.11) are fulfilled. In a situation with $h \gg 1$, Eqns (5.4) and (5.8) indicate that condition (3.40) is satisfied over the entire range established by inequalities (5.41). Likewise, approximate equality (5.11) is fulfilled unless the inequality $h \gg 1$ is too strong. That it cannot be too strong follows from the fact that the growth of parameter h is accompanied by a rise [in agreement with Eqn (5.47)] in the concentration $\eta(-\infty)$ which, however, does not normally exceed $10^5 \ \mathrm{cm}^{-3}$ under practical conditions.

In a situation where $h \ll 1$, it follows from expressions (5.4) and (5.8) that Eqns (3.40) and (5.11) are satisfied only near the upper limit of the range (5.41).

5.4 Method for the calculation of kinetic characteristics of nucleation on soluble nuclei under diffusive growth of supercritical droplets

Now we consider the parameters $\varkappa$ and h to be free as before but restricted via condition (5.36) and the inequalities $h \gg 1$ and $h \ll 1$.

The case of diffusive supercritical droplet growth analyzed in the present section is characterized by an additional limitation imposed by condition (3.44). Let us make explicit this limitation. It follows from Eqns (3.45) and (5.33) that

$$\frac{\Delta\rho}{\rho_\lambda} \sim \frac{3^{1/2}}{2q} \frac{\varkappa\tau}{\tau_D} \frac{v_{\mathrm{n}}^{5/6}}{a^{1/2}} \alpha (n_\infty + n_{\mathrm{g}})^2 v_\alpha^2 \tag{5.51}$$

(in estimates, numerical values are not rounded off to make it easier to follow them). Bearing in mind equalities (3.9), (3.27), and the kinetic relation $D \sim \lambda v_T/3$ for gases and also taking into consideration the estimate given by relation (3.41) for the mean free path λ traveled by a vapor molecule in the vapor–gas medium, we have

$$\frac{\tau}{\tau_D} (n_\infty + n_{\mathrm{g}}) v_\alpha \sim 1 \,. \tag{5.52}$$

Expression (5.51) can be represented with the aid of the last estimate as

$$\frac{\Delta\rho}{\rho_\lambda} \sim \frac{3^{1/2}}{2q} \alpha (n_\infty + n_{\mathrm{g}}) v_\alpha \varkappa \frac{v_{\mathrm{n}}^{5/6}}{a^{1/2}} \,, \tag{5.53}$$

which at first sight coincides with formula (5.37) although the quantities ρ and ρ_λ are now defined by relations (3.25) and (3.45) which are different from Eqns (3.7) and (3.43). The use of relation (5.53) in inequality (3.44) and taking into account approximate equality (5.11) gives

$$\varkappa \gg \frac{2}{3^{1/2}} \frac{1}{\alpha (n_\infty + n_{\mathrm{g}}) v_\alpha} \frac{a^{1/2}}{v_{\mathrm{n}}^{5/6}} \,. \tag{5.54}$$

This inequality is opposite to that given by (5.38) as the limiting case of the diffusive supercritical droplet formation itself is opposite to that of free-molecule growth.

Formulas (5.22), (5.23), and (5.32)–(5.35) will hold in the range of variation of parameters $\varkappa$ and h, permitted by the most rigorous inequality out of (5.36) and (5.54) and constraints $h \gg 1$ or $h \ll 1$. These formulas form a basis for further calculations.

Let us choose the following values of the initial parameters of the theory:

$$\begin{aligned} &a = 10 \,, \quad \alpha = 1 \,, \quad n_\infty = 10^{17} \ \mathrm{cm}^{-3} , \quad n_{\mathrm{g}} = 10^{19} \ \mathrm{cm}^{-3} , \\ &v_\alpha = 10^{-23} \ \mathrm{cm}^3 , \quad \tau = 5.4 \times 10^{-7} \ \mathrm{s} \,, \quad D = 1 \ \mathrm{cm}^2 \, \mathrm{s}^{-1} , \\ &\tau_D = 8.9 \times 10^{-11} \ \mathrm{s} \,, \quad v_{\mathrm{n}}^{1/3} = 10 \,, \quad m = 1 \,. \end{aligned} \tag{5.55}$$

The values given in the last set are different from those in Eqn (5.40) only in that $\alpha = 1$ is assumed instead of $\alpha = 10^{-1}$. However, this difference is responsible for the transition from the free-molecule to diffusive growth of supercritical droplets. The possibility that the coefficient α is close to unity ensues from some experimental findings reported in Ref. [67] and molecular dynamics studies [68, 69]. The value of D given in set (5.55) is quite realistic. For the sake of completeness, the time τ_D is included among the set of initial parameters even though it is a function of n_∞, v_α, and D, in agreement with formula (3.27). The value of τ_D was found with the aid of relation (3.27).

Let us employ the method under consideration for the calculation based on the data from set (5.55). In this case, the inequality (5.54) is more rigorous than (5.36). According to the former inequality, one obtains

$$\varkappa \gg 10^2 \,, \tag{5.56}$$

which determines the admitted region of parameter $\varkappa$ variations.

According to Eqns (5.22), (5.15), and (5.23), we have

$$t_\infty \approx 6.5 \times 10^{-1} \varkappa \ \mathrm{s} \,, \tag{5.57}$$

$$t_* \approx 1.4 \times 10^{-1} \varkappa \ \mathrm{s} \,, \tag{5.58}$$

$$\Delta t \approx 4.1 \times 10^{-4} q^{-1} \varkappa \ \mathrm{s} \,. \tag{5.59}$$

The units for measuring dimensional quantities were specified. The dependence of q on $\varkappa$ and h is given by the equality (5.8). The time moments t_{on} and t_{off} are easy to find using approximate equalities (3.23).

Finally, relations (5.32)–(5.35) give

$$N \approx \begin{cases} 1.8 \times 10^4 q^{1/2} \varkappa^{-3/2} \ \mathrm{cm}^{-3} & (h \gg 1) \,, \\ 1.8 \times 10^4 q^{1/2} h \varkappa^{-3/2} \ \mathrm{cm}^{-3} & (h \ll 1) \,, \end{cases} \tag{5.60}$$

$$\Delta\rho \approx 2.1 \times 10^6 q^{-1} \varkappa \,, \tag{5.61}$$

$$\eta(-\infty) \approx 1.8 \times 10^4 q^{1/2} h \varkappa^{-3/2} \ \mathrm{cm}^{-3} \,. \tag{5.62}$$

The surface area $A = 4\pi R^2$ of a droplet is more conveniently used in experiment than its size ρ introduced by equalities (2.2), (3.25). The area can be obtained from the immediately mentioned expressions as

$$A = (36\pi v_\alpha^2)^{1/3} \rho \,. \tag{5.63}$$

Taking advantage of the proportionality between A and ρ reflected by this equation, we receive for the width ΔA of the supercritical droplet size spectrum on the A-axis:

$$\Delta A = (36\pi v_\alpha^2)^{1/3} \Delta\rho \,. \tag{5.64}$$

It follows from Eqns (5.61), (5.64) that

$$\Delta A \approx 4.6 \times 10^{-9} q^{-1} \varkappa \ \mathrm{cm}^2 \,. \tag{5.65}$$

Let us show how conditions (3.40) and (5.11) are fulfilled. In a situation with $h \gg 1$, relations (5.4) and (5.8) indicate that condition (3.40) is satisfied over the entire range (5.56). Likewise, approximate equality (5.11) is fulfilled (at least for the purpose of estimation) unless the inequalities (5.56) and $h \gg 1$ are too strong. If the inequality (5.56) were too strong, i.e. parameter $\varkappa$ were too large, the time t_* would be very large as well [in accordance with relation (5.58)] and consequently of little practical interest. If the inequality $h \gg 1$ were too strong, the concentration $\eta(-\infty)$ would be very high [in agreement with relation (5.62) and for a not too large parameter $\varkappa$ substantiated] although as was noted it does not normally exceed $10^5\ \text{cm}^{-3}$ under practical conditions.

In the situation where $h \ll 1$, it follows from the expressions (5.4) and (5.8) that inequality (3.40) and approximate equality (5.11) are satisfied over the entire range (5.56) with the exception of too large values of the parameter $\varkappa$ [corresponding, in agreement with Eqn (5.58), to a very large time t_*].

5.5 Accounting for the polydispersity of soluble nuclei

In the kinetic theory of nucleation presented in Sections 5.1 – 5.4 of this review, soluble condensation nuclei were assumed to be identical, i.e. monodispersed. When condensation nuclei are represented by a single type of microscopic heterogeneous centers of condensation (ions, isolated molecules, etc.), the problem of polydispersity is nonexistent. It arises, however, in the case of macroscopic condensation nuclei. The macroscopic size is a characteristic feature of soluble nuclei.

The polydispersity of condensation nuclei implies that the distribution of their initial concentrations over the number ν_{n} of molecules (or ions) contained in them needs to be taken into consideration. Let us adopt the quite realistic assumption that the density of this distribution is practically zero for $\nu_{\text{n}} > \overline{\nu}_{\text{n}}$ but appreciably different from zero for $\nu_{\text{n}} < \overline{\nu}_{\text{n}}$, where $\overline{\nu}_{\text{n}}$ is the number of molecules (ions) in the largest of the nuclei occurring in practice. It is unessential for further reasoning how the density of distribution of the initial nuclei concentrations depends on ν_{n} for $\nu_{\text{n}} < \overline{\nu}_{\text{n}}$. It is important, however, that its dependence on ν_{n} be relatively weak compared with a 'jump' it experiences during transition from values $\nu_{\text{n}} < \overline{\nu}_{\text{n}}$ to $\nu_{\text{n}} > \overline{\nu}_{\text{n}}$.

Bearing in mind the estimative character of further reasoning, we shall use the approximate equality (5.11) without making additional note of it. Expressions (4.10) and (4.24) give the width $\Delta\zeta$ of the vapor prethreshold metastability region on the ζ-axis:

$$\Delta\zeta \sim \nu_{\text{n}}^{-2/3}\zeta_{\text{th}} \,. \tag{5.66}$$

Expressions (4.10) and (4.25) indicate that, with a change of number ν_{n}, the vapor prethreshold metastability region shifts along the ζ-axis at an approximate rate of $\partial\zeta_{\text{th}}/\partial\nu_{\text{n}}$ which, according to formula (4.7), is determined from the relation

$$\frac{\partial\zeta_{\text{th}}}{\partial\nu_{\text{n}}} \sim -\frac{\zeta_{\text{th}}}{\nu_{\text{n}}} \,. \tag{5.67}$$

As the vapor metastable state is being formed, its supersaturation ζ occurs in the prethreshold region not only with respect to the nuclei for which $\nu_{\text{n}} \approx \overline{\nu}_{\text{n}}$ but also with respect to all the nuclei for which ν_{n} lies within the interval $\overline{\nu}_{\text{n}} - \Delta\nu_{\text{n}} < \nu_{\text{n}} < \overline{\nu}_{\text{n}}$ of width $\Delta\nu_{\text{n}}$ satisfying the estimate

$$\Delta\zeta\Big|_{\nu_{\text{n}} \approx \overline{\nu}_{\text{n}}} \sim \left|\frac{\partial\zeta_{\text{th}}}{\partial\nu_{\text{n}}}\right|_{\nu_{\text{n}} \approx \overline{\nu}_{\text{n}}} \Delta\nu_{\text{n}} \,. \tag{5.68}$$

All these nuclei are likely to become centers around which supercritical droplets will form.

It follows from Eqns (5.66) – (5.68) that

$$\frac{\Delta\nu_{\text{n}}}{\overline{\nu}_{\text{n}}} \approx \overline{\nu}_{\text{n}}^{-2/3} \,. \tag{5.69}$$

This expression gives the estimate of the width $\Delta\nu_{\text{n}}$ of the interval $\overline{\nu}_{\text{n}} - \Delta\nu_{\text{n}} < \nu_{\text{n}} < \overline{\nu}_{\text{n}}$ in which supercritical droplets are actually formed. In accordance with the latter expression and the macroscopic nucleus size condition (4.6), one arrives at

$$\frac{\Delta\nu_{\text{n}}}{\overline{\nu}_{\text{n}}} \ll 1 \,. \tag{5.70}$$

This means that the width of the interval $\overline{\nu}_{\text{n}} - \Delta\nu_{\text{n}} < \nu_{\text{n}} < \overline{\nu}_{\text{n}}$ is relatively small.

The total number of newly-formed supercritical droplets being the most important kinetic characteristic of the nucleation process, the following condition must be satisfied in order that the kinetic theory of nucleation as described in Sections 5.1 – 5.4 be applicable in the case of polydispersity of soluble condensation nuclei:

$$\left|\frac{1}{N}\frac{\partial N}{\partial\nu_{\text{n}}}\right|_{\nu_{\text{n}} \approx \overline{\nu}_{\text{n}}} \Delta\nu_{\text{n}} \ll 1 \,. \tag{5.71}$$

This latter condition warrants the smallness of a relative change of the number of droplets N with changing ν_{n} in the range $\overline{\nu}_{\text{n}} - \Delta\nu_{\text{n}} < \nu_{\text{n}} < \overline{\nu}_{\text{n}}$.

According to formula (3.12), the dependence of N on ν_{n} is especially strong when $h \gg 1$. In the same case, this dependence turns out to be the strongest of all the ν_{n}-dependences of the kinetic characteristics of nucleation. Therefore, the condition (5.71) at $h \gg 1$ provides a criterion by which to judge that the polydispersity of condensation nuclei does not practically affect the kinetic characteristics of nucleation over the interval $\overline{\nu}_{\text{n}} - \Delta\nu_{\text{n}} < \nu_{\text{n}} < \overline{\nu}_{\text{n}}$.

When the nucleation stage is dominated by the free-molecule supercritical droplet growth, it follows from relations (3.13), (5.17) at $h \gg 1$ that

$$\frac{\partial N}{\partial\nu_{\text{n}}} \sim \frac{14m+9}{6m}\frac{N}{\nu_{\text{n}}} \,. \tag{5.72}$$

Using Eqns (5.69) and (5.72), condition (5.71) can be reduced to the inequality

$$\frac{14m+9}{6m}\,\overline{\nu}_{\text{n}}^{-2/3} \ll 1 \,. \tag{5.73}$$

For soluble macroscopic condensation nuclei, inequality (5.73) is satisfied if the parameter m is not too small.

When the nucleation stage is dominated by the diffusive growth of supercritical droplets, it follows from relations (3.13), (5.20) at $h \gg 1$ that

$$\frac{\partial N}{\partial\nu_{\text{n}}} \sim \frac{7m+9}{12m}\frac{N}{\nu_{\text{n}}} \,. \tag{5.74}$$

Using Eqns (5.69) and (5.74), condition (5.71) can be reduced to the inequality

$$\frac{7m+9}{12m}\,\overline{\nu}_{\text{n}}^{-2/3} \ll 1 \,. \tag{5.75}$$

For soluble macroscopic condensation nuclei, inequality (5.75) is satisfied if the parameter m is not too small.

Thus, the polydispersity of soluble condensation nuclei may be taken into consideration in the kinetic theory of nucleation detailed in Sections 5.1–5.4 of the present review. To this end, it is necessary in all the formulas of this theory to understand by ν_{n} the quantity $\overline{\nu}_{\mathrm{n}}$ [in agreement with inequality (5.70)] and by $\eta(-\infty)$ the total initial concentration of condensation nuclei for which ν_{n} lies within the interval $\overline{\nu}_{\mathrm{n}} - \Delta\nu_{\mathrm{n}} < \nu_{\mathrm{n}} < \overline{\nu}_{\mathrm{n}}$ where the formation of supercritical droplets occurs. The width $\Delta\nu_{\mathrm{n}}$ of this interval is given by relation (5.69). It is worthwhile to note that the inequalities (5.73) and (5.75) are equivalent to inequality (5.70) to within factors $(14m+9)/(6m)$ and $(7m+9)/(12m)$, respectively, as can be seen from approximate equality (5.69).

It may be concluded that the macroscopic size of soluble condensation nuclei underlying their polydispersity accounts for the very possibility of taking this property into consideration.

6. Thermodynamics of nucleation on insoluble wettable nuclei

Let us now pass to the consideration of thermodynamics of nucleation on macroscopic wettable nuclei insoluble in the condensate. There are two scenarios for the formation of a droplet on an insoluble macroscopic condensation nuclei. According to the first, the process starts from the formation of a uniformly thin film of the condensate around the nucleus. As the condensation progresses, this film becomes thicker and turns into a macroscopic droplet with a central nucleus. In the alternative scenario, isolated small liquid lenses with a finite angle of contact first arise at the nucleus surface. As they increase in size, they may coalesce into a thick continuous film coating the nucleus, which further develops into a droplet. The first of these scenarios of heterogeneous nucleation is of special interest because it allows one to observe an intense nucleation process at a very low vapor supersaturation. Therefore, it will be the central issue of the forthcoming discussion. An obvious distinction between the two scenarios is due to the difference in nuclear sizes and peculiar features of surface wetting. The latter depend on surface forces at the solid–vapor, solid–liquid, and liquid–vapor interfaces. Investigations into conditions for the realization of these scenarios and the role of surface forces in the nucleation process constitute the main task of thermodynamics of heterogeneous nucleation on macroscopic wettable nuclei and will be a subject-matter of further discussion.

6.1 Disjoining pressure and the work of wetting of an insoluble nucleus

The mutual interference between surface layers on the opposite sides of the film is an important issue in the description of the thin film of the condensate enveloping an insoluble wettable macroscopic condensation nucleus. Following Refs [31, 70, 71], we shall regard this reciprocal influence as overlap of the droplet surface layers located between the condensation nucleus and the vapor.

It has been shown in Ref. [31] that the effect of overlapping the surface layers of a thin film in nucleation thermodynamics can be described in terms of disjoining pressure [72, 73] and the work of nucleus wetting in the droplet which depends on its size.

Thus, let an R-radius droplet being formed have a central insoluble, wettable, incompressible, and uncharged nucleus of radius R_{n} (see Fig. 1). Another variable in the description of the droplet, besides R, is ν determined by relation (2.2) and indicating the number of condensate molecules which the droplet could contain had it no condensation nucleus at all. By ν_{n} is meant the number of condensate molecules in the nucleus volume:

$$\nu_{\mathrm{n}} = \frac{4\pi R_{\mathrm{n}}^3}{3 v_\alpha} \,. \tag{6.1}$$

Evidently, the difference $\nu - \nu_{\mathrm{n}}$ is the true number of condensate molecules in the droplet. The difference $R - R_{\mathrm{n}}$ stands for the film thickness h (we hope that the use of the symbol h in a sense different from that which it has in Sections 3, 5, and 7 will cause no misunderstanding).

If the disjoining pressure of an h-thick film is denoted as $\Pi(h)$, the dimensionless chemical potential b_ν of the condensate in a droplet can be represented in the form [74, 31]

$$b_\nu = \frac{2}{3}\, a\nu^{-1/3} - \frac{v_\alpha \Pi(h)}{k_{\mathrm{B}}T} \,. \tag{6.2}$$

For stable films, the isotherm $\Pi(h) > 0$, and the disjoining pressure lowers the chemical potential of the condensate [in agreement with Eqn (6.2)], whereas the capillary pressure, on the contrary, raises it. As a result, the qualitative behavior of the ν-dependence of b_ν given by relation (6.2) corresponds to that shown in Fig. 2.

The dimensionless work F of formation of an R-radius droplet on an insoluble wettable macroscopic nucleus of radius R_{n} can be written, on account of Eqns (2.2) and (6.1), as [31]

$$F = a\nu^{2/3} - b(\nu - \nu_{\mathrm{n}}) + f \,, \tag{6.3}$$

where f is the work of wetting of the nucleus, depending on the droplet size and expressed in $k_{\mathrm{B}}T$ units. Taking into consideration the relationship between the work of droplet formation and the chemical potential and integrating relation (2.22) with the boundary condition

$$F\Big|_{\nu=\nu_{\mathrm{n}}} = 0 \,, \tag{6.4}$$

we arrive, bearing in mind formulas (2.2) and (6.1), at an expression linking the work of wetting to the disjoining pressure [31]:

$$f = -\frac{4\pi}{k_{\mathrm{B}}T}\int_{R_n}^{R} \widetilde{R}^2 \Pi(\widetilde{R} - R_{\mathrm{n}})\,\mathrm{d}\widetilde{R} - a\nu_{\mathrm{n}}^{2/3} \,. \tag{6.5}$$

It follows from the last expression that as $R \to \infty$, we have $f \to f_*$, where

$$f_* = -\frac{4\pi}{k_{\mathrm{B}}T}\int_{R_n}^{\infty} \widetilde{R}^2 \Pi(\widetilde{R} - R_{\mathrm{n}})\,\mathrm{d}\widetilde{R} - a\nu_{\mathrm{n}}^{2/3} \,. \tag{6.6}$$

On the other hand, as $R \to \infty$, the work of wetting of a nucleus in the bulk liquid is described by the Dupré formula

$$f_* = \frac{4\pi R_{\mathrm{n}}^2 (\sigma_{\gamma\alpha} - \sigma_{\gamma\beta})}{k_{\mathrm{B}}T} \,, \tag{6.7}$$

where, $\sigma_{\gamma\alpha}$ and $\sigma_{\gamma\beta}$ stand for the surface tensions at the nucleus – condensate and nucleus – vapor interfaces, respectively. The comparison of relation (6.6) with (6.7), taking into account Eqn (6.1) and the definition (2.29), allows for the conclusion that

$$\frac{1}{R_{\mathrm{n}}^2}\int_{R_{\mathrm{n}}}^{\infty} \widetilde{R}^2 \Pi(\widetilde{R}-R_{\mathrm{n}})\,\mathrm{d}\widetilde{R} = \sigma_{\gamma\beta}-\sigma_{\gamma\alpha}-\gamma\,. \tag{6.8}$$

The quantity

$$S \equiv \sigma_{\gamma\beta}-\sigma_{\gamma\alpha}-\gamma \tag{6.9}$$

is called *the coefficient of spreading*. For the case of complete wetting, when the film entirely and uniformly covers the substrate, $S > 0$. It should be noted that the definition of this quantity includes nonequilibrium surface tension $\sigma_{\gamma\beta}$ over the nucleus surface having no adsorbed vapor molecules. For this reason, the coefficient of spreading obtained in this way is nonequilibrium too. This explains why it may be either negative or positive, unlike the equilibrium coefficient of spreading, $S_{\mathrm{e}} \equiv \sigma_{\gamma\beta}^{(\mathrm{e})}-\sigma_{\gamma\alpha}-\gamma$, found at equilibrium surface tension $\sigma_{\gamma\beta}^{(\mathrm{e})}$ which occurs at the nuclear surface with an equilibrium adsorption layer. For the equilibrium coefficient of spreading, one always finds $S_{\mathrm{e}} \leqslant 0$ [75].

It follows from relations (6.2), (6.3), and (6.5) that condensation around insoluble wettable nuclei represents a situation in which the construction of thermodynamics may be started either from the derivation of an expression for the condensate chemical potential in a droplet (namely, for the contribution of disjoining pressure to the chemical potential) or from giving an explicit expression for the dependence of the work of droplet formation (namely, a work of nucleus wetting) on the thickness of the film condensing on the nucleus.

6.2 Formation of a film uniform in thickness and constraints on the coefficient of condensate spreading and the size of the condensation nucleus

Depending on the surface wetting conditions and nucleus size, the condensed film can be either uniform in thickness [14, 31, 76] or stratified into a thin wetting layer and a lens droplet attached to it [5, 12, 76]. Certainly, the disjoining pressure isotherm totally determines not only the wettability conditions but also the exact film thickness profile [72, 77 – 79]. However, it is difficult to measure the disjoining pressure isotherm as a whole, and its theoretical description also poses a complicated problem because surface forces depend on many factors which acquire significance in different thickness intervals [72]. At the same time, it is not necessary to know the entire disjoining pressure isotherm in the theory of heterogeneous nucleation when discussing the conditions of droplet formation in the form of films uniform in thickness at $S > 0$. In many cases, these conditions may be estimated knowing only the initial segment of the disjoining pressure isotherm $\Pi(h)$ on the h-axis.

The disjoining pressure isotherm for a fairly thin film depends on the surface adsorption properties. For flat adsorption films, the dependence of adsorption Γ on the vapor molecule concentration n in the initial portion of the isotherm may be presented in the form [80]

$$\Gamma = K_{\Gamma}\, n^{1/w}\,, \tag{6.10}$$

where K_{Γ} is a certain constant which depends on the nuclear matter and adsorbate and can be determined experimentally; the parameter w is unity for an energetically uniform adsorbing surface (the Henry isotherm) and does not exceed 5 for an energetically nonuniform adsorbing surface (the Freundlich isotherm).

The adsorption asymptotics of the disjoining pressure $\Pi(h)$, corresponding to the adsorption isotherm (6.10), have the form [81, 82]

$$\Pi(h) = -\frac{w k_{\mathrm{B}} T}{v_{\alpha}} \ln\frac{h}{l_{\mathrm{A}}}\,, \tag{6.11}$$

where $l_{\mathrm{A}} \equiv K_{\Gamma} v_{\alpha} n_{\infty}^{1/w}$ is a certain characteristic thickness of the adsorption film. Despite the minus sign in the right-hand side of Eqn (6.11), $\Pi(h) > 0$ because the asymptotics (6.11) hold for $h < l_{\mathrm{A}}$ where the logarithm is negative.

The substitution of Eqn (6.11) into (6.5) leads to an expression for the adsorption asymptotics of the work of wetting of a nucleus at $h \ll R_{\mathrm{n}}$:

$$f(h) = -\frac{4\pi R_{\mathrm{n}}^2 w h}{v_{\alpha}}\left(1-\ln\frac{h}{l_{\mathrm{A}}}\right) - a v_{\mathrm{n}}^{2/3}\,. \tag{6.12}$$

Such asymptotics for the work of wetting are valid in the region of very thin films a few angstroms in thickness, whereas exponential asymptotics for the work of wetting hold for thicker films (some ten angstroms or more). These asymptotics are conditioned by the structural forces [72, 73, 31]

$$f(h) = f_*\left[1 - C\exp\left(-\frac{h}{l}\right)\right], \tag{6.13}$$

where l is a parameter having the sense of a correlation length in a liquid film around the nucleus, and C is a positive constant. Relation (6.13) implies a monotonic trend towards a limiting work of wetting f_*. It follows from Eqns (6.5), (6.8), and (6.9) that $\Pi(h) \geqslant 0$ and $S > 0$. The asymptotics (6.13) are applicable to the curved surface of a nucleus of radius R_{n} on condition that

$$\frac{R_{\mathrm{n}}}{l} \gg 1\,. \tag{6.14}$$

Evidently, the inequality (6.14) has the sense of the macroscopicity condition for insoluble nuclei.

Regarding the exponential asymptotics (6.13) as valid to the smallest film thickness, as in Ref. [31], it is possible to formulate the necessary condition for the presence of a maximum in the chemical potential curve of the condensate in an embryo. Indeed, it follows from formulas (6.5) and (6.13) that the derivative $\Pi'(h)$ of disjoining pressure with respect to film thickness, taking into account inequality (6.14), takes the form

$$\Pi'(h) = \frac{k_{\mathrm{B}} T}{4\pi R^2}\,\frac{f_* C}{l^2}\exp\left(-\frac{h}{l}\right). \tag{6.15}$$

On account of Eqns (6.2), (2.2), (6.15), and (6.7), Eqn (2.25) may be written as an equation in the radius R_0:

$$\frac{2\gamma}{R_{\mathrm{n}}^2} = \frac{(\sigma_{\gamma\beta}-\sigma_{\gamma\alpha})C}{l^2}\exp\left(-\frac{R_0-R_{\mathrm{n}}}{l}\right). \tag{6.16}$$

The constant C can be found with the aid of condition (6.4) as

$$C = \frac{S}{\sigma_{\gamma\beta}-\sigma_{\gamma\alpha}}\,. \tag{6.17}$$

The substitution of relation (6.17) into Eqn (6.16) gives

$$R_0 = R_\mathrm{n} + l \ln \frac{S R_\mathrm{n}^2}{2\gamma l^2} \,. \tag{6.18}$$

In order to have $R_0 > R_\mathrm{n}$, it is necessary to fulfill the condition

$$S > \frac{2\gamma l^2}{R_\mathrm{n}^2} \,, \tag{6.19}$$

which is apt to be easily broken at a fairly small but positive coefficient S of spreading. If this condition is violated, the chemical potential maximum cannot be realized at a physically meaningful (positive) film thickness.

Condition (6.19) should be understood as a constraint on the applicability of the exponential asymptotics (6.13) for the work of wetting of the nucleus at a small film thickness, since this condition is linked to the finite $\Pi'(h)$ value for the exponential asymptotics as $h \to 0$. Because in reality $\Pi'(h) \to -\infty$ as $h \to 0$, the equation for the maximum chemical potential of the condensate in an embryo always has a physically meaningful root.

This gives reason to assume that there is a thickness h_p such that the adsorption approximation (6.12) operates for $h < h_\mathrm{p}$, and the exponential approximation (6.13) to the work of wetting does for $h > h_\mathrm{p}$, the latter being characterized by a constant C' which, generally speaking, differs from the constant C determined from formula (6.17). The requirement of continuity of the work of wetting and its derivative at the point h_p leads, taking into account Eqns (6.1) and (2.29), to a system of equations

$$f_* \left[1 - C' \exp\left(-\frac{h_\mathrm{p}}{l} \right) \right] = -\frac{4\pi R_\mathrm{n}^2 w h_\mathrm{p}}{v_\alpha} \left(1 - \ln \frac{h_\mathrm{p}}{l_\mathrm{A}} \right) - \frac{4\pi R_\mathrm{n}^2}{k_\mathrm{B} T} \gamma \,,$$

$$f_* \frac{C'}{l} \exp\left(-\frac{h_\mathrm{p}}{l} \right) = \frac{4\pi R_\mathrm{n}^2 w}{v_\alpha} \ln \frac{h_\mathrm{p}}{l_\mathrm{A}} \,. \tag{6.20}$$

In this system, the thickness h_p of patching and constant C' are unknown. The use of the second equation excludes the constant C'. Then, the first equation in the system (6.20), taking into account relations (6.7) and (6.9), assumes the form

$$(l + h_\mathrm{p}) \ln \frac{h_\mathrm{p}}{l_\mathrm{A}} = h_\mathrm{p} - \frac{S v_\alpha}{w k_\mathrm{B} T} \,. \tag{6.21}$$

Bearing in mind that approximation (6.12) holds for $h < l_\mathrm{A}$, it may be concluded that physically correct solutions correspond to negative values of the left-hand side of Eqn (6.21). Hence the solvability condition for the system (6.20) in the form

$$S > \frac{w k_\mathrm{B} T l_\mathrm{A}}{v_\alpha} \,. \tag{6.22}$$

The last condition can be interpreted in the following way. Setting the behavior of the curve of $\Pi(h)$ at a fairly small thickness h by the adsorption asymptotics (6.11), we thus give the integral $\int_0^h \Pi(\xi)\,\mathrm{d}\xi$ for small h. In our case, this integral is positive because approximation (6.11) holds for $h < l_\mathrm{A}$ where the integrand is positive. Taking into consideration formula (6.11), we have

$$\int_0^{l_\mathrm{A}} \Pi(\xi)\,\mathrm{d}\xi > \frac{w k_\mathrm{B} T l_\mathrm{A}}{v_\alpha} \,. \tag{6.23}$$

According to Eqns (6.8) and (6.9), the following relation must be fulfilled for a stable film uniform in thickness in the limit of a flat nucleus surface ($R_\mathrm{n} \to \infty$):

$$S > \int_0^{l_\mathrm{A}} \Pi(\xi)\,\mathrm{d}\xi \,. \tag{6.24}$$

Hence, using relation (6.23), inequality (6.22) ensues as a necessary condition of complete wetting.

We shall now discuss the constraints imposed on the condensation nucleus size by the requirement of uniform film thickness. To this end, films nonuniform in thickness need to be included into consideration.

The equation of the droplet profile, describing the property of constancy of the chemical potential across the film surface, assumes the form

$$P_\mathrm{L} - \Pi = \Delta P = \mathrm{const} \,, \tag{6.25}$$

where P_L and Π are local capillary and disjoining pressures, respectively, and ΔP is the pressure difference between the bulk liquid and gaseous phases at a given chemical potential.

Let us now assume that the profile of a droplet nonuniform in thickness formed on an insoluble nucleus under incomplete wetting has the form of a small lens in contact with the thin film coating the nucleus. In the top part, at $h = H$, this lens is almost spherical and has a certain curvature radius R_d. In the lower part, it features a transition zone to the uniform thin film of thickness h_e. Then, it follows from relation (6.25) that

$$\frac{2\gamma}{R_\mathrm{d}} - \frac{2\gamma}{R_\mathrm{n} + h_\mathrm{e}} = \Pi(H) - \Pi(h_\mathrm{e}) \,. \tag{6.26}$$

It is immediately obvious that a monotonically decreasing $\Pi(h)$ cannot satisfy Eqn (6.26). Consideration of the limiting case of a flat substrate as $R_\mathrm{n} \to \infty$ leads to the conclusion that the curve $\Pi(h)$ must have a negative portion if a lens-like droplet is to be formed. A typical isotherm of disjoining pressure in the case of incomplete wetting is shown in Fig. 6.

If the film thickness h is so small that it falls on the starting branch of the disjoining pressure isotherm with $\Pi(h) > \Pi(h_\mathrm{max})$, such a film cannot layered into an even thinner film and a lens-droplet. Otherwise, it would be in conflict with Eqn (6.26). If the nucleus is so small that the film which condensates on it corresponds to the chemical potential maximum and enters the aforementioned region of very thin

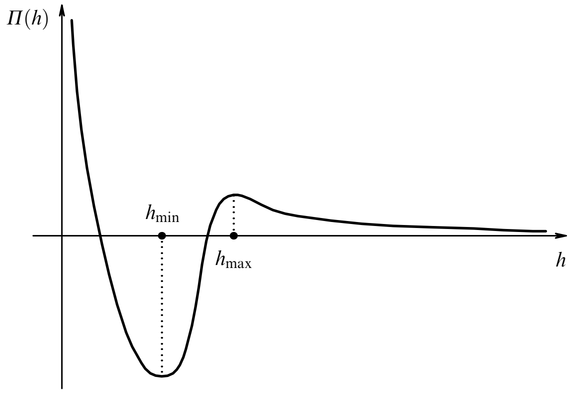

Figure 6. Typical isotherm of the disjoining pressure $\Pi(h)$ for the case of incomplete wetting.

films, the layering is feasible only during further embryo growth. In this case, the vapor threshold supersaturation giving the barrierless nucleation condition is determined in the same manner as in the case of condensation on completely wettable nuclei.

According to Eqns (2.25), (6.2), (2.2), and (2.29), the film thickness h_0 for an embryo with the maximum chemical potential of the condensate is defined as

$$\Pi'(h_0) = -\frac{2\gamma}{(R_n + h_0)^2}\,. \tag{6.27}$$

Assuming that the derivative $\Pi'(h)$ grows monotonically on the initial part of the curve, the condition of a critical embryo falling into the said region of small film thicknesses can be written as

$$\Pi'(h_0) < \Pi'(h_1)\,,$$

where h_1 is the smallest root of the equation $\Pi(h) = 0$, or in the form

$$\frac{2\gamma}{(R_n + h_0)^2} > -\Pi'(h_1)\,.$$

This condition is reduced to a constraint on R_n from above:

$$R_n + h_0 < \sqrt{-\frac{2\gamma}{\Pi'(h_1)}}\,. \tag{6.28}$$

There is no such constraint when conditions (6.19) and (6.22) of the applicability of exponential approximation (6.13) to the films completely wetting nuclei are satisfied.

Deryagin and Zorin [73] have demonstrated that water films on quartz have $h_1 \approx 70$ Å and $\Pi'(h_1) \approx -7 \times 10^{13}$ dyn cm^{-2}. If $\gamma = 70$ dyn cm^{-1}, then $R_n + h_0 < 140$ Å. Because $h_0 \lesssim h_1$, this complies with very small nuclei going almost beyond the condition of disjoining pressure applicability to the description of the properties of thin films formed on these nuclei.

If the difference between the maximum and minimum disjoining pressures is denoted as $\Delta\Pi$, then $\Delta\Pi = \Pi(h_{\max}) - \Pi(h_{\min})$ for the isotherm in Fig. 6. Because $\Pi(H) - \Pi(h_e) \leqslant \Delta\Pi$, the following inequality can be written using Eqn (6.26) and taking $h_e \ll R_n$:

$$\frac{R_n}{R_d} - 1 \leqslant \frac{R_n\,\Delta\Pi}{2\gamma}\,. \tag{6.29}$$

Analysis of this inequality shows that rather a large lens-droplet may cover a major part of the nucleus. When the lense-droplet radius R_d is bigger than that of the nucleus (R_n), the droplet spreads over the entire nuclear surface giving rise to a film uniform in thickness. In this situation, the capillary pressure appears to supersede the fine structure of disjoining pressure. Conversely, when $R_d \ll R_n$, it follows from inequality (6.29) that $R_d \gtrsim 2\gamma/\Delta\Pi$ and therefore $R_n \gg 2\gamma/\Delta\Pi$. According to Ref. [73], for water films on quartz one can find $\Delta\Pi \approx 5 \times 10^3$ dyn cm^{-2}. If $\gamma = 70$ dyn cm^{-1}, then $\gamma/\Delta\Pi \approx 10^{-2}$ cm and the inequality $R_n \gg 2\gamma/\Delta\Pi$ is equivalent to $R_n \gg 10^{-2}$ cm.

It follows from what has been said before about the situation when the radius R_d is larger than R_n that

$$R_n \lesssim \frac{2\gamma}{\Delta\Pi}\,. \tag{6.30}$$

This inequality reflects the condition that a liquid film should uniformly spread over the nucleus. Note that the bigger $\Delta\Pi$ [i.e. the deeper the $\Pi(h)$ minimum or the larger the angle of contact], the narrower the nuclear size region satisfying condition (6.30).

To summarize, if the constraining conditions (6.19) and (6.22) imposed on the initial spreading coefficient are satisfied, there is a range of condensation nucleus sizes within which it is possible to use the exponential approximation (6.13) to the work of wetting of a nucleus in the theory of nucleation. If condition (6.19) is violated, the adsorption asymptotics (6.12) for the work of wetting of a nucleus may be employed in calculations. If condition (6.22) is violated, the range of condensation nucleus sizes over which the adsorption and exponential asymptotics of disjoining pressure are operative in the theory of nucleation for uniformly thick films is significantly restricted by condition (6.28). For all that, the process of heterogeneous nucleation by means of formation of uniformly thick films around nuclei proceeds over the entire range of nuclear sizes satisfying the condition (6.30), even in substances with finite angles of contact.

6.3 Thermodynamic characteristics of nucleation on insoluble wettable nuclei in the prethreshold region of vapor metastability

Let us now assume that either conditions (6.19) and (6.22) or (6.28) and (6.30) are fulfilled. Then, the chemical potential of a fluid condensed on the insoluble wettable nucleus in a droplet is described by formula (6.2) and shows a maximum depending on the droplet size. The linkage between the coordinates of this maximum in variables R and ν is established, in accordance with formula (2.2), by the equation

$$\nu_0 = \frac{4\pi R_0^3}{3 v_\alpha}\,. \tag{6.31}$$

Because of relation (6.2) and the usually satisfied condition

$$\frac{v_\alpha \Pi(h_0)}{k_B T} \ll \frac{2a}{3\nu_0^{1/3}}\,, \tag{6.32}$$

there appears an equation

$$b_{\text{th}} = \frac{2a}{3\nu_0^{1/3}} \tag{6.33}$$

for the threshold value b_{th} of the vapor chemical potential, above which the barrierless droplet formation on condensation nuclei occurs. On the assumption that

$$\nu_0^{1/3} \gg \frac{2a}{3}\,, \tag{6.34}$$

from Eqn (6.33) follows $b_{\text{th}} \ll 1$. Then, taking into account relation (2.21) in agreement with Eqn (6.33), the vapor threshold supersaturation ζ_{th} is given by

$$\zeta_{\text{th}} = \frac{2a}{3\nu_0^{1/3}}\,. \tag{6.35}$$

Let us use relation (4.10), as in Section 4.2 above, to assign the vapor supersaturation ζ through its deviation ε from the threshold value ζ_{th}. In the subthreshold region of vapor metastability, $0 < \zeta < \zeta_{\text{th}}$, we have $0 < \varepsilon < 1$.

Let us introduce p_0 by the formula

$$p_0 \equiv \frac{3^9}{2^3}\frac{\nu_0^7}{a^3}\left(\left|\frac{\partial^2 b_\nu}{\partial \nu^2}\right|_0\right)^3 . \tag{6.36}$$

The use of Eqns (6.33) and (6.36) in the general relations (4.13)–(4.15) yields

$$\begin{aligned} \nu_{\mathrm{e}} &= \nu_0\left(1 - 2^{1/2} 3 p_0^{-1/6}\varepsilon^{1/2}\right) , \\ \nu_{\mathrm{c}} &= \nu_0\left(1 + 2^{1/2} 3 p_0^{-1/6}\varepsilon^{1/2}\right) , \end{aligned} \tag{6.37}$$

$$\Delta\nu_{\mathrm{e}} = \Delta\nu_{\mathrm{c}} = 2^{-1/4}\, 3a^{-1/2}\nu_0^{2/3} p_0^{-1/12}\varepsilon^{-1/4} , \tag{6.38}$$

$$\Delta F = \frac{2^{7/2}}{3}\, a\nu_0^{2/3} p_0^{-1/6}\varepsilon^{3/2} . \tag{6.39}$$

It follows from (6.39) that in the prethreshold region (4.23) of vapor metastability one finds

$$\varepsilon^{1/2} \approx a^{-1/3}\nu_0^{-2/9} p_0^{1/18} , \tag{6.40}$$

where it is taken into consideration that the range of $(\Delta F)^{1/3}$ variation is significantly narrower than that of ΔF variation; therefore, it is roughly assumed that

$$\left(\frac{3\Delta F}{2^{7/2}}\right)^{1/3} \approx 1 .$$

A more refined variant of the relation (6.40) which defines a characteristic quantity $\varepsilon^{1/2}$ in the region (4.23) will be given in Section 7.1.

According to Eqns (6.38) and (6.40), it is readily shown that

$$\Delta\nu_{\mathrm{e}} = \Delta\nu_{\mathrm{c}} \approx 2^{-1/4}\, 3a^{-1/3}\nu_0^{7/9} p_0^{-1/9} . \tag{6.41}$$

Expression (4.23) implies that inequalities (2.18) and (4.22) are fulfilled. The latter inequality taken together with equality (4.21) (which is independent of specific nature of macroscopic condensation nuclei) from Section 4.2 ensures the fulfilment of conditions (2.17) for the applicability of quadratic approximations to the work of formation of near-equilibrium and near-critical droplets.

In the exponential approximation (6.13) to the work of wetting of a nucleus, expressions (6.2), (6.5), (6.7), (6.17), (6.31), and (6.36) collectively lead to

$$p_0 = \frac{\nu_0}{k} , \tag{6.42}$$

where k is determined from the equality

$$k \equiv \frac{4\pi l^3}{3 v_\alpha} . \tag{6.43}$$

If the logarithm in Eqn (6.18) is not too large and the macroscopic nucleus size condition (6.14) is fulfilled, then we get

$$R_0 \approx R_{\mathrm{n}} . \tag{6.44}$$

This relation is satisfied with good accuracy even without the assumption of the exponential approximation to the work of wetting of a nucleus. It can be seen from formulas (6.31) and (6.44) that ν_0 is approximately equal to the number of liquid molecules in a volume equivalent to the nuclear volume.

In accordance with Eqns (6.31), (6.42)–(6.44), one obtains

$$p_0 \approx \left(\frac{R_{\mathrm{n}}}{l}\right)^3 , \tag{6.45}$$

which allows p_0 to be found from R_{n} and l in the framework of the exponential approximation to the work of wetting of a nucleus. It follows from relation (6.45) and the condition (6.14) of nucleus macroscopicity that

$$p_0^{1/3} \gg 1 . \tag{6.46}$$

The strong inequality (6.46) is valid even without the assumption of the exponential approximation to the work of wetting of a nucleus.

If relations (6.40) and (6.41) are represented with the aid of Eqns (6.31), (6.44) and (6.45) as

$$\varepsilon^{1/2} \approx \left(\frac{3}{4\pi}\right)^{2/9} a^{-1/3}\left(\frac{v_\alpha^{1/3}}{l}\right)^{2/3}\left(\frac{l}{R_{\mathrm{n}}}\right)^{1/2} , \tag{6.47}$$

$$\Delta\nu_{\mathrm{e}} = \Delta\nu_{\mathrm{c}} \approx 2^{-1/4}\, 3\left(\frac{4\pi}{3}\right)^{7/9} a^{-1/3}\left(\frac{l}{v_\alpha^{1/3}}\right)^{7/3}\left(\frac{R_{\mathrm{n}}}{l}\right)^2 \tag{6.48}$$

and characteristic estimates $a \sim 10$ and $v_\alpha^{1/3}/l \sim 10^{-1}$ are taken into consideration, condition (6.14) of macroscopic nuclear size also underlies inequalities (4.25) and (2.19).

It follows from Eqns (6.2), (6.5), (6.7), (6.13), (6.17), (6.31), (6.37), and (6.45) that the inequality

$$\frac{1}{3}\left(\frac{2\varepsilon R_{\mathrm{n}}}{l}\right)^{1/2} \ll 1 \tag{6.49}$$

must be fulfilled, if the applicability condition (4.12) for parabolic approximation (4.11) over the interval $\nu_{\mathrm{e}} \leqslant \nu \leqslant \nu_{\mathrm{c}}$ is to be satisfied in the case of exponential approximation to the work of wetting of a nucleus. Taking into account relation (6.47) and the characteristic estimates $a \sim 10$ and $v_\alpha^{1/3}/l \sim 10^{-1}$, leads to the conclusion that the inequality (6.49) really holds.

It follows from Eqns (6.37), (6.46), and (4.25) that

$$\nu_{\mathrm{e}} \approx \nu_0 , \qquad \nu_{\mathrm{c}} \approx \nu_0 . \tag{6.50}$$

Evidently, relations (4.25), (2.19), and (6.50) hold true regardless of the exponential approximation to the work of wetting of a nucleus.

Let us take the quantities ν_0 and p_0 as initial parameters of the kinetic theory of nucleation. The relationship between ν_0 and R_{n} is easy to establish from Eqns (6.31) and (6.44). Also, the relationship between p_0 and l is easily found from approximate equality (6.45) using the exponential approximation to the work of wetting of condensation nuclei; this, however, requires $|\partial^2 b_\nu/\partial\nu^2|_0$ to be known in the general case, in agreement with formula (6.36). It is possible to do both thermodynamically (using the whole disjoining pressure isotherm in thin liquid films at a surface corresponding to the nucleus) and based on experimental nucleation kinetics data (by solving the inverse problem of nucleation kinetics).

The choice of quantities ν_0 and p_0 as initial parameters of the kinetic theory of nucleation on insoluble wettable nuclei provides a basis for the development of this theory in Section 7 in a form independent of whether the exponential approximation to the work of wetting of a nucleus is valid or not.

7. Kinetics of nucleation on insoluble wettable nuclei

We now pass to consideration of the nucleation kinetics of droplets having the form of liquid films enveloping insoluble wettable nuclei. The mechanisms of film formation at a late stage of nucleation (the Ostwald ripening stage) have been described in Refs [83, 84]. Specific features of island films in multicomponent systems have been subjected to analysis in Refs [84, 85]. Condensation kinetics for the instantaneous creation of vapor supersaturation creation on insoluble charged nuclei have been constructed in Refs [40, 86 – 94], and for gradual vapor supersaturation in Refs [35 – 39, 95, 96]. Sections 7.1 – 7.5 will be based on the results of kinetic studies of continuous film nucleation on insoluble macroscopic wettable nuclei reported in Refs [41, 97]. The process of nucleation on insoluble wettable nuclei will be considered using the same approach as in Sections 5.1 – 5.5 concerning soluble nuclei.

7.1 Kinetic characteristics of nucleation on insoluble wettable nuclei

In the case of macroscopic wettable nuclei, relation (5.1) for a current vapor supersaturation at the nucleation stage remains valid regardless of their nature. Moreover, expression (5.2) also holds by virtue of inequality (3.16). Comments on formula (5.2) also remain true.

According to Eqn (3.38) and the equality $\Delta\nu_{\mathrm{e}} = \Delta\nu_{\mathrm{c}}$, the former expression (5.4) holds good in the case of the parabolic approximation (4.11) to the condensate chemical potential (regardless of the growth regime of supercritical droplets and the nature of condensation nuclei).

Similar to Section 5.1, $\tilde{\varepsilon}$ indicates the value of ε at $\zeta = \Phi_*$ introduced in agreement with relation (4.10). In other words, $\tilde{\varepsilon}$ is defined by formula (5.6), as before.

The use of the thermodynamic relation (6.39) in Eqn (5.4), taking into consideration formula (5.6), yields

$$\tilde{\varepsilon}^{1/2} \approx q a^{-1/3} \nu_0^{-2/9} p_0^{1/18}\,, \tag{7.1}$$

where

$$q = \begin{cases} \left[\dfrac{3}{2^{7/2}} \ln\left(\dfrac{\varkappa h}{6\pi \ln 2}\right)\right]^{1/3} & (h \gg 1)\,, \\ \left[\dfrac{3}{2^{7/2}} \ln\left(\dfrac{\varkappa}{6\pi \ln 2}\right)\right]^{1/3} & (h \ll 1)\,. \end{cases} \tag{7.2}$$

According to the last equation, the quantity q (as well as $\Delta F\big|_{\zeta=\Phi_*}$) is a function of dimensionless parameters $\varkappa$ and h. Again, these parameters are a convenient choice as independent free parameters of the theory, compatible, naturally, with its applicability conditions and the limitations $h \gg 1$ or $h \ll 1$ used in it. These limitations will be omitted in the formulas, to simplify their presentation.

Equation (7.1) defines more precisely the relation (6.40) which determines the quantity $\varepsilon^{1/2}$ characteristic of the interval (4.23), i.e. the prethreshold region of vapor metastability. This clarification can be represented, as above, in the form of the approximate equality (5.10), although quantities $\tilde{\varepsilon}^{1/2}$, $\varepsilon^{1/2}$, and q are now different from those in the case of soluble nuclei. It will be shown in Sections 7.3 and 7.4 that the approximate equality (5.11) remains valid in the case of insoluble wettable nuclei too. It follows from this equality and (5.10) that inequalities (5.12) and (4.25) also hold as before.

Substituting (6.39) into (5.9) and using relation (7.1), we obtain

$$\Gamma \approx 2^{5/2} q a^{2/3} \nu_0^{4/9} p_0^{-1/9}\,. \tag{7.3}$$

It follows from formulas (3.35), (3.37) taking into account Eqns (4.8), (5.2), (6.38), (6.50), and (7.1) that

$$t_{\mathrm{s}} \approx \frac{3}{2^{3/2}} \frac{\tau}{q\alpha} \frac{\nu_0^{8/9}}{a^{2/3} p_0^{2/9}}\,. \tag{7.4}$$

It can be found with the aid of Eqns (3.3), (5.2), and (6.35) that

$$t_* \approx \left(\frac{2}{3}\right)^{1/m} t_\infty \frac{a^{1/m}}{\nu_0^{1/(3m)}}\,. \tag{7.5}$$

It seems appropriate to proceed from the consideration of the free-molecule growth of supercritical droplets. The use of Eqns (5.2), (6.35), and (7.3) in (3.10), (3.11) yields

$$c \approx 2^{3/2}\, 3 \left(\frac{3}{2}\right)^{1/m} \frac{q m \tau}{\alpha t_\infty} \frac{\nu_0^{(7m+3)/(9m)}}{a^{(m+3)/(3m)} p_0^{1/9}}\,, \tag{7.6}$$

$$h \approx \frac{1}{12} \left(\frac{2}{3}\right)^{3/m} \frac{\eta(-\infty)}{q^2 n_\infty} \left(\frac{\alpha t_\infty}{m\tau}\right)^3 \frac{a^{(2m+9)/(3m)} p_0^{2/9}}{\nu_0^{(14m+9)/(9m)}}\,. \tag{7.7}$$

It follows from formula (3.47) taking into account Eqns (4.8), (5.2), (6.35), (6.38), (6.50), and (7.1) that

$$\frac{\Delta\rho}{\rho_{\mathrm{c}}} \approx \frac{a^{1/3}}{2^{1/2} q} \left(\frac{\nu_0}{p_0}\right)^{2/9} \frac{\Delta t}{t_{\mathrm{s}}}\,. \tag{7.8}$$

After representing $(\nu_0/p_0)^{2/9}$ with the aid of formulas (6.42) and (6.43) as

$$\left(\frac{4\pi}{3}\right)^{2/9} \left(\frac{l}{v_\alpha^{1/3}}\right)^{2/3},$$

and taking account of the approximate equality (5.11) and characteristic estimates $a \sim 10$, $l/v_\alpha^{1/3} \sim 10$, it is evident that the coefficient of the ratio $\Delta t/t_{\mathrm{s}}$ in Eqn (7.8) is much greater than unity. According to formula (7.8), in this case condition (3.46) is fulfilled with ample reserve provided condition (3.39) is satisfied.

Because the radius R_{c} of the critical droplet is bigger than the radius R_{n} of the condensation nucleus, it follows from the fulfilment of condition (3.46) that at the nucleation stage the characteristic radius of the droplet is much greater than the nuclear radius R_{n}. Therefore, at this stage, the quantity ν defined by equality (2.2) corresponds, with a high accuracy, to the true number of vapor molecules condensed by a droplet containing the insoluble condensation nucleus. This is an important premise of the kinetic theory of nucleation.

Formulas (3.12) – (3.14), (3.17), (3.22), (3.23), and (7.5) taken together with expressions (5.2), (6.35), (7.6), and (7.7) give all the most important kinetic characteristics of nucleation on insoluble wettable nuclei in the case of the free-molecule growth of supercritical droplets.

Let us now consider the diffusive growth of supercritical droplets. Using Eqns (5.2), (6.35), and (7.3) in (3.28), (3.29), we obtain

$$c \approx 2^{3/2}\, 3 \left(\frac{3}{2}\right)^{1/m} \frac{q m \tau_D}{t_\infty} \, \frac{v_0^{(7m+3)/(9m)}}{a^{(m+3)/(3m)} p_0^{1/9}} \,, \tag{7.9}$$

$$h \approx \frac{(3\pi)^{1/2}}{2^{11/4}} \left(\frac{2}{3}\right)^{3/(2m)} \frac{\eta(-\infty)}{q^{1/2} n_\infty} \left(\frac{t_\infty}{m\tau_D}\right)^{3/2} \frac{a^{(m+9)/(6m)} p_0^{1/18}}{v_0^{(7m+9)/(18m)}} \,. \tag{7.10}$$

It has been mentioned in Section 3.4 that condition (3.46) is fulfilled with ample reserve in the case of diffusive growth of supercritical droplets. At the nucleation stage, the quantity v defined by equality (2.2) coincides, with a good accuracy, with the true number of vapor molecules condensed by a droplet containing the insoluble nucleus. The importance of this fact for the kinetic theory of nucleation has been emphasized in previous sections.

Formulas (3.12)–(3.14), (3.17), (3.23), (3.30), and (7.5) taken together with expressions (5.2), (6.35), (7.9), and (7.10) give all the most important kinetic characteristics of nucleation on insoluble wettable nuclei in case of the diffusive growth of supercritical droplets.

A comparison of Eqns (3.22) and (7.6) with (3.30) and (7.9), respectively, shows that the expression for time Δt has an identical form in the case of free-molecule and diffusive growth of supercritical droplets. An analogous inference was deduced in Section 5.1 with regard to the nucleation on soluble nuclei.

7.2 Parametrization of the characteristic time of vapor metastable state formation

The use of formulas (3.22), (7.6), taking into account Eqns (5.2), (6.35), and (7.4), leads in the case of free-molecule growth of supercritical droplets to

$$\frac{\Delta t}{t_{\mathrm{s}}} \approx \frac{1}{2} \left(\frac{2}{3}\right)^{1/m} \frac{\alpha t_\infty}{m\tau} \, \frac{a^{1/m} p_0^{1/3}}{v_0^{(4m+1)/(3m)}} \,. \tag{7.11}$$

An analogous equality can be obtained from formulas (3.30), (7.9) for the diffusive supercritical droplet growth, taking into consideration Eqns (5.2), (6.35), and (7.4). The solution of Eqn (7.11) with respect to t_∞, using definition (5.5), gives

$$t_\infty \approx 2 \left(\frac{3}{2}\right)^{1/m} \frac{\varkappa m \tau}{\alpha} \, \frac{v_0^{(4m+1)/(3m)}}{a^{1/m} p_0^{1/3}} \,, \tag{7.12}$$

which parametrizes the characteristic time t_∞ of vapor metastable state formation by expressing it through the parameter $\varkappa$.

It directly follows from definition (5.5) and relation (7.4) that

$$\Delta t \approx \frac{3}{2^{3/2}} \frac{\varkappa \tau}{q\alpha} \, \frac{v_0^{8/9}}{a^{2/3} p_0^{2/9}} \,. \tag{7.13}$$

It seems appropriate to proceed from the consideration of the free-molecule growth of supercritical droplets. The substitution of relations (7.12) into (7.6) and (7.7) yields

$$c \approx 2^{1/3}\, 3 \, \frac{q p_0^{2/9}}{\varkappa a^{1/3} v_0^{5/9}} \,, \tag{7.14}$$

$$h \approx \frac{2}{3} \frac{\eta(-\infty)}{q^2 n_\infty} \, \frac{\varkappa^3 a^{2/3} v_0^{22/9}}{p_0^{7/9}} \,. \tag{7.15}$$

It follows from relations (3.13), (3.17), taking into consideration Eqns (7.14) and (7.15), that

$$N \approx \frac{3}{2} \frac{q^2 n_\infty p_0^{7/9}}{\varkappa^3 a^{2/3} v_0^{22/9}} \qquad (h \gg 1) \,, \tag{7.16}$$

$$\Delta\rho \approx \frac{1}{2^{1/2}} \frac{\varkappa a^{1/3} v_0^{5/9}}{q p_0^{2/9}} \,. \tag{7.17}$$

The solution of the relation (7.15) with respect to $\eta(-\infty)$ gives

$$\eta(-\infty) \approx \frac{3}{2} \frac{q^2 n_\infty h p_0^{7/9}}{\varkappa^3 a^{2/3} v_0^{22/9}} \,. \tag{7.18}$$

The use of Eqns (3.14) and (7.18) yields

$$N \approx \frac{3}{2} \frac{q^2 n_\infty h p_0^{7/9}}{\varkappa^3 a^{2/3} v_0^{22/9}} \qquad (h \ll 1) \,. \tag{7.19}$$

Formulas (7.12) and (7.18) express the time t_∞ and concentration $\eta(-\infty)$ through the parameters $\varkappa$ and h, whereas formulas (7.13), (7.16), (7.17), and (7.19) express the kinetic characteristics of nucleation Δt, N, and $\Delta\rho$ through the parameters $\varkappa$ and h.

Let us now consider the diffusive growth of supercritical droplets. The substitution of relation (7.12) into formulas (7.9) and (7.10) gives

$$c \approx 2^{1/3}\, 3 \, \frac{q \alpha \tau_D p_0^{2/9}}{\varkappa \tau a^{1/3} v_0^{5/9}} \,, \tag{7.20}$$

$$h \approx \frac{(3\pi)^{1/2}}{2^{5/4}} \frac{\eta(-\infty)}{q^{1/2} n_\infty} \left(\frac{\varkappa\tau}{\alpha\tau_D}\right)^{3/2} \frac{a^{1/6} v_0^{29/18}}{p_0^{4/9}} \,. \tag{7.21}$$

It follows from relations (3.13), (3.17), taking into consideration Eqns (7.20) and (7.21), that

$$N \approx \frac{2^{5/4}}{(3\pi)^{1/2}} q^{1/2} n_\infty \left(\frac{\alpha\tau_D}{\varkappa\tau}\right)^{3/2} \frac{p_0^{4/9}}{a^{1/6} v_0^{29/18}} \qquad (h \gg 1) \,, \tag{7.22}$$

$$\Delta\rho \approx \frac{1}{2^{1/2}} \frac{\varkappa \tau a^{1/3} v_0^{5/9}}{q \alpha \tau_D p_0^{2/9}} \,. \tag{7.23}$$

The solution of the relation (7.21) with respect to $\eta(-\infty)$ produces

$$\eta(-\infty) \approx \frac{2^{5/4}}{(3\pi)^{1/2}} q^{1/2} n_\infty h \left(\frac{\alpha\tau_D}{\varkappa\tau}\right)^{3/2} \frac{p_0^{4/9}}{a^{1/6} v_0^{29/18}} \,. \tag{7.24}$$

The use of Eqns (3.14) and (7.24) yields

$$N \approx \frac{2^{5/4}}{(3\pi)^{1/2}} q^{1/2} n_\infty h \left(\frac{\alpha\tau_D}{\varkappa\tau}\right)^{3/2} \frac{p_0^{4/9}}{a^{1/6} v_0^{29/18}} \qquad (h \ll 1) \,. \tag{7.25}$$

Formulas (7.12) and (7.24) express the time t_∞ and concentration $\eta(-\infty)$ through the parameters $\varkappa$ and h, whereas formulas (7.13), (7.22), (7.23), and (7.25) express the kinetic characteristics of nucleation Δt, N, and $\Delta\rho$ through the parameters $\varkappa$ and h.

It can be seen that in the diffusive growth of supercritical droplets too, the parameters $\varkappa$ and h may be used to construct, in an analytical form, the kinetic theory of nucleation;

moreover, they are more convenient for the purpose than the parameters t_∞ and $\eta(-\infty)$.

As in the case of nucleation on soluble nuclei, an additional advantage of $\varkappa$ and h over t_∞ and $\eta(-\infty)$ consists in the following. The parameter $\varkappa$ in conjunction with inequality (5.36) allows one to judge directly whether the main applicability condition of the kinetic theory (3.39) responsible, in particular, for the fulfilment of the conditions (3.40), (3.46) is satisfied. On the contrary, parameter h allows one to directly estimate the satisfaction of inequalities $h \gg 1$ and $h \ll 1$ used in the theory.

7.3 Method for the calculation of kinetic characteristics of nucleation on insoluble wettable nuclei under free-molecule growth of supercritical droplets

The method for the calculation of kinetic characteristics of nucleation remains the same as for soluble condensation nuclei. Certainly, the application of this method to insoluble wettable nuclei implies the use of specific formulas.

As in Section 7.2, the parameters $\varkappa$ and h are regarded as free but restricted by condition (5.36) and the inequalities $h \gg 1$ or $h \ll 1$. The present section considers the case of free-molecule growth of supercritical droplets with an additional limitation imposed by condition (3.42). Let us make explicit this limitation. It follows from relations (3.43) and (7.17) that

$$\frac{\Delta\rho}{\rho_\lambda} \sim \frac{1}{2^{1/2} q}\,\alpha(n_\infty + n_g)\,v_\alpha\,\frac{\varkappa a^{1/3} v_0^{5/9}}{p_0^{2/9}} \tag{7.26}$$

(in estimates, numerical values are not rounded off to make it easier to follow them). The use of the last formula in inequality (3.42), taking into account the approximate equality (5.11), yields

$$\varkappa \ll \frac{2^{1/2}}{\alpha(n_\infty + n_g)\,v_\alpha}\,\frac{p_0^{2/9}}{a^{1/3} v_0^{5/9}}\,. \tag{7.27}$$

The inequality

$$\frac{2^{1/2}}{\alpha(n_\infty + n_g)\,v_\alpha}\,\frac{p_0^{2/9}}{a^{1/3} v_0^{5/9}} \gg 1 \tag{7.28}$$

needs to be satisfied to ensure a fit between formulas (5.36) and (7.27). If inequality (7.28) containing the initially given parameters of the theory in its left-hand side is satisfied, formulas (7.12), (7.13), (7.16) – (7.19) are valid in the ranges of variation of parameters $\varkappa$ and h, permitted by constraints (5.36), (7.27) and inequalities $h \gg 1$ or $h \ll 1$. These formulas provide a basis for further calculations.

Let us choose the following values of the initial parameters of the theory:

$$\begin{gathered} a = 10\,, \quad \alpha = 10^{-1}\,, \quad n_\infty = 10^{17}\ \text{cm}^{-3}, \quad n_g = 10^{19}\ \text{cm}^{-3}\,, \\ v_\alpha = 10^{-23}\ \text{cm}^3\,, \quad \tau = 5.4 \times 10^{-7}\ \text{s}\,, \quad v_0^{1/3} = 90\,, \\ p_0 = 1.7 \times 10^3\,, \qquad m = 1\,. \end{gathered} \tag{7.29}$$

The values of a, α, n_∞, n_g, v_α, τ, and m given in the last set are the same as in Eqn (5.40). The reality and representativeness of these values were emphasized in Section 5.3. The values of $v_0^{1/3}$ and p_0 satisfy inequalities (6.34) and (6.46). The value of $v_0^{1/3}$ corresponds to $R_n \approx 10^{-6}$ cm, in conformity with Eqns (6.31) and (6.44). In the case of the exponential approximation to the work of wetting of a nucleus, the value of p_0 corresponds, in agreement with estimate (6.45), to $l \approx 10^{-7}$ cm, which is very close to reality [73]. The value of $R_n \approx 10^{-6}$ cm is sufficiently large to ensure that the condition (6.14) of nucleus macroscopicity is satisfied; at the same time, it is so small that the vapor threshold supersaturation $\zeta_{th} \approx 7.4 \times 10^{-2}$ given by the relations (6.31), (6.35), and (6.44) remains amenable to reliable control in experiment.

Let us use the method under consideration for the calculation based on the set (7.29). In this case, inequality (7.28) is satisfied. It follows from inequalities (5.36) and (7.27) that

$$1 \ll \varkappa \ll 2 \times 10^2\,, \tag{7.30}$$

which determines the permitted region of the parameter $\varkappa$ variation.

According to formulas (7.12), (7.5), and (7.13), one obtains

$$t_\infty \approx 7.7 \times 10^2 \varkappa\ \text{s}\,, \tag{7.31}$$

$$t_* \approx 5.8 \times 10\,\varkappa\ \text{s}\,, \tag{7.32}$$

$$\Delta t \approx 3.8 \times 10^{-2} q^{-1} \varkappa\ \text{s}\,. \tag{7.33}$$

The units of measurement of dimensional quantities were specified. The dependence of q on $\varkappa$ and h is given by equality (7.2). The time moments t_{on} and t_{off} are easy to find using approximate equalities (3.23).

Finally, formulas (7.16) – (7.19) give

$$N \approx \begin{cases} 4.9 \times 10^4 q^2 \varkappa^{-3}\ \text{cm}^{-3} & (h \gg 1)\,, \\ 4.9 \times 10^4 q^2 h \varkappa^{-3}\ \text{cm}^{-3} & (h \ll 1)\,, \end{cases} \tag{7.34}$$

$$\Delta\rho \approx 5.3 \times 10^2 q^{-1} \varkappa\,, \tag{7.35}$$

$$\eta(-\infty) \approx 4.9 \times 10^4 q^2 h \varkappa^{-3}\ \text{cm}^{-3}\,. \tag{7.36}$$

The radius R of a droplet is more conveniently used in experiment than its size ρ introduced by equalities (2.2), (3.7). Using relations (5.49) and (7.35), we receive for the width ΔR of the supercritical droplet size spectrum on the R-axis:

$$\Delta R \approx 7 \times 10^{-6} q^{-1} \varkappa\ \text{cm}\,. \tag{7.37}$$

Let us show how conditions (3.40) and (5.11) are fulfilled. In a situation with $h \gg 1$, relations (5.4) and (7.2) indicate that inequality (3.40) is satisfied over the entire range (7.30). Likewise, the approximate equality (5.11) is fulfilled unless the inequality $h \gg 1$ is too strong. That $h \gg 1$ cannot be too strong follows from the fact that the growth of parameter h is accompanied by a rise [in agreement with Eqn (7.36)] in the concentration $\eta(-\infty)$ which, however, does not normally exceed 10^5 cm^{-3} under practical conditions.

In the situation where $h \ll 1$, it follows from expressions (5.4) and (7.2) that conditions (3.40) and (5.11) are satisfied only near the upper bound of region (7.30). Therefore, the realization of a situation in which $h \ll 1$ is actually incompatible with the notion of a significant activation barrier to nucleation. However, such a notion would hold true if the coefficient α and density n_g in the set (7.29) were lowered and the upper limit of region (7.30) were raised, accordingly, in compliance with inequality (7.27).

7.4 Method for the calculation of kinetic characteristics of nucleation on insoluble wettable nuclei under diffusive growth of supercritical droplets

The parameters $\varkappa$ and h are regarded to be free, as before, but restricted by condition (5.36) and the inequalities $h \gg 1$ or $h \ll 1$. The present section considers the case of the diffusive growth of supercritical droplets with an additional limitation imposed by condition (3.44). Let us make explicit this limitation. It follows from relations (3.45) and (7.23) that

$$\frac{\Delta\rho}{\rho_\lambda} \sim \frac{1}{2^{1/2} q} \frac{\varkappa\tau}{\tau_D} \frac{a^{1/3} v_0^{5/9}}{p_0^{2/9}} \alpha (n_\infty + n_{\mathrm{g}})^2 v_\alpha^2 \tag{7.38}$$

(in estimates, numerical values are not rounded off to make it easier to follow them). Using the approximate equality (5.52), expression (7.38) can be represented as

$$\frac{\Delta\rho}{\rho_\lambda} \sim \frac{1}{2^{1/2} q} \alpha (n_\infty + n_{\mathrm{g}})\, v_\alpha \frac{\varkappa a^{1/3} v_0^{5/9}}{p_0^{2/9}} , \tag{7.39}$$

resembling relationship (7.26), although the quantities ρ and ρ_λ are defined by relations (3.25) and (3.45) which differ from (3.7) and (3.43). The use of the above formula in inequality (3.44), taking into account approximate equality (5.11), yields

$$\varkappa \gg \frac{2^{1/2}}{\alpha (n_\infty + n_{\mathrm{g}})\, v_\alpha} \frac{p_0^{2/9}}{a^{1/3} v_0^{5/9}} , \tag{7.40}$$

This expression is opposite to restriction (7.27) as the limiting case of diffusive supercritical droplet formation is opposite to that of the free-molecule growth.

Formulas (7.12), (7.13), and (7.22) – (7.25) hold good in the regions of variations of parameters $\varkappa$ and h permitted by the most rigorous inequalities out of (5.36) and (7.40) and by constraints $h \gg 1$ or $h \ll 1$. These formulas form the basis for further calculations.

Let us choose the following values of the initial parameters of the theory:

$$\begin{gathered} a = 10 , \quad \alpha = 1 , \quad n_\infty = 10^{17}\ \mathrm{cm}^{-3}, \quad n_{\mathrm{g}} = 10^{19}\ \mathrm{cm}^{-3}, \\ v_\alpha = 10^{-23}\ \mathrm{cm}^3 , \quad \tau = 5.4 \times 10^{-7}\ \mathrm{s} , \quad D = 1\ \mathrm{cm}^2\ \mathrm{s}^{-1} , \\ \tau_D = 8.9 \times 10^{-11}\ \mathrm{s} , \quad v_0^{1/3} = 90 , \quad p_0 = 1.7 \times 10^3 , \quad m = 1 . \end{gathered} \tag{7.41}$$

The values in the last set differ from those in set (7.29) only by the assumption of $\alpha = 1$ instead of $\alpha = 10^{-1}$. This difference is however responsible for the transition from the free-molecule growth of supercritical droplets to the diffusive one. It is a very likely possibility that coefficient α is close to unity as has been noted in Section 5.4. The value of D given in set (7.41), same as in the second set (5.55), is quite realistic. For completeness, the time τ_D is included in the initial parameters although, according to formula (3.27), it is a function of n_∞, v_α, and D. The value of τ_D given in set (7.41), the same as in set (5.55), has been found with the aid of relationship (3.27).

Let us use the method under consideration for the calculation based on data from set (7.41). In this case, the inequality (7.40) is more rigorous than (5.36). According to the former inequality, one obtains

$$\varkappa \gg 2 \times 10 , \tag{7.42}$$

which determines the permitted range of parameter $\varkappa$ variations.

According to Eqns (7.12), (7.5), and (7.13), we find

$$t_\infty \approx 7.7 \times 10 \varkappa\ \mathrm{s} , \tag{7.43}$$

$$t_* \approx 5.8 \varkappa\ \mathrm{s} , \tag{7.44}$$

$$\Delta t \approx 3.8 \times 10^{-3} q^{-1} \varkappa\ \mathrm{s} . \tag{7.45}$$

The units of measurement of dimensional quantities were specified. The dependence of q on $\varkappa$ and h is given by the equality (7.2). Time moments t_{on} and t_{off} are easy to find using approximate equalities (3.23).

Finally, equations (7.22) – (7.25) give

$$N \approx \begin{cases} 1.1 \times 10^3 q^{1/2} \varkappa^{-3/2}\ \mathrm{cm}^{-3} & (h \gg 1) , \\ 1.1 \times 10^3 q^{1/2} h \varkappa^{-3/2}\ \mathrm{cm}^{-3} & (h \ll 1) , \end{cases} \tag{7.46}$$

$$\Delta\rho \approx 3.2 \times 10^6 q^{-1} \varkappa , \tag{7.47}$$

$$\eta(-\infty) \approx 1.1 \times 10^3 q^{1/2} h \varkappa^{-3/2}\ \mathrm{cm}^{-3} . \tag{7.48}$$

Surface area $A = 4\pi R^2$ of the droplet is more conveniently used in experiment than its size ρ introduced by equalities (2.2) and (3.25). Using relations (5.64) and (7.47), we receive for the width ΔA of the supercritical droplet size spectrum on the A-axis:

$$\Delta A \approx 7 \times 10^{-9} q^{-1} \varkappa\ \mathrm{cm}^2 . \tag{7.49}$$

Let us show how conditions (3.40) and (5.11) are fulfilled. In a situation with $h \gg 1$, formulas (5.4) and (7.2) indicate that inequality (3.40) is satisfied over the entire range (7.42). Likewise, approximate equality (5.11) is fulfilled (at least as an estimate) unless the inequalities (7.42) and $h \gg 1$ are too strong. If the inequality (7.42) were too strong, i.e. parameter $\varkappa$ were too large, the time t_* would be very large as well (in agreement with relation (7.44)) and of little practical interest. If the inequality $h \gg 1$ were too strong, the concentration $\eta(-\infty)$ would be very high [in agreement with relation (7.48) and at not too large parameter $\varkappa$] although it does not normally exceed $10^5\ \mathrm{cm}^{-3}$ under practical conditions (see above discussion).

On the contrary, in the situation where $h \ll 1$, it follows from the expressions (5.4) and (7.2) that relationships (3.40) and (5.11) are satisfied over the entire range (7.42) with the exception of too large values of the parameter $\varkappa$ [corresponding, to a very large time t_*, in agreement with relation (7.44)].

The similarity of physical substantiations of the condition (3.40) and relation (5.11) in Sections 5.3, 5.4 and 7.3, 7.4 confirms the universal character of the method for calculating kinetic parameters of nucleation, described in these sections.

7.5 Accounting for the polydispersity of insoluble wettable nuclei

The kinetic theory put forward in Sections 7.1 – 7.4 implies that insoluble wettable condensation nuclei are identical, i.e. monodispersed. Let us now consider how the polydispersity of insoluble wettable nuclei can be taken into account.

Nucleus polydispersity requires that the distribution of their initial concentrations by radius R_{n} be taken into consideration. Let us proceed from a quite realistic assumption that the density of this distribution is practically zero for $R_{\mathrm{n}} > \overline{R}_{\mathrm{n}}$ and significantly different from zero for $R_{\mathrm{n}} < \overline{R}_{\mathrm{n}}$, where $\overline{R}_{\mathrm{n}}$ is the radius of the largest nuclei existing under practical conditions. How the distribution density of the initial concentrations of nuclei depends on R_n for $R_n < \overline{R}_n$ is immaterial for the further discussion. It is only important that its R_n-dependence be weak compared with a 'jump', i.e. the transition from $R_n < \overline{R}_n$ to $R_n > \overline{R}_n$ values.

Bearing in mind the estimative nature of the further reasoning, the approximate equality (5.11) and the relation (6.42) valid for the exponential approximation to the work of wetting of a nucleus will be used, making no additional mention of the fact. Expressions (4.10) and (6.40) give an estimate of the width $\Delta\zeta$ of the prethreshold region of vapor metastability on the ζ-axis:

$$\Delta\zeta \sim a^{-2/3} \nu_0^{-4/9} \left(\frac{\nu_0}{k}\right)^{1/9} \zeta_{\mathrm{th}} \,. \tag{7.50}$$

Expressions (4.10) and (4.25) indicate that the prethreshold region of vapor metastability shifts along the ζ-axis at a rate of about $\partial\zeta_{\mathrm{th}}/\partial R_n$ as the radius R_n increases. According to formulas (6.31), (6.35), and (6.44), this rate can be estimated from the relation

$$\frac{\partial\zeta_{\mathrm{th}}}{\partial R_n} \sim -\frac{\zeta_{\mathrm{th}}}{R_n} \,. \tag{7.51}$$

As the vapor metastability state is being formed, the vapor supersaturation ζ obviously falls into the region which is the prethreshold one with respect not only to a nucleus for which $R_n \approx \overline{R}_n$ but also to all the nuclei within the interval $\overline{R}_n - \Delta R_n < R_n < \overline{R}_n$, whose width ΔR_n satisfies the relation

$$\Delta\zeta\bigg|_{R_n \approx \overline{R}_n} \sim \left|\frac{\partial\zeta_{\mathrm{th}}}{\partial R_n}\right|_{R_n \approx \overline{R}_n} \Delta R_n \,. \tag{7.52}$$

All these nuclei are the potential centers of supercritical droplet formation.

Expressions (7.50)–(7.52) submit an estimate

$$\frac{\Delta R_n}{\overline{R}_n} \sim a^{-2/3} \nu_0^{-4/9} \left(\frac{\nu_0}{k}\right)^{1/9} , \tag{7.53}$$

where it is not shown, for simplicity, that ν_0 refers to the value $\overline{R}_n$ of the nuclear radius R_n. The last relation provides an estimate of the width ΔR_n of the interval $\overline{R}_n - \Delta R_n < R_n < \overline{R}_n$ of nuclear radii R_n, within which supercritical droplets actually form. According to the approximate formula (7.53), the following relation holds for macroscopic nuclei:

$$\frac{\Delta R_n}{\overline{R}_n} \ll 1 \,. \tag{7.54}$$

This means that the width of the interval $\overline{R}_n - \Delta R_n < R_n < \overline{R}_n$ is relatively small.

A principal kinetic characteristic of nucleation being the total number of newly-formed supercritical droplets, the following condition must be fulfilled if the kinetic theory of nucleation discussed in Sections 7.1–7.4 is to be employed when dealing with polydispersed insoluble wettable nuclei:

$$\left|\frac{1}{N}\frac{\partial N}{\partial R_n}\right|_{R_n \approx \overline{R}_n} \Delta R_n \ll 1 \,. \tag{7.55}$$

This condition guarantees the smallness of the relative change in the number of droplets N associated with the variation of R_n within the interval $\overline{R}_n - \Delta R_n < R_n < \overline{R}_n$.

It follows from formula (3.12) that the dependence of N on R_n is especially strong when $h \gg 1$. In the same situation, this dependence turns out to be the strongest of all other R_n-dependences of nucleation kinetic characteristics. Therefore, condition (7.55) for $h \gg 1$ may serve as a criterion for the practical absence of effect of nucleus polydispersity on the kinetic characteristics of nucleation within the interval $\overline{R}_n - \Delta R_n < R_n < \overline{R}_n$.

When the stage of effective formation of supercritical droplets is dominated by their free-molecule growth, it follows from relations (3.13), (7.7) for $h \gg 1$, taking into account formulas (6.31), (6.44), that

$$\frac{\partial N}{\partial R_n} \sim \frac{4m+3}{m}\frac{N}{R_n} \,. \tag{7.56}$$

Using relationships (7.53) and (7.56), condition (7.55) can be reduced to the inequality

$$\frac{4m+3}{m} a^{-2/3} \nu_0^{-4/9} \left(\frac{\nu_0}{k}\right)^{1/9} \ll 1 \tag{7.57}$$

(it is not shown that ν_0 refers to the value $\overline{R}_n$ of the nuclear radius R_n). In the case of insoluble macroscopic wettable condensation nuclei, inequality (7.57) is fulfilled if the parameter m is not too small.

However, when the stage of effective formation of supercritical droplets is dominated by their diffusive growth, it follows from formulas (3.13), (7.10) for $h \gg 1$, taking into account relations (6.31), (6.44), that

$$\frac{\partial N}{\partial R_n} \sim \frac{2m+3}{2m}\frac{N}{R_n} \,. \tag{7.58}$$

Using the same relationships (7.53) and (7.58), condition (7.55) can be reduced to the inequality

$$\frac{2m+3}{2m} a^{-2/3} \nu_0^{-4/9} \left(\frac{\nu_0}{k}\right)^{1/9} \ll 1 \tag{7.59}$$

(it is not shown that ν_0 refers to the value $\overline{R}_n$ of the nuclear radius R_n). In the case of insoluble macroscopic wettable condensation nuclei, inequality (7.59) is fulfilled if the parameter m is not too small.

Thus, the polydispersity of insoluble wettable condensation nuclei may be taken into account in the kinetic theory exposed in Sections 7.1–7.4. For this, in all the formulas of this theory, R_n should be understood as $\overline{R}_n$ [in agreement with inequality (7.54)], and $\eta(-\infty)$ as the total initial concentration of condensation nuclei whose radii R_n lie in the interval $\overline{R}_n - \Delta R_n < R_n < \overline{R}_n$ within which supercritical droplets are formed. The width ΔR_n of this interval is given by relation (7.53). It is worthwhile to note that inequalities (7.57) and (7.59) are equivalent to inequality (7.54) up to factors $(4m+3)/m$ and $(2m+3)/(2m)$, as is clear from estimate (7.53).

To conclude, the macroscopic size of insoluble wettable condensation nuclei, responsible for their polydispersity, also made it possible to take into account this polydispersity. This inference was equally true in the case of soluble macroscopic condensation nuclei.

The kinetic theory of nucleation on insoluble wettable nuclei constructed in Sections 7.1–7.4, in which quantities ν_0 and p_0 were taken as the initial parameters, may be used to generalize the kinetic theory of nucleation on soluble nuclei composed of a surface-inactive substance (see Sections 5.1 – 5.4) to nuclei of a surfactant. Indeed, such a generalization can be accomplished, taking advantage of general relations (4.13) – (4.15), by finding the quantities ν_0 and b_{th} in the formulas of Sections 7.1 – 7.4 and the quantity p_0 determined by formula (6.36) with the aid of the algorithm formulated in Section 4.4 for the calculation of the thermodynamic characteristics of nucleation on nuclei of surfactants.

8. The theory of nucleation on partially soluble wettable nuclei and nuclei of mixed composition

Thermodynamic characteristics of heterogeneous nucleation under condensation on completely soluble nuclei and wettable macroscopic nuclei insoluble in newly-formed droplets, considered in Sections 4 and 6, represent limiting physical situations. In practice, the following three intermediate situations are feasible. One arises when the size of the nuclei, even composed of matter readily soluble in the condensate, is such that its maximum chemical potential is reached before the nuclei are completely dissolved in the droplets. In the second case, the nuclei may be composed of a poorly soluble material, but even small amount of it in the solution inside the droplets markedly affects their nucleation potency. In the third situation, nuclei of mixed composition contain both soluble and insoluble components [13, 98 – 100]. In what follows, we shall show with reference to papers [101 – 103] and the thermodynamic approach presented in Sections 4 and 6 how heterogeneous nucleation can be described in these three intermediate physical situations. To avoid misunderstanding, we shall assume here and hereinafter in this section that the soluble component of a nucleus is a surface-inactive substance although all the results can easily be generalized to a soluble surfactant component.

8.1 Sufficient condition for the applicability of the theory to the case of complete nucleus dissolution in a droplet

Let us first formulate a sufficient condition of validity of the nucleation thermodynamics discussed in Section 4 in the case of complete dissolution of the nucleus in a droplet.

Consider a monocomponent nucleus partially or completely dissolved in the liquid condensed from vapor. Regardless of the regime of matter exchange between the droplet and the vapor (free-molecule, diffusive or intermediate), the condition $\dot{\nu} \gtrless 0$ for $b_\nu \gtrless b$ holds for the rate $\dot{\nu}$ at which the number of condensate molecules in the droplet changes with time. Let b_{th} be the vapor threshold chemical potential when the nuclei are completely dissolved in the droplets. This value guarantees that the inequality $\dot{\nu} > 0$ is fulfilled in the case of incomplete nucleus dissolution too, regardless of the value of the vapor chemical potential $b > b_{\text{th}}$, if

$$b_\nu < b_{\text{th}} \tag{8.1}$$

at all ν values at which the nucleus is incompletely dissolved in the droplet.

The removal of nuclear matter in the course of its dissolution in the droplet with a rise in the number of condensate molecules ν is responsible for the inhomogeneity of the nonequilibrium concentration of nuclear matter in the liquid film between the yet undissolved nuclear residue and the vapor – gas medium around the droplet. The chemical potential b_ν of the condensate in the liquid film remains as inhomogeneous as the nuclear matter concentration until a perfect equilibrium is achieved inside the droplet. The matter exchange between the droplet and the surrounding medium will naturally depend on the b_ν value at the surface of the former.

Let us assume that absorption of vapor molecules by a droplet results in an enhanced chemical potential b_ν at the droplet surface. This will induce a release of vapor molecules from the droplet to the surrounding medium, hence the weakening of the inequality $\dot{\nu} > 0$ and slowdown in the condensation process. Also, it will facilitate the establishment of internal equilibrium in the dissolved nuclear matter of the droplet, adsorption equilibrium at its surface, and equilibrium with the nuclear residue. The latter will require that the residue size adjust itself to the either of equilibria [104]. Therefore, the violation of the inequality $\dot{\nu} > 0$ must be preceded by a close-to-equilibrium situation in which the concentration x of dissolved nuclear matter in the droplet is practically homogeneous and coincides with the solubility of the residual nucleus. The chemical potential b_ν of condensate under condition (8.1) should be referred to this solubility. The inequality $\dot{\nu} > 0$ will not be violated if condition (8.1) is fulfilled.

Let x_{n} be the solubility of a nucleus of radius R_{n}. It is related to the equilibrium concentration x_∞ of nuclear matter in a solution on a flat substrate by the Ostwald – Freundlich formula

$$x_{\text{n}} = x_\infty \exp\left(\frac{2\gamma_n v_{\text{n}}}{R_{\text{n}} k_{\text{B}} T}\right), \tag{8.2}$$

where γ_{n} is the mechanical surface tension at the nucleus – solution interface, and v_{n} is the molecular volume of nuclear matter. Because the surface curvature of the residual nucleus exceeds the initial nuclear surface curvature, then, at incomplete dissolution of the nucleus, we have

$$x > x_{\text{n}}\,. \tag{8.3}$$

In the range of ν variation, in which the nucleus is only partly dissolved and the solution concentration x does not necessarily satisfy the inequality $x \ll 1$, the droplet radius R is no longer proportional to $\nu^{1/3}$ as in the case of complete nucleus dissolution. For the purpose of this section, the following inequality may be adopted:

$$R > R_{\text{n}}\,. \tag{8.4}$$

Inequalities (8.3) and (8.4) impose a limitation from below on the solubility x_{n}, necessary to satisfy condition (8.1). This limitation may be regarded as the sufficient usability condition for nucleation thermodynamics in the case of complete nucleus dissolution in a droplet.

In the region of incomplete nucleus dissolution, the contribution to the chemical potential b_ν in a droplet comes not only from the capillary and osmotic pressure but also from the disjoining pressure. Note that the contribution of the latter pressure is negative. Assuming as valid the approximation for a diluted solution, at which the contribution of osmotic pressure to b_ν is $-x$ and taking into account inequality (8.3) to estimate this contribution and inequality (8.4) to estimate the contribution of capillary pressure to b_ν, there is the following inequality in the region of incomplete nucleus dissolution:

$$b_v < -x_n + \frac{2\gamma v_\alpha}{R_n k_B T}\,. \tag{8.5}$$

According to Eqns (4.5), (8.2), (8.5), and (2.29), with

$$v_n = \frac{4\pi R_n^3}{3 v_n} \tag{8.6}$$

condition (8.1) is satisfied if

$$x_\infty > \frac{2\gamma v_\alpha}{R_n k_B T} \exp\left(-\frac{2\gamma_n v_n}{R_n k_B T}\right)\left[1 - \frac{2}{9}\left(\frac{6\gamma v_n}{R_n k_B T}\right)^{1/2}\right], \tag{8.7}$$

which imposes the necessary limitation from below on the solubility x_∞. It is important that the assumption of dilute solution used to derive inequality (8.7) also be observed at a solution concentration which presets the lower limit on x_∞. Indeed, this guarantees the fulfilment of condition (8.1) at a solution concentration specifying the lower bound of the limitation on x_∞. At the same time, it guarantees the fulfilment of condition (8.1) at higher concentrations of the solution too, at which the assumption of dilute solution is no longer true. This is a thermodynamic consequence of solution stability, which accounts for a decrease in the chemical potential of the solvent with a rise in the solution concentration. Thus, the limitation (8.7) is unrelated to whether the assumption of dilute solution is observed at all concentrations x_∞ satisfying inequality (8.7) or not.

The bigger the condensation nuclei, the smaller the right-hand part of inequality (8.7) setting the lower bound of limitation on x_∞. When the condensation nucleus is sufficiently large, the approximation to a dilute solution in a droplet is inevitably valid at the lower bound of this limitation. Then, the limitation itself comes into effect. Condition (8.7) does not take into consideration the disjoining pressure of the liquid film although it admits the fact that this pressure weakens the limitation on solubility. This accounts for the universal character of this restriction unrelated to concrete notions of disjoining pressure isotherms and mechanisms of wetting of condensation nuclei.

In agreement with Eqns (4.3), (2.29), and (8.6), the solution concentration v_n/v_0 in a droplet at the maximum chemical potential of the condensate is small if the following condition is met:

$$R_n \gtrsim \frac{2\gamma v_\alpha}{k_B T}\left(\frac{v_n}{v_\alpha}\right)^{1/3}. \tag{8.8}$$

However, the fulfilment of inequality (8.8) which details the condition (4.6) of macroscopicity of soluble nuclei does not ensure the applicability of limitation (8.7). According to the aforesaid, it is necessary that the concentration setting the lower bound of limitation (8.7) be much smaller than unity. It is clear from Eqn (8.7) that this is possible if

$$R_n \gg \frac{2\gamma v_\alpha}{k_B T}\,. \tag{8.9}$$

The last inequality determines the nuclear size range for which the limitation on solubility (8.7) holds and, accordingly, the sufficient condition for the validity of the theory in the case of complete nucleus dissolution in the droplet is satisfied.

8.2 Maximum of the condensate chemical potential in a droplet under incomplete nucleus dissolution

Let us now turn to the situation in which the solubility of a nucleus is low, and limitation (8.7) is likely to be violated at certain nuclear sizes satisfying inequality (8.9).

Let v'_n be the number of molecules or ions in the undissolved spherical nuclear residue in a droplet, and R'_n be the radius of this residue. Then, one obtains

$$v'_n = \frac{4\pi R'^3_n}{3 v_n}\,. \tag{8.10}$$

Accordingly, the number v of the condensate molecules in the droplet can be represented as

$$v = \frac{4\pi(R^3 - R'^3_n)}{3 v_\alpha}\,. \tag{8.11}$$

As before, the quantity v_α, the surface tension γ, and disjoining pressure parameters in the liquid film around the nucleus in the case of dilute nuclear matter solution are assumed to be the same as in a pure condensate.

By virtue of formulas (8.6), (8.10), and (8.11), the relative concentration of the solution in a droplet can be written in the form

$$x = \frac{v_\alpha}{v_n}\,\frac{R_n^3 - R'^3_n}{R^3 - R'^3_n}\,. \tag{8.12}$$

It has been shown in the preceding section that the concentration of the solution in a droplet may be regarded as equivalent to the equilibrium concentration at the nuclear residue surface (at least on examination when condensation on an incompletely dissolved nucleus begins to proceed through barrierless mechanism). Writing formula (8.2) for the equilibrium with the residual nucleus and taking into account Eqn (8.12), we obtain

$$\frac{R_n^3 - R'^3_n}{R^3 - R'^3_n} = \frac{v_n}{v_\alpha}\, x_\infty \exp\left(\frac{2\gamma_n v_n}{R'_n k_B T}\right). \tag{8.13}$$

This relation links the radius R'_n of the residual nucleus to the droplet radius R. The latter quantity is conveniently used instead of v as a variable in the description of the droplet.

At the initial stage of nucleus dissolution, the chemical potential of the condensate in the droplet is a sum of contributions coming from three sources: capillary pressure, osmotic pressure, and disjoining pressure. In analogy to representations (4.2) and (6.2), it can be written for a dilute solution in the droplet that

$$b_R = -x + \frac{2\gamma v_\alpha}{R k_B T} - \frac{v_\alpha \Pi}{k_B T}\,. \tag{8.14}$$

Bearing in mind, in the first place, aqueous solutions and other strongly structured liquids, we shall use for the disjoining pressure of solution film an approximation ensuing from the exponential asymptotics (6.13) (in the film thickness $h = R - R'_n$) of the work of wetting of a nucleus. It will be shown below that in the interval of droplet radius (R) variation important for the theory the following inequality is fulfilled:

$$R \gg h\,. \tag{8.15}$$

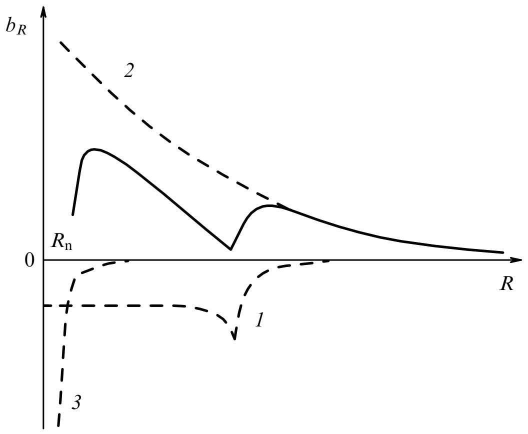

Figure 7. Dependence of the condensate chemical potential b_R (solid line) and contributions to it by osmotic (curve *1*), capillary (curve *2*), and disjoining (curve *3*) pressures on the droplet radius R.

In other words, the film may be regarded as flat. In agreement with formulas (6.5) and (6.13), one obtains

$$\Pi = K \exp\left(-\frac{h}{l}\right), \tag{8.16}$$

where parameters K and l are considered to be empirical.

The qualitative dependence on R of the condensate chemical potential b_R in the droplet and contributions to it from osmotic, capillary and disjoining pressures are depicted in Fig. 7 by the solid and dashed (*1*, *2*, and *3*) lines, respectively. The point of inflection of the solid line and dashed line *1* partitions the regions of incomplete and complete nucleus dissolution in the droplet (there is no contribution of the disjoining pressure to b_R in the complete dissolution region). Which of the two maxima (tentatively depicted in Fig. 7) of the condensate chemical potential b_R is the highest constitutes the subject-matter of the forthcoming discussion.

By detailing the equation

$$\left(\frac{\partial b_R}{\partial R}\right)\bigg|_{R=R_0} = 0 \tag{8.17}$$

which determines the location of chemical potential maxima on the R-axis we find, taking into account formulas (8.14), (8.12), (8.13) and (8.16), that

$$\left\{\left[\frac{2x_\infty \gamma_n v_\mathrm{n}}{R_\mathrm{n}'^2} \exp\left(\frac{2\gamma_n v_\mathrm{n}}{R_\mathrm{n}' k_\mathrm{B} T}\right) - \frac{v_\alpha K}{l} \exp\left(-\frac{h}{l}\right)\right] \frac{\partial R_\mathrm{n}'}{\partial R} - \frac{2\gamma v_\alpha}{R^2} + \frac{v_\alpha K}{l} \exp\left(-\frac{h}{l}\right)\right\}\bigg|_{R=R_0} = 0\,. \tag{8.18}$$

The condition $x_\mathrm{n} \ll 1$ of poor nucleus solubility can be written, by virtue of relation (8.2), in the form

$$x_\infty \exp\left(\frac{2\gamma_n v_\mathrm{n}}{R_\mathrm{n}' k_\mathrm{B} T}\right) \ll 1\,. \tag{8.19}$$

Differentiation of relationship (8.13) with respect to R, taking into consideration inequality (8.19), leads to

$$\frac{\partial R_\mathrm{n}'}{\partial R} = -x_\infty \frac{v_\mathrm{n} R^2}{v_\alpha R_\mathrm{n}'^2} \exp\left(\frac{2\gamma_n v_\mathrm{n}}{R_\mathrm{n}' k_\mathrm{B} T}\right). \tag{8.20}$$

Taking into account the approximate equality

$$R_\mathrm{n}' \approx R\,, \tag{8.21}$$

which ensues from Eqn (8.15), we arrive at the inequality

$$\left|\frac{\partial R_\mathrm{n}'}{\partial R}\right| \ll 1\,. \tag{8.22}$$

It can be seen directly from formulas (8.13) and (8.19) that the approximate equality

$$R_\mathrm{n}' \approx R_\mathrm{n} \tag{8.23}$$

is fulfilled with a much higher accuracy than the approximate equality (8.21). The physical reason for this consists in that the film thickness and the droplet radius at a low concentration of the solution are largely determined by an inflow of matter into the film from the vapor rather than from the nucleus. This reason also makes the weak influence of the degree of nucleus dissolution on variations of the solution concentration understandable.

It follows from inequality (8.22) that the item with derivative $\partial R_\mathrm{n}'/\partial R$ plays no important role in Eqn (8.18). If this item is neglected and approximate equality (8.23) taken into account, it becomes clear that the film thickness h_0 for the maximum chemical potential of the condensate in the region of incomplete nucleus dissolution in a droplet is given by

$$h_0 = l \ln\left(\frac{K R_\mathrm{n}^2}{2l\gamma}\right). \tag{8.24}$$

The last relation indicates that at large condensation nucleus radii, $R_\mathrm{n} \gg l$, of considerable practical interest, such that ensure condensation at low vapor supersaturations, one has $R_\mathrm{n} \gg h_0$. This inequality, in conjunction with formulas (8.21) and (8.22), justifies inequality (8.15) at the point corresponding to the maximum of the condensate chemical potential and, consequently, in the neighborhood of this point, important for the theory. Moreover, this inequality justifies the use of the Ostwald – Freundlich formula (8.2) inapplicable to very small nuclei.

According to Eqns (8.14), (8.24), (8.16), (8.12), (8.13), (8.21), and (8.23), the maximum chemical potential b_{R_0} of the condensate in the region of incomplete nucleus dissolution in a droplet is

$$b_{R_0} = -x_\infty \exp\left(\frac{2\gamma_n v_\mathrm{n}}{R_\mathrm{n} k_\mathrm{B} T}\right) + \frac{2\gamma v_\alpha}{R_\mathrm{n} k_\mathrm{B} T} - \frac{2\gamma v_\alpha l}{R_\mathrm{n}^2 k_\mathrm{B} T}\,. \tag{8.25}$$

To conclude, if the solubility x_∞ of a macroscopic nucleus material is so low that inequality (8.7) fails to be fulfilled, the largest maximum of the condensate chemical potential (in the incomplete nucleus dissolution region) has coordinate $R_\mathrm{n} + h_0$ [see relation (8.24)] on the droplet size R-axis. This maximum is defined by formula (8.25). Accordingly, the vapor threshold chemical potential for barrierless nucleation is determined by the right-hand side of Eqn (8.25). In this case, barrier-assisted nucleation occurs in the prethreshold region of vapor metastability close to the threshold value b_{R_0}. Quantities ν_e, ν_c, $\Delta\nu_\mathrm{e}$, $\Delta\nu_\mathrm{c}$, and ΔF required by barrier condensation kinetics can be easily found from formulas of Section 4.2 with the help of Eqns (8.14), (8.12), (8.16), (8.24), and (8.25). The nucleation kinetics in the case of gradual formation of the metastable vapor state are described by formulas given in Sections 7.1–7.4, where the quantity ν_0 is found for the droplet radius $R_0 = R_n + h_0$, $b_{th} = b_{R_0}$, and the quantity p_0 is determined from Eqns (6.36) and (8.14) with the use of formulas of this section. When inequality (8.7) is fulfilled, the highest maximum of the condensate chemical potential has coordinate ν_0 [see Eqn (4.3)] in the region of complete nucleus dissolution on the droplet size ν-axis. This maximum is defined by formula (4.5). Accordingly, the vapor threshold chemical potential is determined by the right-hand side of Eqn (4.5). In this case, quantities required by barrier condensation kinetics have been found in Section 4.2 and nucleation kinetics for the gradual vapor metastable state formation described in Section 5.

8.3 Accounting for an insoluble nucleus component

In the Earth's atmosphere, condensation nuclei contain insoluble components, besides soluble ones. This is especially true of nuclei containing surfactants formed at the surface of insoluble aerosol particles in photochemical reactions proceeded in the atmosphere [49, 50]. Let us consider the role of insoluble nucleus components in the process of nucleation.

Assume that an insoluble nuclear residue of radius R_{nn} consists of ν_{nn} molecules of a substance practically insoluble in the condensate:

$$\nu_{nn} = \frac{4\pi}{3v_{nn}} R_{nn}^3 , \tag{8.26}$$

where v_{nn} is the volume of molecules in the insoluble nuclear residue. The number of molecules of the soluble nucleus component is denoted by ν_{ns}. Evidently, the results of previous sections may be safely used if $\nu_{ns} \gg \nu_{nn}$. A more interesting situation occurs at $\nu_{ns} \lesssim \nu_{nn}$.

Assuming that the solution in a droplet is diluted in the region of complete dissolution of the surface-inactive soluble nucleus component, we have

$$b_\nu = -\frac{\nu_{ns}}{\nu} + \frac{2\gamma v_\alpha}{R k_B T} , \tag{8.27}$$

where the relationship between the droplet radius R and the number of condensate molecules ν in the droplet is given by formula (8.11) at $R'_n = R_{nn}$, and the surface tension γ of the droplet practically coincides with that of the pure solvent droplet. The coordinate R_0 of the maximum chemical potential b_ν on the R-axis is determined, taking into account Eqns (8.27), (2.25), and (2.29), from the solution of the cubic equation

$$R_0\left(1 - \frac{R_{nn}^3}{R_0^3}\right) = 3\left(\frac{3v_\alpha}{4\pi}\right)^{1/3}\left(\frac{\nu_{ns}}{2a}\right)^{1/2} . \tag{8.28}$$

If the strong inequality

$$\frac{v_\alpha}{v_{nn}}\left(\frac{9\nu_{ns}}{2a}\right)^{3/2} \gg \nu_{nn} \tag{8.29}$$

is fulfilled, relations (8.28) and (8.26) give $R_0 \gg R_{nn}$. For ν_0 and $(b_\nu)_{max}$, formulas (4.3) and (4.5) are obtained, respectively, in which, however, ν_n is replaced by ν_{ns}. It is easy to see that the strong inequality (8.29) is compatible with the condition $\nu_{ns} \lesssim \nu_{nn}$ if ν_{ns} satisfies the condition

$$\nu_{ns}^{1/2} \gg \frac{v_{nn}}{v_\alpha}\left(\frac{2a}{9}\right)^{3/2} . \tag{8.30}$$

Provided this condition is fulfilled, the solution concentration ν_{ns}/ν in the droplet, corresponding to the maximum chemical potential of the condensate, is much smaller than unity as was suggested when equality (8.27) was used to find the maximum of b_ν.

The same line of reasoning as in Section 8.1 leads to the conclusion that the sufficient condition of validity of nucleation thermodynamics in the case of complete dissolution of a nucleus with the initial radius R_n in the droplet has the form

$$x_\infty > \frac{2\gamma v_\alpha}{R_n k_B T} \tag{8.31}$$

(evidently, the quantity x_∞ characterizes here only the solubility of the soluble nucleus component). When conditions (8.29)–(8.31) are satisfied, the thermodynamics and kinetics of nucleation on nuclei containing insoluble components are described in the same way as in the case of completely soluble nuclei, with the sole exception that the total number of molecules ν_n in the nucleus in all formulas should be substituted by the number of molecules ν_{ns} of the soluble component.

When (8.31) is fulfilled while ν_{ns} decreases or ν_{nn} increases, the following strong inequality opposite to Eqn (8.29) is satisfied:

$$\left(\frac{v_\alpha}{v_{nn}}\right)^{1/3}\left(\frac{\nu_{ns}}{2a}\right)^{1/2} \ll \nu_{nn}^{1/3} . \tag{8.32}$$

It follows from Eqn (8.28) that under these conditions

$$R_0 = R_{nn} + \left(\frac{3v_\alpha}{4\pi}\right)^{1/3}\left(\frac{\nu_{ns}}{2a}\right)^{1/2} , \tag{8.33}$$

$$\frac{\nu_{ns}}{\nu_0} = \left(\frac{v_\alpha}{v_{nn}}\right)^{2/3}\left(\frac{2a}{9}\right)^{1/2}\frac{\nu_{ns}^{1/2}}{\nu_{nn}^{2/3}} , \qquad \frac{\nu_{ns}}{\nu_0} \ll 1 . \tag{8.34}$$

Then, the maximum of the condensate chemical potential is estimated as

$$(b_\nu)_{max} \approx \frac{2\gamma v_\alpha}{R_{nn} k_B T} . \tag{8.35}$$

This relation holds even if the surface of an insoluble nuclear residue is not readily wettable. Therefore, even a relatively small number ν_{ns} of the soluble component molecules can provide effective wetting of condensation nuclei containing an insoluble residue and barrierless nucleation on such nuclei.

9. Conclusions

The main results of recent theoretical studies on heterogeneous nucleation presented in this review demonstrate the possibility of constructing an adequate quantitative description of this complicated and varied phenomenon. The elucidation of universal laws of kinetics and thermodynamics of barrier and barrierless heterogeneous nucleation for representative types of condensation centers opens new prospects for both experiments on heterogeneous nucleation and practical applications of its theory.

In the present review, the classical scheme for the construction of the nucleation theory has been adopted in which the thermodynamics of new phase embryos is employed to calculate the key kinetic characteristics of nucleation under conditions of gradual formation of the initial phase metastable state. Special attention was given to the formulation and control of self-consistency of the usability conditions for all thermodynamic and kinetic elements of the theory. We also placed great emphasis on the discussion of the peculiarities of the thermodynamics and kinetics of heterogeneous nucleation on condensation centers of different nature.

A number of important issues related to the theory of the phenomenon under consideration remained beyond the scope of the review. They include nucleation in binary and multicomponent vapors, nucleation in the presence of several types of nuclei in a vapor – gas medium, nucleation on charged soluble nuclei whose matter dissociates upon dissolution, specific kinetic features of nucleation on incompletely wetted nuclei, etc. Many interesting problems await further study.

It seems that an interest in barrier nucleation on macroscopic wettable nuclei has long been suppressed by the absence of a kinetic theory of nucleation under conditions of gradual formation of metastability, which is almost invariably associated with barrier nucleation. Despite the obvious fact that the conditions for the gradual formation of metastable states are widespread both in nature and engineering, no special nucleation experiments have thus far been undertaken under such conditions. This accounts for the absence of the discussion of experimental findings in this review. The authors hope that its publication will give an incentive to relevant experimental studies.

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References

1. Wilson C T R *Philos. Trans. R. Soc. A* **189** (11) 265 (1897)
2. Wilson C T R *Philos. Trans. R. Soc. A* **192** (9) 403 (1899)
3. Wilson C T R *Philos. Trans. R. Soc. A* **193** (9) 289 (1900)
4. Becker R, Döring W *Ann. Phys.* (Leipzig) **24** 719 (1935)
5. Volmer M *Kinetik der Phasenbildung* (Dresden: T. Steinkopf, 1939) [Translated into Russian (Moscow: Nauka, 1986)]
6. Frenkel' Ya I *Kineticheskaya Teoriya Zhidkosteĭ* (Kinetic Theory of Liquids) (Leningrad: Nauka, 1975) [Translated into English (Oxford: The Clarendon Press, 1946)]
7. Tunitskiĭ N N *Zh. Fiz. Khim.* **15** 1061 (1941)
8. Kuni F M, in *Problemy Teoreticheskoĭ Fiziki* (Problems of Theoretical Physics) (Eds Yu N Demkov, Yu V Novozhilov, P P Pavinskiĭ) Vyp. III (Leningrad: Izd. Leningr. Gos. Univ., 1988) p. 192
9. Lifshitz I M, Slezov V V *Zh. Eksp. Teor. Fiz.* **35** 479 (1958) [*Sov. Phys. JETP* **8** 33 (1959)]
10. Slezov V V, Sagalovich V V *Usp. Fiz. Nauk* **151** 67 (1987) [*Sov. Phys. Usp.* **30** 23 (1987)]
11. Gibbs J W *Scientific Papers* (New York: Dover Publ., 1961)
12. Fletcher N H *The Physics of Rainclouds* (Cambridge: Univ. Press, 1962)
13. Dufour L, Defay R *Thermodynamics of Clouds* (New York: Academic Press, 1963)
14. Krystanov L *Meteorol. Zh.* (10) 4 (1936) [*Izbrannye Trudy po Fizike Atmosfery* (Selected Works on Physics of Atmosphere) (Leningrad: Gidrometeoizdat, 1968) p. 11
15. Mészáros E *Idojaras.* **73** 1 (1969)
16. Mészáros E, in *Voprosy Fiziki Oblakov* (Some Problems of Cloud Physics) (Eds I P Mazin et al.) (Leningrad: Gidrometeoizdat, 1978) p. 157
17. Pruppacher H R, Klett J D *Microphysics of Clouds and Precipitation* (Dordrecht: D. Reidel Publ. Co., 1978)
18. Navascués G, Tarazona P *J. Chem. Phys.* **75** 2441 (1981)
19. Rusanov A I, Kuni F M *Kolloidn. Zh.* **44** 934 (1982)
20. Kuni F M, Shchekin A K, Rusanov A I *Kolloidn. Zh.* **44** 1062 (1982)
21. Kuni F M, Shchekin A K, Rusanov A I *Kolloidn. Zh.* **45** 682 (1983)
22. Kuni F M, Shchekin A K, Rusanov A I *Kolloidn. Zh.* **42** 901 (1983)
23. Kuni F M, Shchekin A K, Rusanov A I *Kolloidn. Zh.* **45** 1083 (1983)
24. Rusanov A I, Kuni F M *J. Colloid Interface Sci.* **100** 264 (1984)
25. Shchekin A K, Rusanov A I, Kuni F M *Kolloidn. Zh.* **46** 535 (1984)
26. Sheludko A D *J. Colloid Interface Sci.* **104** 471 (1985)
27. Smorodin V E *Dokl. Akad. Nauk SSSR* **294** 595 (1987)
28. Smorodin V E *Dokl. Akad. Nauk SSSR* **302** 892 (1988)
29. Smorodin V E *Langmuir* **10** 2250 (1994)
30. Laktionov A G *Ravnovesnaya Geterogennaya Kondensatsiya* (Equilibrium Heterogeneous Condensation) (Leningrad: Gidrometeoizdat, 1988)
31. Kuni F M et al. *Adv. Colloid Interface Sci.* **65** 71 (1996)
32. Kashchiev D *Nucleation. Basic Theory with Applications* (Oxford: Butterworth Heinemann, 2000)
33. Kuni F M, Grinin A P *Vestn. Leningr. Univ. Ser. 4* (22) 10 (1982)
34. Rusanov A I *Fazovye Ravnovesiya i Poverkhnostnye Yavleniya* (Phase Equilibria and Surface Phenomena) (Leningrad: Khimiya, 1967)
35. Grinin A P, Kuni F M, Kurasov V B *Kolloidn. Zh.* **52** 430 (1990)
36. Grinin A P, Kuni F M, Kurasov V B *Kolloidn. Zh.* **52** 437 (1990)
37. Grinin A P, Kuni F M, Kurasov V B *Kolloidn. Zh.* **52** 444 (1990)
38. Kuni F M, Grinin A P, Kurasov V B *Lectures on Kinetic Theory of Condensation under Dynamic Conditions* (St. Petersburg: Izd. St. Petersburg Gos. Univ., 1996) p. 46
39. Kuni F M, Grinin A P, Kurasov V B, in *Nucleation Theory and Applications* (Eds J W P Schmelzer, G Roepke, V B Priezzhev) (Dubna: JINR, 1999) p. 160
40. Kuni F M *Kolloidn. Zh.* **46** 674 (1984)
41. Kuni F M, Grinin A P, Shchekin A K *Kolloidn. Zh.* **62** 628 (2000) [*Colloid J.* **62** 562 (2000)]
42. Kuni F M, Shchekin A K, Grinin A P *Kolloidn. Zh.* **62** 191 (2000)[*Colloid J.* **62** 151 (2000)]
43. Kuni F M, Grinin A P, Shchekin A K *Physica A* **252** (1 – 2) 67 (1998)
44. Kuni F M, Trofimov Yu V, Melikhov A A *Kolloidn. Zh.* **56** 182 (1994)
45. Kuni F M et al. *Kolloidn. Zh.* **60** 202 (1998)[*Colloid J.* **60** 179 (1998)]
46. Kohler H *Trans. Faraday Soc.* **32** 1152 (1936)
47. Kuni F M, Shchekin A K, Rusanov A I *Kolloidn. Zh.* **55** 34 (1993)
48. Hänel G, in *The Properties of Atmospheric Aerosol Particles as Functions of the Relative Humidity at Thermodynamic Equilibrium with the Surrounding Moist Air* (Advances in Geophysics, Vol. 19, Eds H E Landsberg, J Van Mieghem) (New York: Academic Press, 1976) p. 73
49. Gill P S, Graedel T E, Weschler C J *Rev. Geophys. Space Phys.* **21** 903 (1983)
50. Hansson H C et al. *J. Aerosol Sci.* **25** (SUP1) S129 (1994)
51. Shulman M L et al. *Geophys. Res. Lett.* **23** 277 (1996)
52. Shulman M et al. *J. Aerosol Sci.* **28** 737 (1997)
53. Shchekin A K et al. *Kolloidn. Zh.* **57** (1) 105 (1995)
54. Shchekin A K et al. *Kolloidn. Zh.* **57** (2) 261 (1995)
55. Rusanov A I, Kuni F M, Shchekin A K *Kolloidn. Zh.* **55** 55 (1993)
56. Kuni F M, Shchekin A K, Rusanov A I *Kolloidn. Zh.* **55** 64 (1993)
57. Kuni F M, Shchekin A K, Rusanov A I *Kolloidn. Zh.* **55** 73 (1993)
58. Shchekin A K, Rusanov A I, Kuni F M *Kolloidn. Zh.* **55** 91 (1993)
59. Rusanov A I, Kuni F M, Shchekin A K *Mendeleev Communications* **3** (5) 196 (1993)
60. Kuni F M et al. *Mendeleev Communications* **5** (5) 202 (1995)
61. Svitova T F et al. *Kolloidn. Zh.* **56** (3) 441 (1994)
62. Kuni F M, Shchekin A K, Rusanov A I *Kolloidn. Zh.* **55** 45 (1993)
63. Kuni F M et al. *Mendeleev Communications* **7** (4) 165 (1997)
64. Kuni F M et al. *Kolloidn. Zh.* **59** 187 (1997)
65. Kuni F M et al. *Kolloidn. Zh.* **60** 361 (1998) [*Colloid J.* **60** 329 (1998)]
66. Kuni F M et al. *Kolloidn. Zh.* **60** 499 (1998) [*Colloid J.* **60** 456 (1998)]
67. Barnes G T *Adv. Colloid Interface Sci.* **25** (1 – 4) 89 (1986)
68. Yasuoka K, Matsumoto M, Kataoka Y *J. Chem. Phys.* **101** 7904 (1994)
69. Matsumoto M, Yasuoka K, Kataoka Y *J. Chem. Phys.* **101** 7912 (1994)
70. Rusanov A I, Kuni F M *Dokl. Akad. Nauk SSSR* **318** 1410 (1991)
71. Rusanov A I, Kuni F M *Colloids Surfaces* **61** 349 (1991)

72. Deryagin B V, Churaev N V, Muller V M *Poverkhnostnye Sily* (Surface Forces) (Moscow: Nauka, 1985) [Translated into English (New York: Consultants Bureau, 1987)]
73. Deryagin B V, Zorin Z M *Zh. Fiz. Khim.* **29** 1755 (1955)
74. Schuchowitzki A A *Kolloid Z.* **66** 139 (1934)
75. Rowlinson J S, Widom B *Molecular Theory of Capillarity* (Oxford: Clarendon Press, 1982) [Translated into Russian (Moscow: Mir, 1985)]
76. Van der Hage J C H *J. Colloid Interface Sci.* **101** (1) 10 (1984)
77. Churaev N V, Starov V M, Derjaguin B V *J. Colloid Interface Sci.* **89** (1) 16 (1982)
78. Indekeu J O *Physica A* **183** 439 (1992)
79. Dobbs H T, Indekeu J O *Physica A* **201** 457 (1993)
80. Donohue M D, Aranovich G L *Adv. Colloid Interface Sci.* **76 – 77** 137 (1998)
81. Shchekin A K, Tatianenko D V, Kuni F M, in *Nucleation Theory and Applications* (Eds J W P Schmelzer, G Roepke, V B Priezzhev) (Dubna: JINR, 1999) p. 320
82. Tat'yanenko D V, Shchekin A K, Kuni F M *Kolloidn. Zh.* **62** 536 (2000) [*Colloid J.* **62** 479 (2000)]
83. Kukushkin S A, Slezov V V *Dispersnye Sistemy na Poverkhnosti Tverdykh Tel*: *Mekhanizmy Obrazovaniya Tonkikh Plenok* (*Evolyutsionnyĭ Podkhod*) [Dispersed Systems at Solid Surfaces: Mechanisms of Thin-Film Formation (Evolutionary Approach)] (St. Petersburg: Nauka, 1996)
84. Kukushkin S A, Osipov A V *Usp. Fiz. Nauk* **168** 1083 (1998) [*Phys. Usp.* **41** 983 (1998)]
85. Kukushkin S A, Osipov A V *J. Phys. Chem. Solids* **56** 831 (1995)
86. Kuni F M *Kolloidn. Zh.* **46** 902 (1984)
87. Kuni F M *Kolloidn. Zh.* **46** 1120 (1984)
88. Kuni F M, Shchekin A K, Kopeĭkin K V *Kolloidn. Zh.* **47** 295 (1985)
89. Kuni F M, Novozhilova T Yu, Terent'ev I A *Vestn. Leningr. Univ. Ser. 4* (1) 117 (1986)
90. Kuni F M, Novozhilova T Yu, Terent'ev I A *Vestn. Leningr. Univ. Ser. 4* (3) 97 (1986)
91. Kuni F M, Novozhilova T Yu, Terent'ev I A *Teor. Mat. Fiz.* **68** 276 (1986)
92. Kuni F M, Novozhylova T Yu, Terentiev I A *Lett. Math. Phys.* **14** 161 (1987)
93. Kuni F M *Kolloidn. Zh.* **49** 467 (1987)
94. Shchekin A K, Sasim T V *Kolloidn. Zh.* **50** 782 (1988)
95. Kuni F M, Kurasov V B, Grinin A P *Vestn. Leningr. Univ. Ser. 4* (4) 8 (1986)
96. Kurasov V B, Kuni F M, Grinin A P, in *Voprosy Fiziki Formoobrazovaniya i Fazovykh Prevrashcheniĭ* (Problems of Physics of Formative Processes and Phase Transformations) (Eds L M Shcherbakov et al.) (Kalinin: Izd. Kalininskogo Gos. Univ., 1986) p. 3
97. Kuni F M, Shchekin A K, Grinin A P, in *Nucleation Theory and Applications* (Eds J W P Schmelzer, G Roepke, V B Priezzhev) (Dubna: JINR, 1999) p. 208
98. Gorbunov B, Hamilton R *J. Aerosol Sci.* **28** 239 (1997)
99. Gorbunov B et al. *Atmospheric Res.* **47 – 48** 271 (1998)
100. Gorbunov B *J. Chem. Phys.* **110** 10035 (1999)
101. Kuni F M, Shchekin A K, Rusanov A I *Kolloidn. Zh.* **55** (5) 80 (1993)
102. Shchekin A K, Rusanov A I, Kuni F M *Kolloidn. Zh.* **55** (5) 185 (1993)
103. Shchekin A K, Rusanov A I, Kuni F M *Mendeleev Communications* **7** (3) 122 (1997)
104. Shchekin A K, Grinin A P, Kini F M *Kolloidn. Zh.* **60** 118 (1998) [*Colloid J.* **60** 111 (1998)]