Role of surface forces in heterogeneous nucleation on wettable nuclei

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Abstract

The condition has been formulated and the role of the surface forces at a solid–liquid interface has been established for the barrierless heterogeneous formation of a droplet on a macroscopic wettable insoluble solid nucleus in supersaturated vapour. The threshold value of the vapour supersaturation starting from which heterogeneous nucleation occurs as a barrierless process and all thermodynamic characteristics of heterogeneous formation of a droplet which are necessary for kinetic description of phase transition below the threshold have been found as a function of parameters of the exponential and the power-law approximations to the work of wetting of the nucleus associated with the surface forces and size of condensation nuclei: the coordinates and the half-widths of the potential hump and the potential well in the curve of the work of heterogeneous formation of a droplet; the activation barrier which droplets have to overcome by fluctuations in the process of formation of the stable phase.

Contents

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Introduction: historical background

Realization of the homogeneous mechanism of phase transition usually requires such high supersaturations of an initial metastable phase that the mechanism is hardly encountered in nature. More readily realized is the heterogeneous mechanism of phase transition on foreign particles that are practically always present in the initial metastable phase, even if only in small numbers, and can serve as nucleating centres of a stable phase.

The idea about the predominance of heterogeneous nucleation over homogeneous nucleation was introduced by Volmer. He was the first to substantiate this predominance in the case of heterogeneous nucleation on ions and in the case of condensation on macroscopic boundaries of metastable phase both from thermodynamic and kinetic points of view [1]. The case of wettable solid nucleus completely covered by thick liquid film was considered first by Krastanov [2].

It is recognized in the present state of the art that the advantage of the heterogeneous mechanism of phase transition over the homogeneous mechanism is determined by the gain in the energy of formation of a stable phase embryo. This gain in the energy is associated with surface forces at interfaces.

The role of surface forces is especially complex in heterogeneous phase transitions, and so this role has been little studied theoretically until now even in the most typical case of vapour nucleation on solid nuclei. The reason why surface forces can provide the possibility of intensive heterogeneous condensation on solid insoluble nuclei at low

supersaturations of vapour has itself been unclear. It is usually assumed, following Krastanov [2], that the heterogeneous formation of a stable phase embryo requires smaller work in comparison with the homogeneous formation, i.e. is more favourable energetically, if the work of transfer of a heterogeneous nucleus from the metastable phase into the stable phase is negative. Even though this condition, as we will see later, indeed is necessary, it is not sufficient to explain the essential predominance of heterogeneous nucleation over homogeneous nucleation. The number of foreign particles present in the metastable phase and serving as the centres for heterogeneous formation of the stable phase is, as a rule, smaller by many orders than the number of metastable phase molecules serving as the centres of homogeneous nucleation. In order that heterogeneous phase transition might nevertheless occur sufficiently intensively, the energetic advantage of the heterogeneous mechanism over the homogeneous should be extremely high. This happens practically in the situation when heterogeneous nucleation proceeds as a barrierless or near-barrierless process.

Revealing the ability of such a situation and consideration of its association with the surface forces at interfaces will be the principal goal of the investigation presented below.

Being interested in the principal side of the problem, we will suppose for certainty that the initial metastable phase is a supersaturated vapour and the final stable phase is a liquid. We will refer to this liquid as a condensate. The nucleus in a stable phase embryo will be assumed wettable and enveloped by the film of condensate uniformly from all sides. In this way, we exclude from consideration the mechanism of heterogeneous phase transition through the formation of separate droplet caps with a finite contact angle on the nucleus surface [3,4]. The mechanism of creation of a continuous wetting film of condensate [5,6] and the question about the role of inhomogeneity of the nucleus surface [7,8] are also beyond the scope of the investigation.

Explanation of the origin of the energetic advantage of the heterogeneous mechanism of phase transition over the homogeneous mechanism will be given in the investigation on the basis of the idea about overlapping of the surface layers of condensate film between the nucleus of condensation and vapour. The overlapping of the surface layers is provided by the long-range character of surface forces at the interface between nucleus and condensate, and it will be taken into account in the investigation through the difference of the work of wetting of a nucleus by the condensate film in comparison with wetting by the liquid

bulk phase. As we will see below, just this overlapping of surface layers, which is typical for thin condensate films, affords a possibility of barrierless nucleation on wettable nuclei. This possibility was excluded in the approximation of thick film used by Krastanov [2].

The effect of overlapping surface layers of the liquid film between the nucleus and the vapour was discussed first in the thermodynamics of heterogeneous nucleation by Shcherbakov [9] and by Shcherbakov and Tereshin [10,11]. They announced that the expression for the work of droplet formation on a wettable nucleus should include an additional term which accounted for the van der Waals forces between nucleus and condensate. This term displayed a power-law dependence on the thickness of the droplet liquid film and could not be reduced to "volume" and "surface" terms present in the case of a thick liquid film on the nucleus. However, an activation barrier of nucleation and the preexponential factor in equilibrium distribution of sizes for heterogeneously nucleated droplets were defined incorrectly in Refs. [9–11]. As a result, the statement that the activation barrier for heterogeneous nucleation vanishes when the work of formation of the critical embryo goes to zero was in error.

Further, the contributions to the chemical potential of the spherical film of condensate due to the van der Waals forces between the solid nucleus and the vapour were calculated by Belosludov and Nabutovski [12,13] by means of a study of the fluctuating electromagnetic field in the systems with spherical interfaces. These contributions gave in an explicit form the molecular constituent of the overlapping of the surface layers of the condensate film between the nucleus and vapour. In distinction to preceding authors [2,9–11], Belosludov and Nabutovski correctly defined the activation barrier of heterogeneous nucleation on wettable insoluble particles as the difference in the values of the work of formation for critical and equilibrium droplets. They showed that the threshold for barrierless nucleation, i.e. the vapour supersaturation at which the activation barrier of nucleation goes to zero, could exist in the case when the condensation nuclei had greater optical density than the film of condensate. Structural surface forces were not considered in Refs. [12,13].

The competition between surface forces and curvature to determining the thickness of wetting layers, and the resulting wetting phase diagram, have also been studied from the point of view of the statistical mechanics of surface phase transitions by Upton et al. [14].

Structural surface forces in the thermodynamics of vapour nucleation on macroscopic solid nuclei were first accounted for by Rusanov and

Kuni [15,16]. They showed the possibility of barrierless heterogeneous nucleation in the presence of structural forces and found the dependence of vapour supersaturation at the threshold of barrierless heterogeneous nucleation on the characteristics of the forces and on the size of the condensation nuclei.

The specific distinctions of the kinetics of overcoming the activation barrier for nucleation on insoluble nuclei in comparison with the kinetics of homogeneous nucleation have not been discussed in the literature previously. But it is just the kinetics that make a link between theory and experiment. As follows from previously obtained thermodynamic results [15,16], if the energetic advantage of heterogeneous nucleation over homogeneous nucleation is to be realized at low supersaturations of vapour, the nuclei of condensation must be macroscopic (though their radii may be rather small say, a fraction of a micron). As we will see below, the macroscopic size of nuclei makes the activation barrier of nucleation, as well as the nucleation rate, very sensitive to vapour supersaturation. It will bring an essential simplification permitting formulation of the theory in an analytical form.

In Part I we will consider the principles of thermodynamics of heterogeneous nucleation on wettable macroscopic insoluble nuclei and establish the relation between the thermodynamic and kinetic theories. In Part II we will study the role of both structural and molecular surface forces and formulate the condition for barrierless heterogeneous formation of a droplet around a wettable macroscopic insoluble nucleus of condensation in supersaturated vapour. Determining all thermodynamic quantities which are necessary for the kinetic description of a phase transition, as functions of surface force characteristics and size of the condensation nucleus, the theory will give in this way an answer to all questions raised by experiment.

I. Thermodynamic principles of heterogeneous nucleation on wettable nuclei

1. Chemical potential of condensate in a droplet

Consider a droplet of condensate (phase α) of radius R containing at the centre an insoluble, incompressible, and wettable nucleus (phase γ) with a given radius R_n (Fig. 1). From the outside, the droplet is surrounded by vapour (phase β) of the condensate. The temperature of the
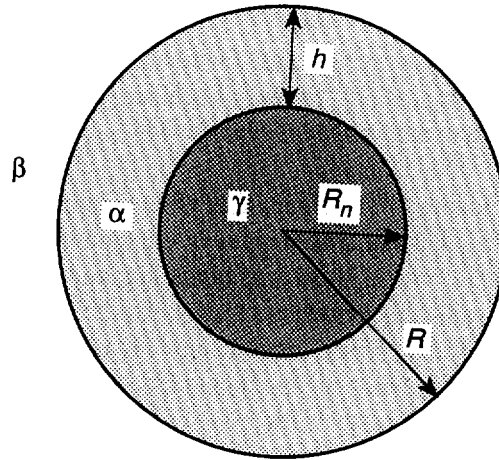
Fig. 1. Liquid drop on a solid wettable condensation nucleus.

droplet is assumed to coincide with the temperature T of the surrounding vapour. The validity of the assumption about the droplet thermalization is provided by passive gas-carrier which practically always is present outside the droplet in large amount (in comparison with vapour) and has little ability to exchange molecules with the droplet. The droplet and the vapour-gas surrounding are in mechanical equilibrium, but chemical (diffusion) equilibrium is not necessarily achieved.

Let v denote the number of molecules which would be in the droplet if it were completely liquid without any nucleus:

$$v = \frac{4\pi R^3}{3\upsilon^\alpha} \tag{1.1}$$

Here υ^α is the volume per molecule in the condensate (the condensate is supposed to be incompressible). We will denote by v_n, the number of molecules of the condensate which might be contained inside the volume of the nucleus:

$$v_n = \frac{4\pi R_n^3}{3\upsilon^\alpha} \tag{1.2}$$

Naturally, $R_n/R < 1$. According to Eqs. (1) and (2), the inequality $(v_n/v)^{1/3} < 1$ also holds with the same accuracy. It is evident that $v - v_n$, represents

the actual number of molecules of condensate in the droplet. One may say that v and v_n represent the volumes of the droplet and the nucleus in units of v^α. We will use the quantity v together with R as a variable of droplet state.

Denote by μ_v the chemical potential of condensate in the droplet. Let us introduce a dimensionless chemical potential of condensate contained in the droplet: $b_v \equiv (\mu_v - \mu_\infty)/kT$. We express the chemical potential b_v in the thermal energy units kT, where k is Boltzmann's constant, and measure it from the value μ_∞/kT corresponding to the condensate–vapour equilibrium with a plane interface.

Choosing v as a variable of droplet state, let us discuss the dependence of b_v on v. It includes, for every value of v, a positive contribution due to capillary pressure of the curved droplet surface. This contribution for droplets of macroscopic size has, with account taken of Eq. (1.1), the form $(2/3)av^{-1/3}$, where

$$a \equiv \frac{4\pi\gamma}{kT}\left(\frac{3v^\alpha}{4\pi}\right)^{2/3}$$ (1.3)

and where γ is the mechanically determined surface tension of the condensate–vapour interface. Since $\gamma \cong const$ for droplet of large size, the contribution to the chemical potential b_v due to capillary pressure decreases monotonously with increase of v. This contribution is leading in the case of homogeneous nucleation.

The presence of an additional contribution in the expression for the chemical potential b_v, which counteracts the capillary pressure, is a specific feature and even an indication of heterogeneous nucleation. Denoting this contribution by β_v, we have

$$b_v = \frac{2}{3}av^{-1/3} + \beta_v$$ (1.4)

The contribution β_v is opposite in sign to the contribution of the capillary pressure and grows in absolute value relatively faster with decreasing droplet size. The specific form of this counterpart and its association with surface forces for condensation nuclei of various kinds will be clarified in Section II. Here we need only state the fact that competition between the contributions β_v and $(2/3)av^{-1/3}$ leads to the appearance of a maximum in the curve of the dependence of condensate chemical potential b_v on v for heterogeneously nucleated droplets.
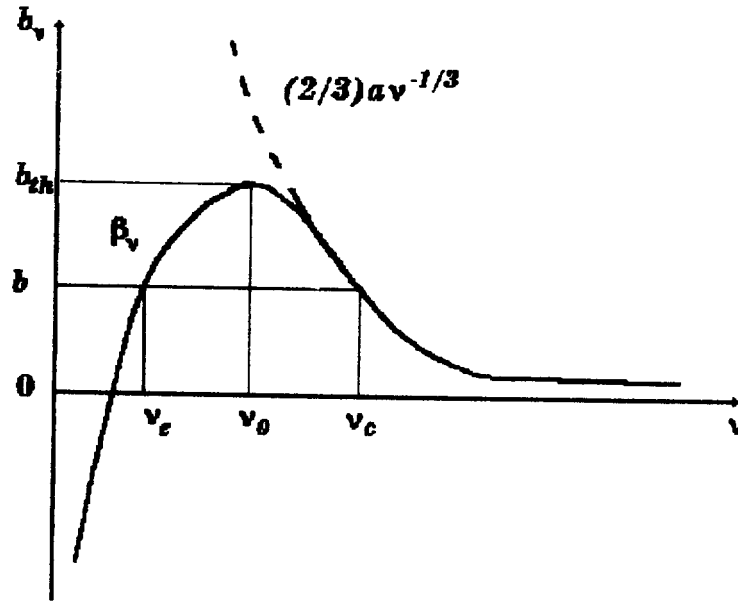
Fig. 2. Dependence on v of the chemical potential b_v of condensate in a droplet.

A typical plot for dependence of b_v on v is presented on Fig. 2. The solid curve shows the behaviour of b_v in heterogeneous nucleation. The broken line represents the contribution to b_v of capillary pressure. The corresponding curve would represent b_v in homogeneous nucleation. As we see, the chemical potential of the condensate reaches its maximum at $v = v_0$. We will denote further by subscript 0 the values of quantities at the extreme points of b_v. It is obvious in the case considered that

$$(\partial b_v / \partial v)_0 = 0 \tag{1.5}$$

$$(\partial^2 b_v / \partial v^2)_0 < 0 \tag{1.6}$$

(see Fig. 2).

Denote by μ^β the chemical potential of vapour. Let us introduce the dimensionless chemical potential of vapour

$$b \equiv (\mu^\beta - \mu_\infty) / kT \tag{1.7}$$

If the vapour may be considered as an ideal gas, the chemical potential b is related to the vapour supersaturation $\zeta \equiv (p - p_\infty)/p_\infty$ (p is the vapour pressure) as

$$b = \ln (1 + \varsigma) \tag{1.8}$$

For $b < (b_v)_0$, the heterogeneously nucleated droplet can be in stable (equilibrium droplet) and unstable (critical droplet) equilibrium with vapour. We will use subscripts e and c to identify variables referring to equilibrium and critical droplets. We have

$$(b_v)_e = b, \quad (b_v)_c = b \tag{1.9}$$

$$(\partial b_v / \partial v)_e > 0, \quad (\partial b_v / \partial v)_c < 0 \tag{1.10}$$

(see Fig. 2).

Critical and equilibrium droplets coincide, $v_e = v_c$, when the vapour chemical potential approaches the value

$$b_{th} = \max(b_v) = (b_v)_0 \tag{1.11}$$

For $b > b_{th}$, equilibrium and critical droplets are absent entirely. Only an equilibrium droplet exists at $b < 0$. This allows us to conclude that Eq. (1.11) determines the threshold value b_{th} for the vapour chemical potential b, that is expressed (as b_v) in units of the thermal energy kT and measured from μ_∞/kT. For $b > b_{th}$, nucleation of a droplet around the condensation nucleus proceeds barrierlessly.

For $b > b_{th}$, all the thermodynamic information important for kinetics and experiment consists of value b_{th}. Therefore, finding b_{th} as a function of the size of "dry" condensation nuclei and physical and chemical parameters of nuclei and condensate becomes the actual problem. This problem for macroscopic wettable uncharged and insoluble condensation nuclei will be solved in Section II.

The subthreshold region of values of vapour chemical potential $0 < b < b_{th}$, where heterogeneous nucleation proceeds with a barrier, turns out to be nontrivial for the kinetics and for experiment. We will return to analysis of this region in the next section.

Note in conclusion of this section, that the threshold value b_{th} of vapour chemical potential is limited from below. This limit has a thermodynamic origin. We neglected the pressure of the surrounding vapour–gas in comparison with the capillary pressure in the droplet when we considered contributions to the chemical potential of the condensate. Meanwhile, the capillary pressure can be comparable with and even smaller than the surrounding pressure for drops of large size in surroundings enriched by a passive gas. Taking pressure of the surroundings into account, we find an additional term $v^\alpha(n_g + n^\beta - n_\infty^\beta)$

in the expression for the chemical potential b_v of the condensate, where n_g, n^β and n^β_∞ are the densities of the numbers of molecules of the passive gas, the vapour that is present and the saturated vapour above the plane surface of the condensate, respectively. The same term, in view of its independence of v, will be in the threshold value b_{th} of the vapour chemical potential. As a result, the value b_{th}, increases by a term $v^\alpha n_g$, if we recognize that $n_g \gg n^\beta - n^\beta_\infty$ for surroundings enriched by passive gas. Therefore, if the threshold value b_{th}, which does not take into account the pressure of the surroundings, can approach very small values in its dependence on the parameters of nucleus and condensate, then the term $v^\alpha n_g$ will limit the smallest threshold value of the vapour chemical potential.

2. The work of droplet formation

In modern thermodynamics, the work of transfer from the initial state 1 to the final state 2 is usually found as the difference of an appropriate thermodynamic potential for the above two states. The choice of potential depends on the external conditions. If the formation of a droplet proceeds, e.g., at fixed temperature, volume of the system, and amounts of all components, the work W of heterogeneous droplet formation is the difference in free energy Φ for the system in the final and the initial states:

$$W = \Phi_2 - \Phi_1 \tag{2.1}$$

For our purposes, it will be convenient to express the work W also through the grand thermodynamic potential Ω which is related to the free energy by the identity $\Phi = \sum_i \mu_i N_i + \Omega$, where μ_i and N_i are the chemical potential and number of molecules of component i of the fluid part of the system. Putting this identity into Eq. (2.1) yields

$$W = \sum_i (\mu_{i2} - \mu_{i1}) N_i + \Omega_2 - \Omega_1 \tag{2.1a}$$

In the initial state, the system includes only the nucleus (phase γ), vapour and passive gas (phase β), so that

$$\Omega_1 = \Omega_1^\gamma + \Omega_1^\beta + \overline{\Omega}^{\gamma\beta}$$

where here and below single superscripts denote bulk phases and double

superscripts denote corresponding interfaces; surface excess quantities are barred. The final stage includes, in addition, a liquid film of condensate (phase α) between phases γ and β which, generally speaking, need not be equilibrated with the surrounding vapour (the film and the vapour may have different chemical potentials):

$$\Omega_2 = \Omega_2^\alpha + \Omega_2^\beta + \Omega_2^\gamma + \overline{\Omega}^{\,\alpha\beta} + \overline{\Omega}^{\,\gamma\alpha}$$

Putting now the above expressions for Ω_1 and Ω_2 into Eq. (2.1a) and recruiting notation introduced in the previous section, one can write Eq. (2.1) in the form

$$W = (v - v_n)\,(\mu_v - \mu^\beta) + \overline{\Omega}^{\alpha\beta} + \overline{\Omega}^{\gamma\alpha} + \overline{\Omega}^{\gamma\beta} + \Omega_{R_n R}^\alpha(\mu_v) - \Omega_{R_n R}^\beta(\mu^\beta) \qquad (2.2)$$

It is implied in Eq. (2.2) that the chemical potentials, as well as the pressure, of the vapour and passive gas-carrier stay practically fixed during the process of droplet formation. This is fulfilled well for a sufficiently large system. The quantity $\Omega_{R_n R}^\alpha(\mu_v)$ in Eq. (2.2) stands for grand thermodynamic potential which we will refer to as the bulk part of the film of condensate. If the surface layers of the film do not affect each other, then $\Omega_{R_n R}^\alpha(\mu_v)$ coincides with the grand thermodynamic potential of the condensate having chemical potential μ_v and contained between spherical surfaces with radii R_n and R. Both with the interference of surface layers and without it, the sum $\overline{\Omega}^{\,\alpha\beta} + \overline{\Omega}^{\,\gamma\alpha} + \Omega_{R_n R}^\alpha(\mu_v)$ describes the whole grand thermodynamic potential of the condensate film. Considering the excess grand thermodynamic potentials $\overline{\Omega}^{\,\gamma\alpha}$ and $\overline{\Omega}^{\,\alpha\beta}$ to be the same as in the case of interfaces between corresponding phases of infinite extent, we will incorporate the whole effect of surface-layer interference into quantity $\Omega_{R_n R}^\alpha(\mu_v)$. The quantity $\Omega_{R_n R}^\beta(\mu^\beta)$ in Eq. (2.2) stands for the grand thermodynamic potential of vapour (having chemical potential μ^β) and passive gas which are contained between spherical surfaces with radii R_n and R.

Let the droplet radius R and nucleus radius R_n coincide with the radii of the corresponding equimolecular surfaces of the droplet with respect to the condensate. Then, in the approximation of incompressible condensate in the film, we have

$$\Omega_{R_n R}^\alpha(\mu_v) \cong \Omega_{R_n R}^\alpha(\mu_\infty) - (v - v_n)\,(\mu_v - \mu_\infty) \qquad (2.3)$$

Considering the vapour and passive gas as a mixture of ideal gases, we may write the grand thermodynamic potential $\Omega_{R_n R}^\beta(\mu^\beta)$ in the form

$$\Omega^{\beta}_{R_{n},R}(\mu^{\beta}) \cong \Omega^{\beta}_{R_{n},R}(\mu_{\infty}) - v^{\beta}_{R_{n},R} \, \varsigma \, kT \tag{2.4}$$

where $v^{\beta}_{R_{n},R}$ is the number of vapour molecules per unit volume of the spherical layer between radii R_{n} and R at $\mu^{\beta} = \mu_{\infty}$. Evidently, the following strong inequality is fulfilled:

$$\varsigma \, v^{\beta}_{R_{n},R} \ll v - v_{n} \tag{2.5}$$

Let us introduce thermodynamically defined surface tensions $\sigma^{\alpha\beta}$, $\sigma^{\gamma\alpha}$, and $\sigma^{\gamma\beta}$ for the interfaces liquid–gas, nucleus–liquid and nucleus–gas by the relationships

$$\sigma^{\alpha\beta} = \overline{\Omega}^{\,\alpha\beta} / 4\pi R^{2} \tag{2.6}$$

$$\sigma^{\gamma\alpha} = \overline{\Omega}^{\,\gamma\alpha} / 4\pi R_{n}^{2} \tag{2.7}$$

$$\sigma^{\gamma\beta} = \overline{\Omega}^{\,\gamma\beta} / 4\pi R_{n}^{2} \tag{2.8}$$

If the nucleus carries an electric charge, then the thermodynamically defined surface tensions $\sigma^{\alpha\beta}$, $\sigma^{\gamma\alpha}$, and $\sigma^{\gamma\beta}$ do not coincide with the mechanically defined surface tensions for the corresponding interfaces [17,18]. Considering henceforth uncharged nuclei of macroscopic size and, accordingly, macroscopic droplets, we will assume

$$\sigma^{\alpha\beta} \cong \sigma^{\alpha\beta}_{\infty} = \gamma, \qquad \sigma^{\gamma\alpha} \cong \sigma^{\gamma\alpha}_{\infty}, \qquad \sigma^{\gamma\beta} \cong \sigma^{\gamma\beta}_{\infty} \tag{2.9}$$

The quantity

$$f \equiv \frac{\Omega^{\alpha}_{R_{n},R}(\mu_{\infty}) - \Omega^{\beta}_{R_{n},R}(\mu_{\infty}) + \overline{\Omega}^{\gamma\alpha} - \overline{\Omega}^{\gamma\beta}}{kT} \tag{2.10}$$

represents the work of wetting of a nucleus by a film of condensate bounded by spherical surfaces with radii R_{n} and R. This work is expressed in units of the thermal energy kT. Both the film and vapour quantities are taken in Eq. (2.10) at the same value of the chemical potential, $\mu = \mu_{\infty}$. Further we will refer to the work f as the work of wetting of a nucleus in a droplet.

The quantity f depends on the character of the surface forces at the interface between the nucleus and condensate in the droplet and on the thickness of the condensate film. If the nucleus of condensation is absent and $R_n = 0$ or if the nucleus consists of the same condensate, then the pressures in the liquid and gas phases are equal, and we have $\Omega^{\alpha}_{R_n,R}(\mu_{\infty}) = \Omega^{\beta}_{R_n,R}(\mu_{\infty})$. If the nucleus is absent, then $\sigma^{\gamma\alpha} = \sigma^{\gamma\beta} = 0$ and, as is seen from Eqs. (2.7)–(2.10), $f = 0$. If the nucleus is a droplet of condensate of radius R_n, then $\sigma^{\gamma\alpha} = 0$, $\sigma^{\gamma\beta} = 0$ and, as follows from Eqs. (2.7)–(2.10), $f = -4\pi R_n^2 \gamma/kT$.

It is convenient to use the work of droplet formation F expressed in units of the thermal energy kT, instead of W:

$$F = W / kT \tag{2.11}$$

Recognizing Eqs. (2.3)–(2.11), Eqs. (1.1)–(1.3), and Eq. (1.7), we find from Eq. (2.2)

$$F = a v^{2/3} - b(v - v_n) + f \tag{2.12}$$

In the presence of thermal and mechanical equilibrium of the droplet with the surrounding vapour–gas, we have the differential thermodynamic relation [19]

$$\partial F / \partial v = b_v - b \tag{2.13}$$

which takes into account the fact that the amount of matter in the nucleus of the droplet remains unchanged and the droplet does not exchange molecules with the passive gas. The relation is equivalent to the condition of aggregation equilibrium in the vapour and is satisfied at every value of the vapour chemical potential b (either positive for supersaturated vapour, or negative for undersaturated vapour).

Using Eq. (2.13) and taking into account successively Eqs. (1.9), (1.10), and (1.5), we obtain

$$(\partial F / \partial v)_e = 0, \quad (\partial F / \partial v)_c = 0 \tag{2.14}$$

$$(\partial^2 F / \partial v^2)_e > 0, \quad (\partial^2 F / \partial v^2)_c < 0 \tag{2.15}$$

$$(\partial^2 F / \partial v^2)_0 = 0 \tag{2.16}$$

Thus, at the points $v = v_e$, $v = v_c$ and $v = v_0$ the work F as a function of v has a minimum, a maximum, and a point of inflection, respectively.

The dependence of F on v that follows from Eq. (2.13) and Fig. 2 (and is in agreement with Eqs. (2.14)–(2.16)) is shown in Fig. 3. We have taken into account the fact that $F|_{v=v_n} = 0$: the nucleus of condensation
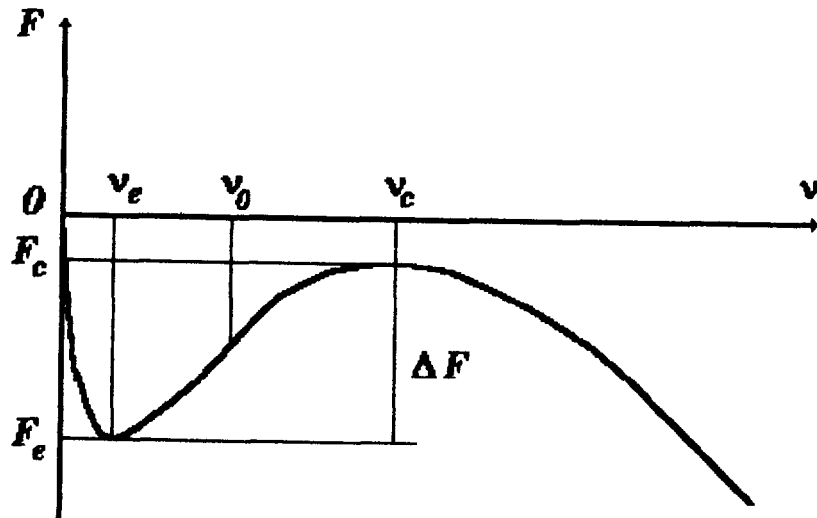
Fig. 3. Dependence on v of the work F of heterogeneous droplet formation at $0 < b < b_{th}$.

is originally present in the vapour–gas medium, and therefore no work is required for its formation. As a consequence, $F_e < 0$. As is seen from Fig. 2, with decreasing vapour supersaturation down from the threshold value b_{th}, the points $v = v_e$ and $v = v_c$ move away to the left and right of the point $v = v_0$, which does not depend on vapour supersaturation. At the same time, the minimum F_e and maximum F_c of the work F, which have merged at $b = b_{th}$ at the point of inflection $v = v_0$, increase. There comes a moment, at some value of the vapour supersaturation, at which the inequality $F_c < 0$ (its validity is assumed in Fig. 3) is violated. However, the inequality $F_e < 0$ always remains valid. Among other things, this inequality implies $F\,|\,^{v=v_0}_{b=b_{th}} < 0$.

If $b > b_{th}$, then the work F, according to Eq. (2.13) and the condition $F\,|\,_{v=v_n} = 0$, decreases monotonously, starting from zero at the point $v = v_n$, with increasing v within the entire physical range $v > 0$. Just this shows that the heterogeneous phase transition certainly proceeds in a barrierless way at $b > b_{th}$. The fact that at $b = b_{th}$ the derivative $\partial F / \partial v$ goes to zero at the single point $v = v_0$ of the maximum of b_v, does not affect the conclusion.

Taking the derivative of F with respect to v, with account of Eq. (2.12), substituting the result into the left-hand side of Eq. (2.13), and comparing it with Eq. (1.4), we conclude

$$\partial f / \partial v = \beta_v \qquad\qquad\qquad (2.17)$$

It is obvious from Eq. (2.17), that only a v-dependent contribution to the work of wetting of the nucleus in the droplet can provide the specific features of heterogeneous nucleation, and, in particular, the existence of the point of inflection, $v = v_0$, and the inequality $F|_{b=b_{th}}^{v=v_0} < 0$.

3. Thermodynamic characteristics of nucleation in subthreshold and prethreshold region of vapour metastable state

Let us return to the study of the subthreshold region of the vapour metastable state, $0 < b < b_{th}$, that we started in Section 1. We write the vapour chemical potential in the form

$$b = b_{th}(1 - \varepsilon) \tag{3.1}$$

where ε is the relative deviation of b below b_{th}. Our immediate program will be to find all the thermodynamic characteristics that are important for the kinetics of heterogeneous nucleation and are exhibited in experiment as functions of ε in the subthreshold region where $0 < \varepsilon < 1$.

Expanding b_v in a Taylor series in the neighbourhood of the point $v = v_0$, and using Eqs. (1.5), (1.6), and (1.11), we obtain

$$b_v = b_{th} - \frac{1}{2}\left|\frac{\partial^2 b_v}{\partial v^2}\right|_0 (v - v_0)^2 \tag{3.2}$$

It is obvious that the parabolic approximation is valid if the neglected term with the third derivative of b_v with respect to v at the point $v = v_0$ is small with respect to the retained term with the second derivative of b_v with respect to v at the same point. This requires

$$\frac{1}{3}\left|\frac{(v - v_0)\,(\partial^3 b_v/\partial v^3)_0}{(\partial^2 b_v/\partial v^2)_0}\right| \ll 1 \tag{3.3}$$

Using Eqs. (3.2), (1.9), and (3.1), we find

$$v_e = v_0 - \left(2\varepsilon b_{th}\,/\left|\partial^2 b_v/\partial v^2\right|_0\right)^{1/2}$$

$$v_c = v_0 + \left(2\varepsilon b_{th}\,/\left|\partial^2 b_v/\partial v^2\right|_0\right)^{1/2} \tag{3.4}$$

Fulfilment of Eq. (3.3) for $v = v_e$ and $v = v_c$ presupposes, as is clear from Eq. (3.4),

$$\frac{1}{3} \left(2\varepsilon b_{th}\right)^{1/2} \left|\frac{\partial^3 b_v}{\partial v^3}\right|_0 \Big/ \left|\frac{\partial^2 b_v}{\partial v^2}\right|_0^{3/2} \ll 1 \tag{3.5}$$

We will continue to keep Eqs. (3.3) and (3.5) in mind, as the conditions for the validity of the theory.

From Eqs. (3.2) and (2.13), taking into account Eq. (3.1), we have

$$\frac{\partial F}{\partial v} = b_{th} \left[\varepsilon - \frac{1}{2b_{th}} \left|\frac{\partial^2 b_v}{\partial v^2}\right|_0 (v - v_0)^2\right] \tag{3.6}$$

The approximation, Eq. (3.6), is justified within the whole region where Eq. (3.3) holds. If Eq. (3.5) is valid, the interval $v_e \le v \le v_c$ falls into this region.

Characteristic of nucleation important in the kinetics is the activation energy

$$\Delta F = F_c - F_e \tag{3.7}$$

— the difference between the ordinates of the potential hump and the potential well in the work of droplet formation (see Fig. 3). Integrating Eq. (3.6) with respect to v from v_e to v_c, and taking into account Eq. (3.4), we obtain

$$\Delta F = \frac{4}{3} \varepsilon^{3/2} b_{th}^{3/2} \left[\frac{2}{|\partial^2 b_v / \partial v^2|_0}\right]^{1/2} \tag{3.8}$$

Recognizing Eqs. (2.14) and (2.15), we write the following approximations

$$F = F_e + \left[\frac{(v - v_e)}{\Delta v_e}\right]^2 \qquad (|v - v_e| \le \Delta v_e) \tag{3.9}$$

$$F = F_c - \left[\frac{(v - v_c)}{\Delta v_c}\right]^2 \qquad (|v - v_c| \le \Delta v_c) \tag{3.10}$$

where

$$\Delta v_e = \left[\frac{2}{(\partial^2 F / \partial v^2)_e} \right]^{1/2}, \qquad \Delta v_c = \left| \frac{2}{(\partial^2 F / \partial v^2)_c} \right|^{1/2} \qquad (3.11)$$

Obviously, Δv_e and Δv_c are the "half-widths" of the potential well and the potential hump in the work F. The work F becomes larger by kT than the minimal work F_e at $|v - v_e| = \Delta v_e$ and smaller by kT than the maximal work F_c at $|v - v_c| = \Delta v_c$. Subcritical droplets gather at the bottom of the potential well in F, approximately inside half-width Δv_e, before, by fluctuation, overcoming the potential hump in F with half-width Δv_c. The smaller Δv_e and Δv_c, i.e. the narrower the well and the hump in F, the more readily does the heterogeneous phase transition proceed. We will call near-equilibrium and near-critical the droplets for which the variable v lies in the neighbourhoods $|v - v_e| \le \Delta v_e$ and $|v - v_c| \le \Delta v_c$ of the points $v = v_e$ and $v = v_c$, respectively.

The condition of smallness of the terms omitted in Eqs. (3.9) and (3.10), with the third derivative of F with respect to v at the points $v = v_e$ and $v = v_c$, relative to the terms retained in Eqs. (3.9) and (3.10), with the second derivative of F with respect to v at the points $v = v_e$ and $v = v_c$, is, as is clear from Eq. (3.6), given by the inequalities

$$\frac{\Delta v_e}{3(v_0 - v_e)} \ll 1, \qquad \frac{\Delta v_c}{3(v_c - v_0)} \ll 1 \qquad (3.12)$$

They also reflect the condition that the heterogeneous phase transition proceeds subject to a barrier (ie., that the potential well and the potential hump in the work F are fully manifested). The justification of the inequalities present in Eq. (3.12) will be given below.

Using Eqs. (3.6) and (3.11), and taking into account Eq. (3.4), we obtain

$$\Delta v_e = \Delta v_c = \left(\frac{2}{\varepsilon b_{th} \, |\partial^2 b_v / \partial v^2|_0} \right)^{1/4} \qquad (3.13)$$

It follows from Eqs. (3.11), (3.8), and (3.13) that

$$\frac{\Delta v_e}{v_0 - v_e} = \frac{\Delta v_c}{v_c - v_0} = \frac{2}{(3\Delta F)^{1/2}} \qquad (3.14)$$

Note the universality of the last relation which allows us to rewrite Eq. (3.12), the condition that the heterogeneous phase transition be characterized by a barrier, in the form of a restriction on the value of the activation energy ΔF from below

$$(\Delta F)^{1/2} \gg 2 / 3^{3/2} \tag{3.15}$$

The intensity of heterogeneous nucleation of supercritical droplets which grow without limit depends on ΔF through $\exp(-\Delta F)$. For practically any concentration of condensation nuclei in the surrounding vapour–gas, the only part of the entire subthreshold region of the vapour metastable state that will be of interest for the theory is in fact

$$3 \leq \Delta F \leq 30 \tag{3.16}$$

Indeed, for $\Delta F \geq 30$, the exponential $\exp(-\Delta F)$ is so small that heterogeneous nucleation hardly takes place at all. For $\Delta F \leq 3$, the inequality in Eq. (3.15) is violated, and the exponential $\exp(-\Delta F)$ will no longer be small. The heterogeneous nucleation then takes place practically in the barrierless regime, and this so greatly simplifies the kinetics of heterogeneous phase transition that, among all the thermodynamic relations obtained above, all that remains important for the kinetics is (as in the region $b > b_{th}$) just the value b_{th}.

We will call the region of vapour metastable state in which Eq. (3.16) holds the "prethreshold region". Further, when we will consider specific condensation nuclei, we will demand that Eq. (3.5) be fulfilled for every ε that, through Eqs. (3.8) and (3.16), belong to the prethreshold region of the vapour metastable state. Obviously, this will give some restrictions on the accessible values of parameters of the condensation nuclei determining v_0, b_{th}, $(\partial^2 b_v / \partial v^2)_0$, $(\partial^3 b_v / \partial v^3)_0$. As we will see in a subsequent section, for macroscopic condensation nuclei in the subthreshold region $0 < \varepsilon < 1$ the prethreshold region occupies only a very narrow gap with width of the order of the distance of the gap from the upper limit of the subthreshold region.

If Eq. (3.5) is satisfied in the prethreshold region, then the inequalities

$$\Delta v_e / v_e \ll 1, \qquad \Delta v_c / v_c \ll 1 \tag{3.17}$$

hold in the prethreshold region even more strongly than the inequalities in Eq. (3.12). Equation (3.17) justifies Eq. (3.6) not only within the interval $v_e \leq v \leq v_c$ but also within the interval $v_e - \Delta v_e \leq v \leq v_c + \Delta v_c$. The validity of Eq. (3.17) itself will be proved in a subsequent section when we will consider particular approximations for the dependence of the

chemical potential of condensate in the droplet, b_v, on v.

If ΔF satisfies Eq. (3.16), the right-hand side of Eq. (3.14) is bounded from below by the value $2/(90)^{1/2}$. This means

$$\Delta v_e \gg 1, \qquad \Delta v_c \gg 1 \qquad (3.18)$$

for droplets with $v \gg 1$ and, consequently, with $v_0 - v_e \gg 1$ and $v_c - v_0 \gg 1$. The inequalities are important, in particular, because they show [21] that the variable v (which is essentially discrete) can be justifiably regarded as continuous within the potential well and the potential hump in F.

4. Relation between thermodynamic and kinetic theories of nucleation

The kinetics of nucleation plays the linking role between thermodynamics of nucleation and experiment. According to the results of the preceding section, the kinetics of heterogeneous nucleation is of the most interest in the prethreshold region of the vapour metastable state in which the kinetics opens up the possibility of external control of the development of the phase transition in time and the possibility of maximal retrieval of inverse information about molecular properties of the condensate from experimental data.

When discussing the kinetics of heterogeneous nucleation, we will bear in mind the first stage of the phase transition in supersaturated vapour, the stage of effective nucleation of droplets. Development of subsequent stages of nucleation in their dependence on regularities of the first stage and also on external conditions of creation of the vapour metastable state and on the change in time of the vapour concentration of condensation nuclei was investigated in general earlier in Refs. [22,23].

The general character of the approach presented below is provided by the fundamental thermodynamic starting points used to describe heterogeneous nucleation: the threshold value of the vapour chemical potential, the locations and halfwidths of the potential well and the potential hump in the work of heterogeneous droplet formation, and the activation energy.

To construct a kinetic equation governing the process by which fluctuations allow near-critical embryos to overcome the activation barrier, we need to know, first, their equilibrium distribution and, second, the rate of change in time of the variable that describes them.

We denote by $n^{(e)}(v)$ the equilibrium distribution of droplets as a function of the variable v, referred to unit volume of vapour. For

simplicity, we shall assume that the condensation nuclei are all identical. We denote their number in unit volume of the vapour by n_n.

Because the work F_e is negative and is large in absolute magnitude in the prethreshold region of the vapour metastable state (large as compared with the thermal energy kT), practically each of the condensation nuclei captures such a number of vapour molecules for which the newly formed droplet is at the bottom of the potential well in the work F. As a result, an equilibrium distribution of the heterogeneously nucleating droplets will also be formed.

Recognizing that the equilibrium distribution has the form of a Gibbs distribution, we then obtain

$$n^{(e)}(v) = \frac{n_n}{\pi^{1/2}\Delta v_e} \exp\left[-(F - F_e)\right] \tag{4.1}$$

To prove the correctness of the normalization factor in this distribution, we integrate it over the near-equilibrium neighbourhood $|v - v_e| < \Delta v_e$ where it is mainly concentrated. Using Eq. (3.9), we conclude that the integral is, as it must be, equal to n_n.

The idea, expressed by Eqs. (4.1) and (3.9), that heterogeneously produced droplets accumulate at the bottom of the potential well in the work of droplet formation before they overcome the activation barrier in a fluctuation process was used earlier [20] in the theory of ion-induced nucleation in a metastable vapour.

In the near-critical neighbourhood $|v - v_c| < \Delta v_c$ of the point $v = v_c$ of the maximum of the work of droplet formation, which is important for kinetics, the work F can be written in the form of Eq. (3.10). In this neighbourhood, in which the equilibrium distribution is small and has a purely formal meaning, we obtain from Eq. (4.1), taking into account Eqs. (3.10) and (3.7),

$$n^{(e)}(v) = \frac{n_n}{\pi^{1/2}\Delta v_e} \exp(-\Delta F) \exp\left[\left(\frac{v - v_c}{\Delta v_c}\right)^2\right] \quad (|v - v_c| \leq \Delta v_c) \tag{4.2}$$

The fact that F_e and F_c have appeared in Eq. (4.2) in the form of the difference $F_c - F_e$ shows why it was sufficient to start from the differential (and not finite-difference) relation in Eq. (2.13), which determines the work F only up to a constant term.

Let us now turn to the finding of the rate of change $\dot{v}$ with respect to the time in a near critical droplet. Considering the vapour as an ideal

gas, we relate the chemical potential b of the vapour, which is present in the system, and the chemical potential b_v of the imaginary vapour which is in equilibrium with a droplet consisting of v molecules of condensate at temperature T, to the vapour density,

$$n^\beta = n^\beta_\infty \exp(b), \qquad n^\beta_v = n^\beta_\infty \exp(b_v) \tag{4.3}$$

To describe free-molecule material exchange between droplet and vapour, we will use the well-known Knudsen formula,

$$\dot{v} = w(1 - n^\beta_v / n^\beta) \tag{4.4}$$

where

$$w = \pi \alpha_C v_T n^\beta R^2 \tag{4.5}$$

with α_C the sticking coefficient for vapour molecules and v_T the mean thermal velocity of vapour molecules. The assumption that the material exchange between the droplet and the vapour is in the free-molecule regime imposes an upper limit on R [24]. The limitation, however, as we will see further, is so weak that it is practically always fulfilled in the stage of the nucleation of supercritical droplets, even for condensation nuclei of macroscopic size.

Using Eqs. (4.3) and (2.13) in Eq. (4.4), we find

$$\dot{v} = w[1 - \exp(\partial F / \partial v)] \tag{4.6}$$

In accordance with Eq. (3.10) and with the second inequality from Eq. (3.18), we have in the near-critical neighbourhood $|v - v_c| \leq \Delta v_c$ the approximation $|\partial F/\partial v| \ll 1$. Using it in Eq. (4.6), substituting Eq. (3.10) and recognizing that, if Eq. (3.3) is fulfilled in the prethreshold region, w can be replaced by its value w_0 at $v = v_0$, we obtain

$$\dot{v} = 2W_{th} \frac{v - v_{th}}{(\Delta v_c)^2} \qquad (|v - v_c| \leq \Delta v_c) \tag{4.7}$$

The kinetic equation that governs the process by which near-critical droplets overcome the activation barrier by fluctuation is the Fokker–Planck equation linearized in the neighbourhood of the critical droplet [25–27].

It has the form of the continuity equation

$$\partial_t n(v,t) = -\partial_v j \tag{4.8}$$

where t is the time, $n(v,t)$ is the distribution of droplets with respect to the variable v that describes them, and j is the flux of the droplets. We have used the abbreviated notation $\partial_t \equiv \partial/\partial t$ and $\partial_v \equiv \partial/\partial v$ for the operators of differentiation with respect to t and v. We assume below that $n(v,t)$, like the equilibrium distribution $n^{(e)}(v)$, refers to unit volume of the vapour-passive gas system.

In accordance with the general principles of physical kinetics,

$$j = (\dot{v} + \alpha\partial_v)\, n(v,t) \tag{4.9}$$

The term with the operator ∂_v describes the fluctuation development of droplets. This is superimposed on the regular development of an individual droplet described by the term with $\dot{v}$. The unknown coefficient α of the term with the operator ∂_v is determined from the condition of vanishing of the flux of droplets when they have their equilibrium distribution.

Taking into account Eqs. (4.2) and (4.7) in Eq. (4.9), we then obtain

$$j = -w_0 \left[\partial_v - 2\frac{v - v_c}{(\Delta v_c)^2} \right] n(v,t) \tag{4.10}$$

Substituting Eq. (4.10) into Eq. (4.8), we finally arrive at

$$\partial_t n(v,t) = w_0\partial_v \left[\partial_v - 2\frac{v - v_c}{(\Delta v_c)^2} \right] n(v,t) \tag{4.11}$$

The operator ∂_v acts on all factors to the right of it.

The kinetic equation, Eq. (4.11), is written in the same form as in the classical theory of homogeneous nucleation [26,27]. However, the parameters v_c, Δv_c, and w_0 turn out to be essentially different from those in the theory of homogeneous nucleation.

For the distribution $n(v,t)$ we impose the natural boundary conditions for kinetics of phase transitions [27,28]:

$$n(v,t)\,/n^{(e)}(v) \cong 1 \qquad (v \cong v_c - \Delta v_c)$$

$$n(v,t)\,/n^{(e)}(v) \cong 0 \qquad (v \cong v_c + \Delta v_c) \tag{4.12}$$

Under these conditions, the equilibrium distribution $n^{(e)}(v)$ given by Eq. (4.2) also differs essentially from the one in the classical theory of nucleation.

The second of the inequalities in Eq. (3.17) justifies the neglect in Eq. (4.11) of the derivatives of $n(v,t)$ with respect to v of higher than second order, i.e. it justifies the validity of the Fokker–Planck approximation in this equation. Indeed, the second inequality shows that the change of variable v in an individual event in which the droplet captures or emits a vapour molecule (the change is equal to 1 or –1) is small compared with the half-width Δv_c of the potential hump in the work F, which specifies the scale of the variation of the distribution $n(v,t)$ with variation of v.

The linearization of the kinetic equation, Eq. (4.11), in the neighbourhood of the critical droplet is due to the validity of the parabolic approximation, Eq. (3.10), for the work of formation of the near-critical droplet.

Let us now investigate the steady-state solution of Eq. (4.11). We shall identify it by the index s.

In the steady state, the quantities do not depend on t, and the flux, by virtue of Eq. (4.8), is also independent of v. In accordance with Eqs. (4.10), (4.12), and (4.2), we then have

$$n^{(s)}(v) = \frac{n_n \exp(-\Delta F)}{\pi^{1/2} \Delta v_e \Delta v_c} \exp\left[\left(\frac{v - v_c}{\Delta v_c}\right)^2\right] \int\limits_v^\infty dv' \exp\left[-\left(\frac{v' - v_c}{\Delta v_c}\right)^2\right] \tag{4.13}$$

Substituting then Eq. (4.13) in Eq. (4.10), we obtain

$$j^{(s)} = \frac{n_n w_0}{\pi \Delta v_e \Delta v_c} \exp(-\Delta F) \tag{4.14}$$

and this determines a quantity that is important for the kinetics, the steady rate of heterogeneous nucleation of supercritical droplets which then grow without limit. The factor $w_0/\pi \Delta v_e \Delta v_c$ in Eq. (4.14) is the heterogeneous analog of the "Zeldovich factor".

The work of heterogeneous formation of a droplet is represented in the argument of the exponential in Eq. (4.14), as is seen from Eq. (3.7), by the difference $F_c - F_e$. This confirms that the activation energy of heterogeneous nucleation is determined by the sum of the height of the potential hump and the depth of the potential well in the work of droplet formation, and not only by the height of the potential hump as in the case of homogeneous nucleation.

Using the results obtained in Refs. [28,29] in the investigation of an Equation of the form of Eq. (4.11) with the boundary conditions given by Eq. (4.12), we could also describe analytically the process of the establishment in time of a steady state of the near-critical droplets. In particular, we have

$$t_s = \frac{(\Delta v_c)^2}{2w_0} \tag{4.15}$$

for the time t_s of establishment of this state and, therefore, the establishment of a steady rate of nucleation.

The time t_s can be observed in an experiment. It is called the incubation time (or the time lag). When it has elapsed, supercritical embryos of the stable phase begin to arise systematically in the metastable phase with a regular frequency, in number $j^{(s)}$ per unit time in unit volume of the metastable phase.

It can be seen from Eqs. (4.14) and (4.15) with $\Delta v_e = \Delta v_c$ (the equality is fulfilled, according to Eq. (3.13), with high accuracy in the prethreshold region of the vapour metastable state) that the number of supercritical droplets that arise in the steady regime during the time t_s, in unit volume of the vapour–gas system, is the fraction $(1/\pi)\exp(-\Delta F)$ of the number n_n of condensation nuclei in the same volume. This fraction is completely negligible in the prethreshold region of the vapour metastable state where the activation energy ΔF is already substantial.

One can say that the time t_s specifies the scale of the characteristic time of development of the heterogeneous phase transition in the prethreshold region of the vapour metastable state. The work F of formation of a droplet is represented in Eq. (4.15) for the time t_s by the half-width Δv_c of its potential hump.

If t_s is small compared with the time during which there is a significant change of the steady nucleation rate $j^{(s)}$ when the values of b, n_n, and T (and also the volume occupied by vapour and gas) vary in time, then the steady state of the near-critical droplets will be maintained as a quasisteady state, i.e. it will correspond to the instantaneous values of these quantities.

In the laboratory experiment allowing instant generation of the initial value of vapour supersaturation, it is hard to fit accurately into the prethreshold region of the vapour metastable state if the threshold value of vapour supersaturation is itself small. The supersaturation generated may fit into the lower part of the superthreshold region

at $b > b_{th}$. In accordance with this, we note that the time t_s defined by Eq. (4.15) specifies the scale of the characteristic time of development of the heterogeneous phase transition not only in the prethreshold region of the vapour metastable state, but also in the lower part of its superthreshold region $b > b_{th}$. As follows from Eq. (3.1), $\varepsilon < 0$ in the superthreshold region and $|\varepsilon|^{1/2}$ satisfies Eq. (3.5), which can be reduced, as was noted above, to the inequality $|\varepsilon|^{1/2} \ll 1$.

Let us prove this. Equation (2.13), as well as Eq. (3.6), is not limited by the case $b < b_{th}$, i.e. $\varepsilon > 0$. As can be seen from Eqs. (3.6) and (4.6), the inequality $\dot{v} > 0$ always holds at $\varepsilon < 0$. The positivity of velocity $\dot{v}$ of regular change in time of the variable v at $\varepsilon < 0$ allows one to neglect the fluctuation contribution in the estimate of the rate of heterogeneous growth of droplets and, consequently, to consider this growth as an entirely determined (not stochastic) process with rate $\dot{v}$. As follows from Eq. (3.6) at $\varepsilon < 0$, $\partial F/\partial v$ is negative and grows in absolute value with increasing $|v - v_0|$. According to Eq. (4.6), rate $\dot{v}$ reaches its minimum value (positive at $\varepsilon < 0$) at the point $v = v_0$ and grows with increasing $|v - v_0|$. The smaller $|\varepsilon|$, the relatively faster is the growth of $\dot{v}$. Due to this fact we can estimate the characteristic time τ of the development of the heterogeneous phase transition at $\varepsilon < 0$ and $|\varepsilon|^{1/2} \ll 1$ as

$$\tau \sim \int_{-\infty}^{\infty} \frac{dv}{\dot{v}} \qquad (4.16)$$

where the main contribution to the integral comes from the region with $\dot{v} \ll 1$. This region coincides at $|\varepsilon|^{1/2} \ll 1$ with the neighbourhood $|v - v_0| < (2b_{th} / |\partial^2 b_v / \partial v^2|_0)^{1/2} |\varepsilon|^{1/2}$ of the point $v = v_0$ where, as follows from Eqs. (3.6) and (4.5), $\partial F/\partial v \ll 1$ and $w \cong w_0$. Substituting Eq. (4.6) in Eq. (4.16) and taking into account Eq. (3.6) and what was said above, we obtain

$$\tau \sim \pi \left(\frac{2}{|\varepsilon| b_{th} |\partial^2 b_v / \partial v^2|_0} \right)^{1/2} \frac{1}{w_0} \qquad (4.17)$$

Comparing the time τ with the time t_s, recognizing Eqs. (4.15) and (3.13) and considering the value of $|\varepsilon|$ in Eq. (4.17) to be the same as the value of ε in Eq. (3.13), we have

$$\tau/t_s \sim 1 \qquad (4.18)$$

Although Eq. (4.18) overestimates the real time of development of the heterogeneous phase transition in the superthreshold region, $b > b_{th}$, of

the vapour metastable state (neglected fluctuations accelerate this development), Eq. (4.18) nevertheless shows that the time t_s specifies the characteristic time of development of the heterogeneous phase transition even in the lower part of the superthreshold region of the vapour metastable state.

Let us formulate the condition for validity of the assumption, adopted in Eq. (4.4), about the free-molecule regime of material exchange between droplet and vapour. This condition can be reduced [24] to the form

$$R_0 << l_m/\alpha_C \tag{4.19}$$

where l_m is the mean free path for molecules of the surrounding vapour–gas. Estimating $l_m \sim (4\pi)^{2/3}/(3\upsilon^\alpha)^{2/3}(n_g + n^\beta)$ and taking into account the relation between R_0 and ν_0 and the explicit relation for ν_0, we could rewrite Eq. (4.19) in the form of a limitation on the accessible values of the initial parameters of the problem. Let us remember that an additional limitation on the values of the parameters of the condensation nuclei is imposed by Eq. (3.5).

II. Nucleation on macroscopic uncharged nuclei

5. The disjoining pressure of a condensing liquid film and the work of wetting of a nucleus

The formation of the droplet around the wettable macroscopic nucleus of condensation starts from the formation of a thin film of condensate which we cannot describe thermodynamically with neglect of the mutual interference of surface layers on opposite film sides. We shall speak about the interference as overlapping of the droplet surface layers between the condensation nucleus and the surrounding vapour–gas.

The effect of overlapping of the surface layers of the thin film can be described in terms of the disjoining pressure. The disjoining pressure Π is defined as the difference between the normal component of pressure inside the flat film, which is equal to the external pressure, and the pressure in the bulk phase of the film matter at the same values of the temperature and chemical potentials as in the film. For a one-component liquid phase, its chemical potential μ^α at a given temperature is determined solely by the pressure p^α inside phase α:

$$d\mu^\alpha = \upsilon^\alpha dp^\alpha \tag{5.1}$$

For a condensed phase $\upsilon^\alpha = const$, and integration of Eq. (5.1) with respect to p^α from the value p^α_∞ which corresponds to the equilibrium of phases α and β with a flat interface gives

$$\mu^\alpha - \mu_\infty = \upsilon^\alpha(p^\alpha - p^\alpha_\infty) \tag{5.2}$$

Since the external pressure on the film is equal to the pressure p^β of the surrounding vapour–gas, the chemical potential of the molecules in the flat film, according to Eq. (5.2) and to the definition of Π, is

$$\mu^\alpha = \mu_\infty + \upsilon^\alpha(p^\beta - \Pi - p^\alpha_\infty) \tag{5.3}$$

In the case of a slightly curved thin film, the condition of mechanical equilibrium of the film with the liquid phase can be written in the form

$$p^\alpha = p^\beta + 2\gamma \, / \, R - \Pi \tag{5.4}$$

(see, for instance, Refs. [30–32]) where the second term on the right-hand side is the capillary pressure.

Substituting Eq. (5.4) in Eq. (5.2) yields

$$\mu^\alpha = \mu_\infty + \upsilon^\alpha(p^\beta - p^\beta_\infty + 2\gamma \, / \, R - \Pi) \tag{5.5}$$

where we have taken into account $p^\alpha_\infty = p^\beta_\infty$. If the pressure in the surroundings is held constant (during the condensation process it may be provided, for example, by a passive carrier gas, as in the case of condensation of water in the Earth's atmosphere), then $p^\beta - p^\beta_\infty = 0$, and we obtain from Eq. (5.5)

$$\mu^\alpha = \mu_\infty + \upsilon^\alpha(2\gamma \, / \, (R_n + h) - \Pi) \tag{5.6}$$

where

$$h \equiv R - R_n \tag{5.7}$$

is the thickness of the liquid film.

Equation (5.6) relates the dependence of the chemical potential of the condensate in the film on the thickness h of the film to the isotherm $\Pi(h)$ of the disjoining pressure in the film. For stable films $\Pi > 0$ and the disjoining pressure, as follows from Eq. (5.6), lowers the chemical

potential, whereas the capillary pressure, on the contrary, raises it. Thus we have the typical situation which was generally described in Section 1. Evidently, the contribution β_v that counteracts the contribution of the capillary pressure in Eq. (1.4) to the chemical potential of the condensate in the droplet can be written as

$$\beta_v = -\upsilon^\alpha \Pi \ / \ kT \tag{5.8}$$

According to Eq. (2.17), Eq. (5.8) establishes a relation between the disjoining pressure Π and the work f of wetting of a nucleus. Since the disjoining pressure is experimentally determined only for flat films and Eq. (2.10) for the work f can be applied both for slightly and highly curved films, then, with a given approximation for f, Eq. (2.17) allows us to define the disjoining pressure for the curved film. Subsequent sections will be based on approximations for the dependence of the work of wetting of a nucleus on the thickness of the condensate film around the nucleus. We will check the dependence in the limiting case of a flat film by comparing it with experimental determinations of the dependence of Π on h.

Let us integrate Eq. (2.17) taking into account Eq. (2.12) and the boundary condition, $F|_{v=v_n} = 0$. Substituting Eq. (5.8) in Eq. (2.17), using Eqs. (1.1)–(1.3), and considering the disjoining pressure Π to be known for arbitrary thickness of the liquid film around the nucleus, we have

$$f = \frac{4\pi}{kT} \int\limits_{R_n}^{R} dR R^2 \Pi - \frac{4\pi R_n^2 \gamma}{kT} \tag{5.9}$$

Setting $\Pi = 0$ (i.e. assuming that the nucleus consists of matter which is similar in its characteristics to the condensate), we find $f = -\gamma 4\pi R_n^2/kT$, which coincides with the result obtained for the analogous case in Section 2.

Let $f_\ast$ denote the value of the work of wetting of a nucleus in the condensate of infinite extent (at $R = \infty$). It follows from Eq. (5.9) that

$$f_\ast = -\frac{4\pi}{kT} \int\limits_{R_n}^{\infty} dR R^2 \Pi - \frac{4\pi R_n^2 \gamma}{kT} \tag{5.10}$$

where the upper limit of the integral is taken to be ∞ due to the rapid decrease of Π to zero with increasing thickness of the condensate film. On the other hand, as $R \to \infty$ the quantity $\Omega^\alpha_{R_n R}(\mu_\infty)$ tends to $\Omega^\beta_{R_n R}(\mu_\infty)$. In view of Eq. (2.10), and taking account of Eqs. (2.7)–(2.9), we then have

$$f_* = (\sigma_\infty^{\gamma\alpha} - \sigma_\infty^{\gamma\beta})\, 4\pi R_n^2 \tag{5.11}$$

which expresses Dupre's rule (for the generalization of the rule and associated rigorous relations see Ref. [33]).

Let us define

$$\Delta\sigma = \sigma_\infty^{\gamma\alpha} - \sigma_\infty^{\gamma\beta} \tag{5.12}$$

For the nucleus surface which is wettable by the condensate, $\Delta\sigma < 0$, while $\Delta\sigma > 0$ for non-wettable surface. Comparing Eqs. (5.10) and (5.11), we see that the equality

$$\frac{1}{R_n^2} \int_{R_n}^{\infty} dR R^2 \Pi = s \tag{5.13}$$

should hold for the nucleation on wettable nuclei. The quantity

$$s \equiv \sigma_\infty^{\gamma\beta} - \sigma_\infty^{\gamma\alpha} - \gamma \tag{5.14}$$

stands for the coefficient of spreading of the condensate over the flat surface of the nucleus substance; more precisely, the initial value of this coefficient, before the adsorption of vapour on the nucleus surface. As is seen from Eq. (5.13) for wettable nuclei (for $\Pi > 0$), one should have

$$s > 0 \tag{5.15}$$

which is a more restrictive condition than $\Delta\sigma < 0$. However, as we will show in the next section, even this condition will not be sufficient for barrierless heterogeneous nucleation.

Note that Eq. (5.15) does not hold for the equilibrium values of the spreading coefficient. As was shown by Gibbs [34] (a detailed discussion has been given by Rowlinson and Widom in Ref. [5]), even with complete wetting of the nucleus the equilibrium value of s does not exceed zero. This is due to the fact that the equilibrium value of the surface tension of the $\gamma\beta$ interface is smaller than $\sigma_\infty^{\gamma\beta}$.

In the case of macroscopic condensation nuclei with a condensate film, for which the maximal film thickness with $\Pi \neq 0$ is much smaller than the nucleus radius R_n, we can write instead of Eq. (5.13)

$$\int_0^{\infty} dh \Pi = s \tag{5.16}$$

with the thickness h defined according to Eq. (5.7).

Let us consider now one more thermodynamic consequence of the ideas presented in this section, concerning the reversal of phases at nucleation.

Equation (5.13) should be correct independently of the specific choice of phases α and β. If phases α and β replace each other and a spherical layer cavity filled with a vapour (phase β) forms around a solid particle (phase γ) inside the bulk of liquid (phase α), then, instead of Eq. (5.13), we have

$$\frac{1}{R_n^2} \int_{R_n}^{\infty} dR R^2 \Pi^\beta = \sigma_\infty^{\gamma\alpha} - \sigma_\infty^{\gamma\beta} - \gamma \tag{5.17}$$

where we label Π with the superscript β to make a distinction with the case of a liquid film. As follows from Eqs. (5.14) and (5.15), the right-hand side of Eq. (5.17) should be negative. Consequently, $\Pi^\beta < 0$, and the cavity is unstable. This means that cavitation in a liquid cannot be stimulated by those solid particles which allow barrierless heterogeneous nucleation in the supersaturated vapour of the same liquid. So cavitation should occur by the homogeneous mechanism in this case.

The same is true for the case of nucleation in systems with liquid–liquid miscibility gap. Let us illustrate this by Fig. 4. The figure shows the temperature–composition coexistence curve (the binodal) for the equilibrium of two liquid phases, α and β, in a two-component liquid mixture (the outer curve). The inner curve (the spinodal) is the bulk
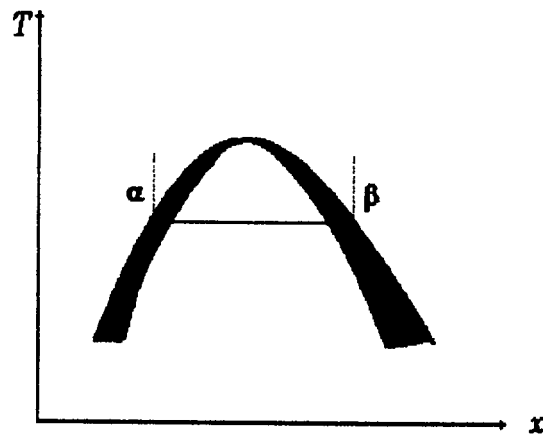

Fig. 4. The binodal and the spinodal for the liquid–liquid system in the temperature–composition plane. The vertical dashed lines correspond to supercoolings at fixed composition.

stability boundary separating metastable (shaded area) and unstable regions in the phase diagram. Both the curves are known to be more symmetrical the closer to the critical point.

The vertical dashed lines in the figure represent attempted super-coolings at fixed composition — starting in the one-phase region and lowering the temperature below that of the equilibrium phase separation and entering the metastable region where the fluid still remains homogeneous. We can imagine particles of a third phase, γ, to be immersed into those phases to see how such particles will stimulate the nucleation process on either side of the critical point. If the interface $\gamma\beta$ is wetted by the phase α, and Eq. (5.13) holds, the system cannot be deeply supercooled on the β-phase side of the critical point, because phase α will nucleate at small supercoolings practically without encountering the activation barrier. But, according to the discussion above, the system can be supercooled on the α-phase side of the critical point, since phase α will nucleate only homogeneously in this case.

A similar behaviour, but in the situation when phases α and β were in contact with the container walls, was observed by Heady and Cahn [35]. Thus, the known symmetry of the physical picture near the critical point is remarkably disturbed in the phenomenon of nucleation due to the influence of surface forces at a solid nucleus.

6. Exponential approximation to the work of wetting of a nucleus

Let us consider the exponential approximation to the work of wetting of the nucleus in a droplet. One can relate the exponential character of the work of wetting of the nucleus to the exponential character of interactions which is very common in nature. Whatever the nature of the interaction forces at large distances, there is a molecular correlation effect that manifests itself at intermediate distances (usually in an exponential form) and can be regarded as universal [36–39]. On the other hand, for some liquids (and, first of all, for water) there are manifested so-called structural forces, ie. the same correlation effects but acting over the longest distances (i.e., characterized by largest correlation length). Therefore

$$f = f^{\circ} \{1 - c \cdot \exp \left[-(R - R_n) / l \right]\} \tag{6.1}$$

can be a representative approximation for the work f as a function of R. Here c is a certain positive coefficient and the quantity l is the correlation length of the film of condensate around the nucleus. We shall

consider some positive quantity l as a given parameter of the theory. The fact that the nucleus is macroscopic means

$$l / R_n << 1 \tag{6.2}$$

To compact the notation we introduce the auxiliary quantity,

$$\kappa = 4\pi l^3 / 3\upsilon^\alpha \tag{6.3}$$

which is the number of molecules of condensate contained inside the imaginary sphere with radius l. As follows from Eqs. (1.2) and (6.2), the condition that the nucleus is of macroscopic size can be rewritten as

$$(\kappa / \nu_n)^{1/3} << 1 \tag{6.4}$$

Let us find the expression for β_ν which corresponds to the approximation given by Eq. (6.1) Differentiating f with respect to ν and using Eqs. (1.1), (2.17), and (6.3), we obtain

$$\beta_\nu = \frac{1}{3} cf_* \kappa^{-\frac{1}{3}} \nu^{-\frac{2}{3}} \exp\left[-(R - R_n) / l\right] \tag{6.5}$$

According to Eqs. (5.15), (5.14), and (5.11) the sign of f_* in Eq. (6.5) is negative $(\Delta\sigma < 0)$. Therefore, the coefficient c in Eqs. (6.1) and (6.5) must be positive. This coefficient can be found with the help of the boundary condition, $F|_{\nu=\nu_n} = 0$, for the work of heterogeneous formation of a droplet if one recognizes Eq. (6.1) to be valid down to $R = R_n$. Taking into account Eqs. (1.2), (1.3), (5.11), (5.12), and (5.14), we find from Eqs. (2.12) and (6.1)

$$c = s/|\Delta\sigma| \tag{6.6}$$

Using Eq. (6.6) in Eq. (6.5) and substituting the resulting relation for b_ν into Eq. (1.4), and taking account of Eq. (5.11), we have

$$b_\nu = \frac{2}{3} a\nu^{-\frac{1}{3}} - \frac{4\pi R_n^2 s}{3kT} \kappa^{-\frac{1}{3}} \nu^{-\frac{2}{3}} \exp\left[-(R - R_n) / l\right] \tag{6.7}$$

Differentiating b_ν with respect to ν, recognizing Eqs. (1.1), (6.3), and substituting the result into the left-hand side of Eq. (1.5), we obtain the equation for the coordinate ν of the point of maximum of b_ν:

$$-\frac{2}{9} a v_0^{-4/3} + \frac{4\pi R_n^2 s}{9kT} \kappa^{-2/3} v_0^{-4/3} \exp\left[-(R_0 - R_n)/l\right] = 0 \tag{6.8}$$

where, in accordance with $(v_n / v)^{1/3} < 1$ and the inequality (6.4), we have neglected small terms of the order of $(\kappa/v)^{1/3}$.

Equation (6.8) can be solved analytically. We have

$$v_0 = 4\pi R_0^3 / 3\upsilon^\alpha \tag{6.9}$$

where

$$R_0 = R_n + l \ln\left(\frac{sR_n^2}{2\gamma l^2}\right) \tag{6.10}$$

As follows from Eq. (6.10), in order to satisfy $R_0 > R_n$ we must have

$$s > 2\gamma l^2 / R_n^2 \tag{6.11}$$

In view of Eqs. (5.12) and (5.14), Eq. (6.11) can be rewritten as

$$\Delta\sigma / \gamma > 1 + 2l^2 / R_n^2 \tag{6.12}$$

The fulfilment of Eq. (6.11) means that the maximum of the chemical potential of the condensate, $(b_v)_0$, really exists, and thus the process of heterogeneous nucleation on condensation nuclei will be barrierless at $b \geq (b_v)_0$. We see that Eq. (6.11) represents not only the necessary condition (as Eq. (5.15)) but also the sufficient condition for barrierless heterogeneous nucleation on macroscopic insoluble nuclei that are characterized by parameters $\Delta\sigma$, l, and R_n.

Let us write the inequality $R > R_n$ in the form

$$(v_n / v_0)^{1/3} < 1 \tag{6.13}$$

and the inequality $l/R_0 \ll 1$ as

$$(\kappa / v_0)^{1/3} \ll 1 \tag{6.14}$$

With increasing R_n, and with l fixed, the ratio R_0/R_n decreases and the quantities R_0 and $R_0 - R_n$ grow. Along with this, the inequality in Eq. (6.13) becomes weaker and the inequality in Eq. (6.14), by contrast,

becomes stronger. Increase of the ratio s/γ leads to increase of all three quantities R_0/R_n, R_0, $R_0 - R_n$ and, as a result, strengthens both the inequality in Eq. (6.13) and the inequality in Eq. (6.14).

Substituting Eqs. (6.9) and (6.10) in Eq. (6.7), and taking into account Eqs. (6.3) and (1.11), we obtain the expression for the threshold value of the vapour chemical potential,

$$b_{th} = \frac{2}{3} a v_0^{-1/3} \left[1 - \left(\frac{\kappa}{v_0} \right)^{1/3} \right] \tag{6.15}$$

In view of Eq. (6.14), Eq. (6.15) is replaced with high accuracy by

$$b_{th} = \frac{2}{3} a v_0^{-1/3} \tag{6.16}$$

According to Eqs. (6.16), (6.9), and (6.10), in the case of macroscopic nuclei we have always $b_{th} \ll 1$. Equation (6.16) shows that b_{th} coincides with the value of the vapour chemical potential at which a homogeneously formed critical droplet contains v molecules, i.e., is of radius R_0. At $b = b_{th}$ ($b_{th} \ll 1$) the work of homogeneous formation of a critical droplet that determines the activation barrier to homogeneous nucleation appears so large that homogeneous nucleation does not occur. Meanwhile, at $b = b_{th}$ the heterogeneous nucleation is already barrierless.

Equation (6.16) shows also that the value of b_{th} is smaller by the factor $(v_0/v_n)^{1/3}$ ($(v_0/v_n)^{1/3} > 1$) than the chemical potential of the vapour in equilibrium with which the homogeneously formed critical droplet has a radius that coincides with the radius R_n of the condensation nucleus.

Recognizing what was said above about the behaviour of R_0 and R_0/R_n with variation of R_n and s/γ, we conclude that with increasing R_n and s/γ the value of b_{th} decreases.

Differentiating the left-hand and the right-hand sides of Eq. (6.7) twice with respect to v, substituting Eqs. (6.9) and (6.10) and using Eqs. (1.3) and (6.3), we have

$$\left(\frac{\partial^2 b_v}{\partial v^2} \right)_0 = -\frac{2}{27} a \kappa^{-1/3} v_0^{-2} \left[1 - 4 \left(\frac{\kappa}{v_0} \right)^{1/3} \right] \tag{6.17}$$

The correction $4(\kappa/v_0)^{1/3}$ in Eq. (6.17) describes the relative role of the contribution to $(\partial^2 b_v / \partial v^2)_0$ from the surface energy $a v^{2/3}$ in comparison with the contribution from the work f of wetting of the nucleus. We see,

that the role of the contribution of the work f increases on including higher-order derivatives and the role of the contribution of the surface energy decreases. With fulfilment of Eq. (6.14), the third-order derivative $(\partial^3 b_v / \partial v^3)_0$ can be easily calculated to first order in the small parameter $(\kappa/v_0)^{1/3}$. Differentiating the exponential in the second term on the right-hand side of Eq. (6.7) with respect to v three times and taking into account Eqs. (1.1), (6.3), (6.10), and (1.3), we have

$$\left(\frac{\partial^3 b_v}{\partial v^3}\right)_0 = \frac{2}{81}\, a\kappa^{-2/3}\, v_0^{-8/3} \tag{6.18}$$

Equations (6.16)–(6.18) which express the chemical potential b_v and its derivatives at $v = v_0$ allow us to find the main characteristics of heterogeneous nucleation in the prethreshold region of the vapour metastable state according to the program formulated in Section 3. As follows from Eqs. (6.17) and (6.18), the condition for validity of the parabolic approximation for b_v in the neighbourhood of the point $v = v_0$, which is given by Eq. (3.3), is fulfilled with

$$\frac{1}{9}\, \kappa^{-1/3}\, v_0^{-2/3}\, |v - v_0| \ll 1 \tag{6.19}$$

Substituting Eqs. (6.16) and (6.17) in Eq. (3.4) yields for the equilibrium $(v = v_e)$ and the critical $(v = v_c)$ droplets

$$v_e = v_0 \left[1 - 3 \cdot 2^{1/2}(\kappa\, /v_0)^{1/6}\, \varepsilon^{1/2} \right]$$

$$v_c = v_0 \left[1 + 3 \cdot 2^{1/2}(\kappa\, /v_0)^{1/6}\, \varepsilon^{1/2} \right] \tag{6.20}$$

By the same token, we find from Eqs. (6.16), (6.17), and (3.13) the following relation for the half-widths Δv_e and Δv_c of the potential well and the potential hump in the work of heterogeneous formation of a droplet:

$$\Delta v_e = \Delta v_c = 3 \cdot 2^{-1/4}\, a^{-1/2}\, v_0^{2/3}(\kappa\, /v_0)^{1/12}\, \varepsilon^{-1/4} \tag{6.21}$$

Finally, using Eqs. (6.16), (6.17), and (3.8), we obtain the relation for the activation energy ΔF

$$\Delta F = \frac{2^{7/2}}{3} a v_0^{2/3} (\kappa / v_0)^{1/6} \varepsilon^{3/2} \tag{6.22}$$

In order to satisfy Eq. (6.19) at $v = v_e$ and $v = v_c$, we need, as is clear from Eq. (6.20),

$$\varepsilon^{1/2} \ll (\kappa / v_0)^{1/6} \tag{6.23}$$

In view of Eq. (6.14), the quantity on the right-hand side of Eq. (6.23) is small. According to Eqs. (6.9) and (6.10), this quantity decreases with increasing size of the nucleus. Note now that with the aid of Eqs. (6.22) and (3.16) the value of $\varepsilon^{1/2}$ may be estimated in the prethreshold region of the vapour metastable state as

$$\varepsilon^{1/2} \sim a^{-1/3} \kappa^{-1/18} v_0^{-1/6} \tag{6.24}$$

It is seen that the right-hand side of Eq. (6.24), as well as the right-hand side of Eq. (6.23), is considerably smaller than unity. This allows us to restrict consideration to values of $\varepsilon^{1/2}$ and, the more so, ε which are much less than unity.

Let us reduce Eq. (6.23), with the aid of Eq. (6.24), to the form

$$a^{-1/3} \kappa^{-2/9} \ll 1 \tag{6.25}$$

Since $a \sim 10$ and $\kappa \gg 1$, Eq. (6.25) holds, even though by a small margin. With fulfilment of Eq. (6.25), Eqs. (6.23) and (6.24) are consistent, and this justifies using the parabolic approximation, Eq. (3.2), for b_v in calculations of thermodynamic quantities within the prethreshold region of the vapour metastable state. The fact that Eq. (6.25) is not related explicitly to the condition of macroscopic size of the nucleus, Eq. (6.4), is not surprising because that condition is the basis of Eq. (6.14), the left-hand side of which has defined the small parameter of the theory, $(\kappa/v_0)^{1/3}$. The latter has been used to derive the expressions for $(\partial^2 b_v / \partial v^2)_0$ and $(\partial^3 b_v / \partial v^3)_0$.

To fulfil Eqs. (3.17) and (3.18), it is required that the condensation nucleus be of macroscopic size. Let us recall that Eq. (3.17) is responsible for the validity of the parabolic approximation in Eq. (3.2) for b_v in the cases of near-equilibrium and near-critical droplets while Eq. (3.18) allows us to regard the variable v as continuous for these droplets. Substituting Eq. (6.24)in Eq. (6.21), we find

$$\Delta v_e = \Delta v_c \sim a^{-\frac{1}{3}} \kappa^{\frac{1}{9}} v_0^{\frac{2}{3}} \tag{6.26}$$

whence, with $v_0^{1/3} \gg 1$ (this is certain when Eq. (6.14) holds), it follows that $\Delta v_e \gg 1$ and $\Delta v_c \gg 1$. Finding, then, with the aid of Eqs. (6.26) and (6.20), the ratios $\Delta v_e/v_e$ and $\Delta v_c/v_c$ and recognizing Eq. (6.24), we obtain

$$\Delta v_e / v_e = \Delta v_c / v_c \sim a^{-\frac{1}{3}} \kappa^{\frac{1}{9}} v_0^{-\frac{1}{3}} \tag{6.27}$$

whence, with $v_0^{1/3} \gg 1$, we have a confirmation of Eq. (3.17).

7. Power-law approximation to the work of wetting of a nucleus

Power-law forces are common in nature. It is enough to recall the van der Waals forces and, first of all, dispersion interactions. The power-law behaviour of these forces over large distances (with retardation and without it) is established by science for certain. Therefore, together with the exponential approximation, Eq. (6.1), to the work of wetting of the condensation nucleus in a droplet, the power-law approximation to the work f as a function of thickness $h = R - R_n$ of the film of condensate between the nucleus and the vapour is also representative:

$$f = f^* \left\{ 1 - c_p \cdot \left(\frac{R_n}{R - R_n} \right)^m \right\} \tag{7.1}$$

where c_p and m are positive parameters and the work f_* of wetting the nucleus by the bulk condensate phase is given, as before, by Eq. (5.11).

Let us see how the main results of the theory look using Eq. (7.1) instead of Eq. (6.1). We need consider only the formulae that must be changed in passing from Eq. (6.1) to Eq. (7.1).

Differentiating the left-hand side and the right-hand side of Eq. (7.1) with respect to v, and taking into account Eqs. (2.17), (5.11), (5.12), and (1.1), we find

$$\beta_v = -\frac{1}{3} a v^{-\frac{2}{3}} \frac{|\Delta\sigma|}{\gamma} \left(\frac{4\pi}{3v^\alpha} \right)^{\frac{1}{3}} m c_p \frac{R_n^{m+2}}{(R - R_n)^{m+1}} \tag{7.2}$$

According to Eqs. (1.4) and (7.2), the chemical potential b_v can be written as

$$b_v = \frac{2}{3} a v^{-\frac{1}{3}} - \frac{1}{3} a v^{-\frac{2}{3}} \frac{|\Delta\sigma|}{\gamma} \left(\frac{4\pi}{3v^\alpha} \right)^{\frac{1}{3}} m c_p \frac{R_n^{m+2}}{(R - R_n)^{m+1}} \tag{7.3}$$

In order to write the relation for the point $v = v_0$ of the maximum of b_v in an analytical form, let us restrict ourselves to the case of thin films, for which there is $(R - R_n)/R_n \ll 1$. We will assume that the condition that the condensation nucleus be of macroscopic size also holds. In the case under consideration the condition can be written as $(v^\alpha)^{1/3}/R \ll 1$, and, in view of Eq. (1.2), this is equivalent to $v_n^{1/3} \gg 1$.

Instead of Eq. (6.8), in order to find v_0 we have now the following equation:

$$-\frac{2}{9} a v^{-4/3} + \frac{1}{9} a v_0^{-4/3} \frac{|\Delta\sigma|}{\gamma} m(m+1) c_p \frac{R_n^{m+2}}{(R_0 - R_n)^{m+2}} = 0 \tag{7.4}$$

Note that in deriving Eq. (7.4) we have neglected terms of the order of $(R_0 - R_n)/R_n$ in relative magnitude.

Solving Eq. (7.4), we find

$$R_0 = R_n(1 + \delta) \tag{7.5}$$

where

$$\delta \equiv \left[c_p m(m+1) \frac{|\Delta\sigma|}{2\gamma} \right]^{1/(m+2)} \tag{7.6}$$

In order to satisfy the inequality

$$(R_0 - R_n)/R_n \ll 1 \tag{7.7}$$

according to Eq. (7.5) we must have

$$\delta \ll 1 \tag{7.8}$$

As seen from Eq. (7.6), Eq. (7.8) holds for sufficiently small values of the coefficient c_p. An explicit definition of c_p will be given in the next section.

Instead of Eq. (6.15), we have now

$$b_{th} = \frac{2}{3} a v^{-1/3} \left[1 - \frac{\delta}{m+1} \frac{R_n}{R_0} \right] \tag{7.9}$$

In view of Eqs. (7.5) and (7.8), one can consider

$$b_{th} = \frac{2}{3} a v_n^{-1/3} \tag{7.10}$$

as an appropriate approximation to the threshold value of the vapour chemical potential. With $v_n^{1/3} \gg 1$ we have, as before, $b_{th} \ll 1$.

Similarly to the case of the exponential approximation, in passing from the first-order derivative to higher-order derivatives of the chemical potential b_v of condensate with respect to v the contribution of the disjoining pressure increases relatively to the contribution of the capillary pressure. Keeping only terms which are of first order in the small parameter given by Eq. (7.8), we obtain

$$\left(\frac{\partial^2 b_v}{\partial v^2} \right)_0 = - \frac{2}{27} (m + 2) a v_0^{-7/3} \delta^{-1} \tag{7.11}$$

$$\left(\frac{\partial^3 b_v}{\partial v^3} \right)_0 = \frac{2}{81} (m + 2) (m + 3) a v_0^{-10/3} \delta^{-2} \tag{7.12}$$

Instead of Eqs. (6.19)–(6.22), we have now

$$\frac{m + 3}{9} \frac{|v - v_0|}{v_0} \delta^{-1} \ll 1 \tag{7.13}$$

$$v_e = v_0 \left[1 - 3 \cdot 2^{1/2}(m + 2)^{-1/2} \delta^{1/2} \varepsilon^{1/2} \right]$$

$$v_c = v_0 \left[1 + 3 \cdot 2^{1/2}(m + 2)^{-1/2} \delta^{1/2} \varepsilon^{1/2} \right] \tag{7.14}$$

$$\Delta v_e = \Delta v_c = 3 \cdot 2^{-1/4}(m + 2)^{-1/4} a^{-1/2} v_0^{2/3} \delta^{1/4} \varepsilon^{-1/4} \tag{7.15}$$

$$\Delta F = \frac{2^{7/2}}{3} (m + 2)^{-1/2} a v_0^{2/3} \delta^{1/2} \varepsilon^{3/2} \tag{7.16}$$

In order to satisfy Eq. (7.13) at $v = v_e$ and $v = v_c$ with v_e and v_c given by Eq. (7.14), the inequality,

$$\varepsilon^{1/2} \ll \frac{(m + 2)^{1/2}}{m + 3} \delta^{1/2} \tag{7.17}$$

must hold. This inequality is similar to Eq. (6.23). In view of Eq. (7.8), it follows from Eq. (7.17) that $\varepsilon^{1/2} \ll 1$.

From Eqs. (7.16) and (3.16) in the prethreshold region of the vapour metastable state, we find

$$\varepsilon^{1/2} \sim (m + 2)^{1/6} a^{-1/3} v_0^{-2/9} \delta^{-1/6} \tag{7.18}$$

Consistency of Eqs. (7.17) and (7.18) requires

$$\frac{m + 3}{(m + 2)^{1/3}} a^{-1/3} v_0^{-2/9} \delta^{-2/3} \ll 1 \tag{7.19}$$

With a sufficiently large value of v_0 (which is provided by a nuclei of macroscopic size), one may expect Eq. (7.19) to be fulfilled.

8. Patching the exponential and the power-law approximations to the work of wetting of a nucleus

As was said above, the power-law, Eq. (7.1), and the exponential Eq. (6.1), approximations to the work of wetting of a nucleus reflect the power-law and the exponential behaviour of molecular correlations in a liquid in their dependence on the distances between molecules.

According to the asymptotic theory of capillary systems [40] one should expect the power-law approximation, Eq. (7.1), to the work of wetting of a nucleus to be close to reality when the thickness $R - R_n$ of the liquid film of condensate between the nucleus and vapour satisfies the inequality $(R - R_n)/(v^\alpha)^{1/3} \gg 1$ by a substantial margin. Since $(v^\alpha)^{1/3}$ estimates the mean intermolecular distance in a liquid, the quantity on the left-hand side of the inequality represents the approximate number of monolayers in the film. This number should be large enough to ensure the practical non-overlapping of the surface layers of the film at its boundaries with the nucleus and the vapour. Note that the inequality $(R - R_n)/(v^\alpha)^{1/3} \gg 1$ may be consistent with Eq. (7.7) which has allowed us to obtain in analytical form all the results for the power-law approximation to the work of wetting. Indeed, the right-hand side of Eq. (7.7) is equal to the product of $(R - R_n)/(v^\alpha)^{1/3}$ and $(v^\alpha)^{1/3}/R_n$ and with strong fulfilment of the condition of macroscopic size of the nucleus, $(v^\alpha)^{1/3}/R_n \ll 1$, Eq. (7.7) can be fulfilled even with $(R - R_n)/(v^\alpha)^{1/3} \gg 1$.

According to the asymptotic theory of capillary systems [40] and gradient theory for structural forces in thin liquid films [38,39], one should also expect the exponential approximation, Eq. (6.1), to the work of wetting to be close to reality when the thickness $R - R_n$ of the liquid film is relatively small and the number of monolayers in the film is not yet so large.

Thus, we come to the following conclusion. If the radius R_0 given by Eq. (6.10) does not exceed the radius R_n by too many multiples of the liquid monolayer thickness, then one should use the exponential approximation, Eq. (6.1), in the theory. Otherwise, if the radius R_0 given by Eqs. (7.5) and (7.6) considerably exceeds the radius R_n by many multiples of the liquid monolayer thickness, then one should use the power-law approximation, Eq. (7.1), in the theory.

It is clear from Eqs. (6.10), (7.5), and (7.6) that with increasing radius R_n and ratio s/γ one passes inevitably from the situation where the theory needs the exponential approximation, Eq. (6.1), to the situation where the theory needs the power-law approximation, Eq. (7.1).

The situations described by Eqs. (6.1) and (7.1) are extremal. In between, there is an intermediate region of variation of parameters R_n and s/γ to describe which we need more detailed information on the dependence of the work f of wetting on the thickness of the liquid film between the nucleus and the vapour. It follows from the general formulation, Eqs. (2.10), (2.7), (2.8), and (5.11), that in the case of insoluble uncharged nuclei the shift $f-f_*$ is equal to the difference in grand thermodynamic potential between the vapour which is perturbed by the presence of a nucleus of condensation and located outside the sphere of radius R and the liquid which is perturbed by the nucleus and located outside the same sphere of radius R. Thus, we have an opportunity for direct calculation of the shift $f-f_*$ by methods of statistical thermodynamics. However, this is an independent problem going outside the scope of the present investigation.

We estimate the coefficient c_p in Eq. (7.1) in the following way. Considering Eqs. (6.1) and (7.1) as limiting at small and large R (with the radius R_n of the nucleus and the ratio s/γ fixed), let us patch these two approximations together at droplet radius $R = \tilde{R}$ which lies between the regions of validity for the power-law and the exponential approximations. Taking into account the equality at $R = \tilde{R}$ of the approximations themselves and their first-order derivatives with respect to R, we find

$$\tilde{R} = R_n + ml \tag{8.1}$$

$$c_p = \left(\frac{ml}{R_n e}\right)^m \frac{s}{|\Delta\sigma|} \tag{8.2}$$

where e is the base of natural logarithms.

Substituting Eq. (8.2) in Eq. (7.1), we conclude that the factor before $(R-R_n)^{-m}$ does not depend on the nucleus radius R_n, which is as it should be, but depends on such characteristics of the nucleus and condensate as s, $|\Delta\sigma|$, l, and m.

The parameter m in Eq. (7.1) is equal to 2 or 3 depending on whether the van der Waals forces or the forces concerned with electromagnetic retardation predominate at large distances between molecules of the substance considered. This follows from Eqs. (7.2), (5.8), and the results obtained for the disjoining pressure in Refs. [12,30,40].

With $m = 2$ and $m = 3$ we see from Eqs. (6.1) and (8.1) that $f|_{R=\tilde{R}} \cong f_*$ and the value $\tilde{R}$ of the droplet radius R lies at the upper edge of the region of validity for the exponential approximation. At the same time we see from Eqs. (7.1) and (8.1) that the value $\tilde{R}$ lies at the left edge of the validity region for the power-law approximation which requires, as was mentioned above, $(R - R_n)/(\upsilon^\alpha)^{1/3} \gg 1$.

Substituting Eq. (8.2) in Eq. (7.6) yields

$$\delta \equiv \left[m^{m+1}(m + 1)\frac{s}{2\gamma e^m}\right]^{1/m+2}\left(\frac{l}{R_n}\right)^{m/m+2} \tag{8.3}$$

Substituting Eq. (8.3) with $m = 2$ in Eq. (7.8), we obtain

$$(s/\gamma)^{1/4}(l/R_n)^{1/2} \ll 1 \tag{8.4}$$

Equation (8.4) defines in an explicit form the condition on the parameters of a nucleus and film of condensate that ensures smallness of the film thickness at $R = R_0$ in comparison with the nucleus radius. The inequality $(R_0 - R_n)/(\upsilon^\alpha)^{1/3} \gg 1$ is fulfilled by this if we have

$$(s/\gamma)^{1/4}(lR_n)^{1/2}(\upsilon^\alpha)^{-1/3} \gg 1 \tag{8.5}$$

With characteristic values of the parameters s, γ, l, υ^α, and R_n, Eqs. (8.4) and (8.5) are fulfilled with a large margin.

Let us return to the estimate of the left-hand side of Eq. (7.19). Substituting Eq. (8.3) in Eq. (7.19) at $m = 2$, taking into account Eqs. (1.2), (6.3) and supposing $v_0^{-2/9} \cong v_n^{-2/9}$, we find that Eq. (7.19) holds with

$$(\gamma/s)^{\frac{1}{6}}\, a^{-\frac{1}{3}}\, \kappa^{-\frac{1}{9}}\, v_n^{-\frac{1}{9}} \ll 1 \tag{8.6}$$

With $s > 2\gamma l/R_n^2$ (i.e. with fulfilment of Eq. (6.11)), the left-hand side of Eq. (8.6) satisfies, with account taken of Eqs. (1.2) and (6.3), inequality

$$(\gamma/s)^{\frac{1}{6}}\, a^{-\frac{1}{3}}\, \kappa^{-\frac{1}{9}}\, v_n^{-\frac{1}{9}} \ll a^{-\frac{1}{3}}\, \kappa^{-\frac{2}{9}} \tag{8.7}$$

Hence we see that Eq. (8.6) certainly holds with $a^{-1/3}\kappa^{-2/9} \ll 1$ (i.e. with fulfilment of Eq. (6.25)). Thus, the sufficient condition for barrierless heterogeneous nucleation, Eq. (6.11), and the condition of validity for the exponential approximation, Eq. (6.25), are sufficient to ensure validity of the analytical results for the power-law approximation to the work of wetting in the prethreshold region of the vapour metastable state.

Together with the estimate given by Eq. (8.2) from the patching procedure for the exponential and the power-law approximations, we can give a rigorous expression for the coefficient c_p which follows from the results of direct calculation of the asymptotic form for the disjoining pressure by means of the microscopic theory of dispersion interactions [40]. According to Eq. (62) from Ref. [40], we have to the first order in the thickness h of a film, neglecting the effects of retardation and formation of adsorbed layers,

$$\Pi = B_1/h^3, \qquad h \ll R_n \tag{8.8}$$

where, in our notation,

$$B_1 = (\pi/6)\, A(1/v^\alpha - 1/v^\beta)(1/v^\gamma - 1/v^\alpha) \tag{8.9}$$

with v^γ the volume per molecule of the nucleus substance and A the force constant for the dispersion-force interaction of molecules.

Comparing Eq. (8.8) (with account taken of Eqs. (5.7) and (5.8)) with Eq. (7.2) at $m = 2$, putting $v^{-2/3} \cong v_n^{-2/3}$ and using Eq. (1.2), we obtain

$$c_p = \frac{\pi A}{12 v^\alpha R_n^2 \,|\Delta\sigma|} \left(\frac{1}{v^\gamma} - \frac{1}{v^\alpha} \right) \tag{8.10}$$

We see from Eqs. (8.10) and (8.2) that the parameters A, l, and s must be related, even though only approximately, by

$$A \left(\frac{1}{\upsilon^\gamma} - \frac{1}{\upsilon^\alpha} \right) \sim \upsilon^\alpha \, l^2 \, s \qquad\qquad (8.11)$$

Depending on the long-range character of the structural forces described by the exponential approximation to the work of wetting, the patching of the exponential and power-law approximations may occur for rather large thicknesses of film, when the forces are weak. Nevertheless, even in this case these forces play an important role in nucleation processes.

9. Experimental foundation for the exponential and the power-law approximations to the work of wetting of a nucleus

Let us trace the relation of the theory of condensation on wettable solid insoluble nuclei to the disjoining pressure isotherms $\Pi = \Pi(h)$ known from experiment [30,31,41–44]. The function $\Pi(h)$ is monotonic in the case of nonpolar liquids. A corresponding dependence of β_v on h for this case according to Eq. (5.8) is depicted in Fig. 5. The dependence of β_v on h on the left side of the curve is of a form close to $\exp(-h/l)$, the small parameter l, the correlation length, being of the order of the
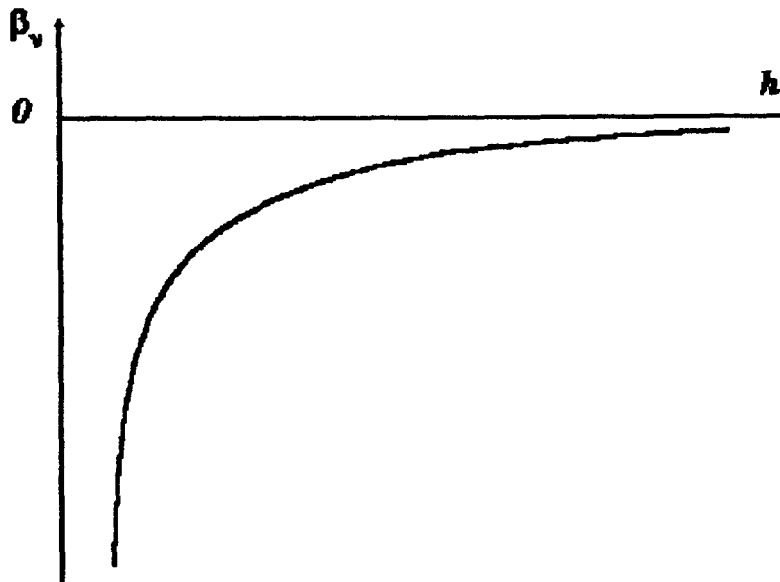

Fig. 5. Dependence of b_v on thickness h in the case of film of nonpolar liquid on quartz.

intermolecular distance in a liquid. The right side of the curve for the dependence of β_v on h obeys a power law approximately of the form h^{-3}.

The larger the radius R_n of the nucleus, the weaker is the capillary effect and the smaller the deviation of the curve b_v from β_v. Then the larger becomes the value of v at which the capillary effect competes with the effect of disjoining pressure and the larger becomes the coordinate v_0 of a maximum of b_v in accordance with Eqs. (6.10), (7.5), (8.3), and (1.1). Thus, the exponential approximation, Eq. (6.1), to the work of wetting of a condensation nucleus is applicable if the radius R_n is not too large and if Eq. (6.10) does not yet take R_0 and $h_0 = R_0 - R_n$ out of the region of validity of the exponential approximation for the dependence of β_v on h in Fig. 5. Then the results obtained in Section 6 may be used.

If, however, the radius R_n is so large that Eqs. (7.5) and (8.3) ensure that R_0 and $h_0 = R_0 - R_n$ enter the region of validity of the power approximation to the dependence of β_v on h in Fig. 5, the power-law approximation with $m = 2$ for the work of wetting of a condensation nucleus holds. Then the results of Section 7 may be used. The smallness of the correlation length parameter l in the case of nonpolar liquids makes, in this case, rather real the applicability of the power-law approximation to the dependence of β_v on h in heterogeneous nucleation.

In the case of polar liquids and, especially, of polar liquids with hydrogen bonds, the disjoining pressure isotherm $\Pi(h)$ is nonmonotonic due to a contribution of structural forces. A dependence of β_v on h according to Eq. (5.8) corresponding to this case is depicted in Fig. 6 with the left α-branch and the right β-branch. The region of unstable states of a film is shown with the broken line in Fig. 6. In its stable part (corresponding to a stable equilibrium of a film with undersaturated vapour) the α-branch runs up to a film thickness h of about $7 \cdot 10^{-7}$ to $8 \cdot 10^{-7}$ cm [41] and is of the form $\exp(-h/l)$, the correlation length parameter l being anomalously large and exceeding the intermolecular distance in a liquid by a factor 10.

The capillary effect suppresses the β-branch for the dependence of β_v on h even at a rather large radius R_n of a nucleus when the capillary effect is weak. Practically, the threshold value of the vapour chemical potential due to the α-branch turns out to be always much higher than the threshold value of the vapour chemical potential due to the β-branch. Thus, the α-branch limits, on the vapour supersaturation scale, the possibility of barrierless heterogeneous nucleation and, hence, only the α-branch is important in heterogeneous condensation. As a result, the typical behaviour of the condensate chemical potential b_v depicted in
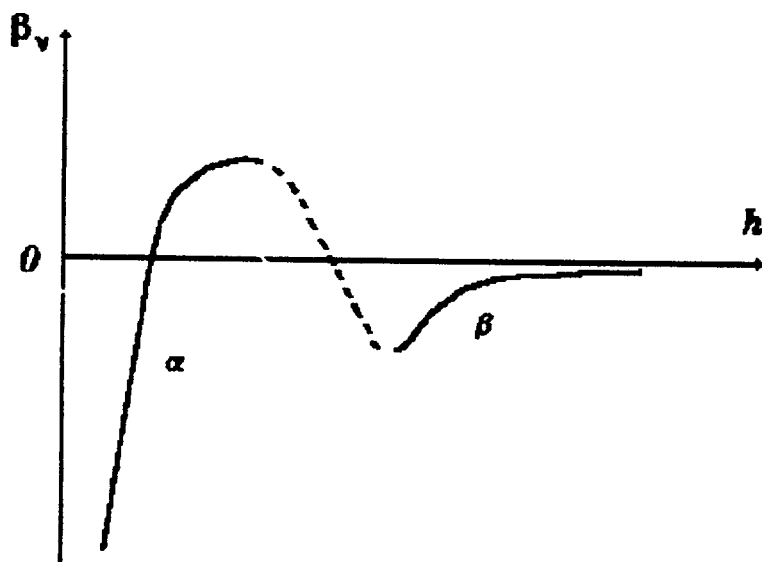
Fig. 6. Dependence of b_v on thickness h in the case of film of polar liquid on quartz.

Fig. 1 is maintained also in the case of polar liquids. We emphasize that it is the capillary effect that makes the behaviour of the drop chemical potential in the case of polar liquids with hydrogen bonds qualitatively similar to that in the case of nonpolar liquids.

The exponential approximation is applicable in the theory of heterogeneous nucleation if the radius R_n is not too large and Eq. (6.10) does not yet take R_0 and h_0 out of the region of validity of the exponential approximation for the dependence of β_v on h.

What is said above should be complemented with the following. The above subdivision of liquids into nonpolar and polar is rather arbitrary. Actually, not only the nature of a liquid, but also the nature of the nucleus matter should be taken into account. One should remember that, both in the case of nonpolar liquids and in the case of polar liquids, the quantity β_v tends to $-\infty$ as $h \to 0$, as was depicted qualitatively in Figs. 5 and 6. The approach of β_v to $-\infty$ proceeds logarithmically irrespective of whether the isotherm of adsorption on the nucleus surface is linear or a power at small v and at small vapour pressures. Thus, the exponential approximation to the dependence of β_v on h (and, hence, the exponential approximation to the work f of wetting of the nucleus) becomes invalid for certain as $v \to v_n$. Nevertheless, this will not lead, as we will show now, to significant corrections to the results obtained in Section 6.

Let us describe the procedure of matching the exponential approximation to the work of wetting of the nucleus by a condensate film with the experimental dependence of f on v resulting from the behaviour observed for β_v near the point $v = v_n$. The experimental dependence of f on v will be called the "pre-exponential approximation" (it is not necessarily determined by the Henry adsorption law which is applied only for a smooth homogeneous surface of the nucleus).

We will mark with superscripts 1 and 2 quantities calculated using the exponential approximation and the pre-exponential approximation, respectively. We have

$$f^{(1)} = f_* \left\{ 1 - c_e \exp \left[-(R - R_n) / l \right] \right\}$$

(9.1)

where the factor c_e differs from the right-hand side of Eq. (6.6) since the approximation given by Eq. (9.1) may not be extended all the way to the value $v = v_n$. Just this factor will be the quantity sought.

The contribution to the condensate chemical potential $\beta_v^{(2)}$, (as a function of h or v) is considered to be known from experiment. With regard to $\beta_v^{(2)}$, we obtain from Eqs. (5.8), (5.9), (1.1)–(1.3)

$$f^{(2)} = \int_{v_n}^{v} \beta_v^{(2)} \, dv' - a v_n^{2/3}$$

(9.2)

It is of note that the integral in (9.2) converges because $\beta_v^{(2)}$ behaves as $\ln h$ as $h \to 0$.

The dependence of $\beta_v^{(1)}$ and $\beta_v^{(2)}$ on v is depicted qualitatively by the curves 1 and 2 in Fig. 7 where the coordinate of their intersection point is designated as v_x. This coordinate, as well as curve 1 itself, is a function of the factor c_e we sought: $v_x = v_x(c_e)$. Evidently, $\beta_v^{(2)} - \beta_v^{(1)} < 0$ at $v < v_x$ and $\beta_v^{(2)} - \beta_v^{(1)} > 0$ at $v > v_x$.

We choose the factor c_e and the coordinate v_x in such a way as to satisfy $f^{(2)}|_{v=v_x} = f^{(1)}|_{v=v_x}$. As is clear from Fig. 7 and Eq. (2.17), the dependence of $f^{(1)}$ and $f^{(2)}$ on v will then be depicted qualitatively by curves 1 and 2 in Fig. 8. The values of the work f at $v = v_n$ indicated in Fig. 8 correspond to the asymptotic forms given by Eqs. (9.1) and (9.2). Naturally, the asymptotic form given by Eq. (9.1) has a physical meaning only at $v > v_x$ and the asymptotic form given by Eq. (9.2) only at $v < v_x$. The value f_* indicated in Fig. 8 is attained asymptotically by the function described by Eq. (9.1) as $v \to \infty$.
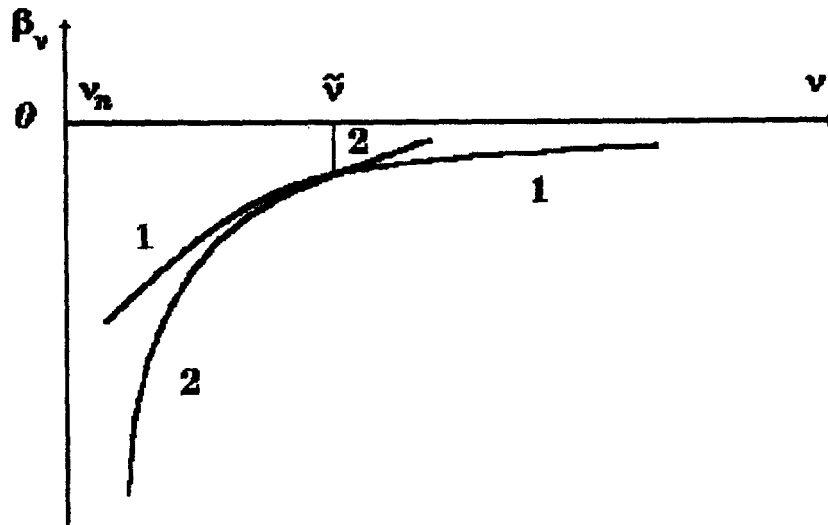
Fig. 7. Dependence of the chemical potential β_v on v according to the exponential approximation (curve 1) and pre-exponential approximation (curve 2).
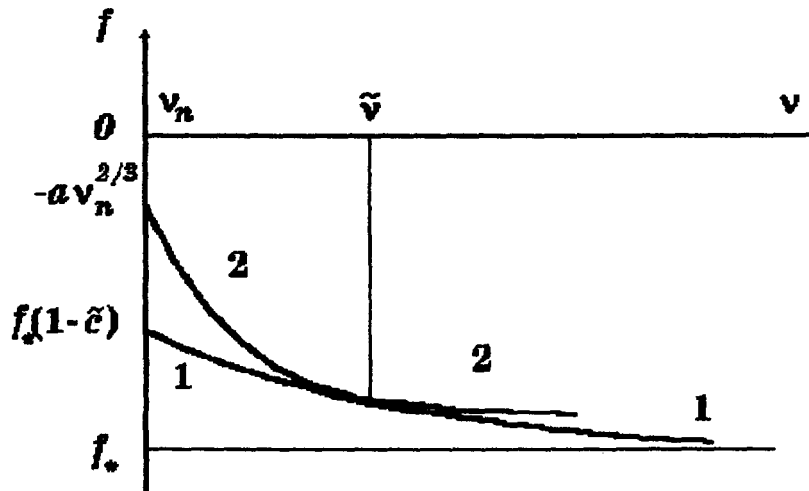

Fig. 8. Dependence of the work f on v according to the exponential approximation (curve 1) and pre-exponential approximation (curve 2).

In contrast with the curves 1 and 2 in Fig. 7, curves 1 and 2 in Fig. 8 do not intersect, but only touch each other at the point $v = v_x$. It is seen that

$$f_* < f^{(1)}\big|_{v=v_n} < f^{(2)}\big|_{v=v_n} < 0 \tag{9.3}$$

With Eqs. (5.11), (5.12), (5.14), (5.15), (9.1), (9.2), (1.2), (1.3), and (6.6) in mind, we conclude from Eq. (9.3) that

$$0 < c_e < c < 1 \tag{9.4}$$

Thus, on using the exponential approximation for the work f in the vicinity of the point $v = v_0$ (lying on the v-axis much to the right from the point $v = v_n$), which is the only region important for theory, all the influence of a deviation of f from the true behaviour of the work of wetting near the point $v = v_n$ (in the region where the film thickness is of molecular dimensions) is reduced to decreasing the factor in the exponent. As is seen from Fig. 8, the ratio c_e/c will not strongly differ from unity if the vicinity of the point $v = v_n$ where a deviation from the exponential approximation is observed, is comparatively narrow. A small difference between c and c_e will not influence significantly the results of the thermodynamic theory presented in Sections 6–8 since the factor c (or c_e) appears in the theory only through a R_0-value where c enters only in the argument of the logarithm, as is seen from Eqs. (6.6) and (6.10), and through a δ-value where c enters as $c_p^{1/(m+2)}$, as is seen from Eqs. (6.6), (7.6), and (8.2).

If the experimental exponential approximation to the disjoining pressure of a film is written in the form [30,31,41,44]

$$\Pi(h) = K \exp(-h/l) \tag{9.5}$$

then, from Eqs. (5.8), (6.5), (6.6), (5.11), (5.12), (6.3), and (1.2), in the quasi-flat approximation and with Eq. (9.4) in mind, we obtain

$$K < s/l \tag{9.6}$$

It is of note that the same relation between the parameters K, s, and l follows from the general formula given by Eq. (5.16).

Numerical estimates: water vapour nucleation on quartz particles

The relationships obtained in the previous sections for the characteristics of heterogeneous nucleation will now be illustrated with numerical estimates. For the sake of illustration, we choose the case where a polar liquid is condensed on solid insoluble macroscopic nuclei. More specifically, we will consider water as a condensate and quartz grits as condensation nuclei. In this case, the exponential approximation for the effect of overlapping of the surface layers of a condensate film on a

nucleus is realized (the value of $h_0 = R_0 - R_n$ runs into the stable part of the α-branch of the disjoining pressure isotherm).

For a water film on quartz, we have $\upsilon^{\alpha} = 3 \cdot 10^{-23}$ cm^3 (the monolayer thickness is about $3 \cdot 10^{-8}$ cm), $l = 2.33 \cdot 10^{-7}$ cm (which corresponds to the data from Refs. [31,41]), and $a = 9.4$ (at 273 K). We set $R_n = 3.4 \cdot 10^{-6}$ cm and $|\Delta\sigma|/\gamma = 1.3$ (which satisfies the restriction expressed by Eq. (6.11)). Herewith we find from Eqs. (6.3) and (1.2): $\kappa = 1.8 \cdot 10^3$, $v_n = 5.5 \cdot 10^6$; the nucleus macroscopicity parameter $l/R_n \equiv (\kappa/v_n)^{1/3}$ is about 0.07 and, hence, is small.

According to Eq. (6.10), we have $R_0 = 4.2 \cdot 10^{-6}$ cm and $R_0 - R_n = 8 \cdot 10^{-7}$ cm. This shows the applicability of the exponential approximation, Eq. (6.1) (the maximum of b_v running into the stability region of the α-branch of the disjoining pressure isotherm). According to Eq. (1.1), we also have $v_0 = 10^7$, $(v_n/v_0)^{1/3} = 0.8$, and $(\kappa/v_n)^{1/3} = 0.06$, so that the conditions expressed in Eqs. (6.13) and (6.14) are fulfilled with certainty.

According to Eq. (6.16), we have $b_{th} = 0.029$ so that $b_{th} \ll 1$. Further, we have $\Delta F = 4.2 \cdot 10^5 \, \varepsilon^{3/2}$. It is seen from Eq. (6.24) that $\varepsilon^{1/2} \sim 2 \cdot 10^{-2}$.

The quantity $a^{-1/3}\kappa^{-2/9}$ on the left-hand side of the inequality (6.25) is equal to 0.09, so that this inequality is satisfied.

Further, according to Eq. (6.26), we have in the pre-threshold region of vapour supersaturation $\Delta v_e = \Delta v_c \sim 5 \cdot 10^4$.

Using the data on the constants K and l from Refs. [31,41] ($K = 9.94 \cdot 10^7$ dyne/cm^2) and with the value $|\Delta\sigma|/\gamma = 1.3$ chosen for these calculations, Eqs. (5.12), (5.14), and (9.6) yield $\gamma > 77$ dyne/cm, to be compared with the tabulated value $\gamma = 75.6$ dyne/cm [45], which confirms the plausibility of the chosen value $|\Delta\sigma|/\gamma = 1.3$.

We now show that the above parameter values satisfy the condition, Eq. (4.19), of free-molecule exchange of matter between a heterogeneously formed drop and vapour. The free molecular path in vapour l_m can be estimated as 0.02 cm under the normal conditions ($n_g = 10^{18}$ cm^{-3}, $T = 273$ K). Recognizing the condensation coefficient to be $\alpha_C \sim 1$ to 10^{-2} for water [24,46], we estimate the right-hand side of Eq. (4.19) as $l_m/\alpha_C \sim 0.02$ to 2 cm. Taking into account the above estimate of R_0, we see the condition (4.19) to be satisfied.

At free molecular exchange of matter between a drop and vapour, the quantity w characterizing the rate of exchange is determined by Eq. (4.5). We have $w_0 = 5.5 \cdot 10^{10} \, \alpha_C \, c^{-1}$ at $n^{\beta} = 10^{17}$ cm^{-3} and $R = R_0$. Knowing w_0 and Δv_c and using Eq. (4.15), we find the characteristic time t_s, for the development of phase transition on insoluble macroscopic nuclei: $t_s \sim 0.02 \, \alpha_C^{-1} \, c$.

Conclusion

The numerical estimates obtained for the situation when the exponential approximation for the effect of overlapping surface layers of a liquid film on a condensation nucleus is valid, confirm the primary ideas and the conclusions of the theory.

The fact that the b_{th}-values turned out to be much smaller than unity, exhibits the reality of the barrierless heterogeneous phase transformation of a metastable phase on macroscopic nuclei dispersed through the whole of its volume (not at its outer boundaries) already at a rather small supersaturation of the metastable phase.

A nucleus is surrounded by a rather thick liquid film in the prethreshold region of vapour metastability (which is just the region of interest for theory) both in "near-critical" drops (for which $|v - v_c| < \Delta v_c$) and in "near-equilibrium" drops (for which $|v - v_e| < \Delta v_e$). Although the effect of overlapping of the film surface layers due to the influence of surface forces of a condensation nucleus is relatively weak for the thick film, the effect already ensures an extremely high energetic preference for heterogeneous as against homogeneous nucleation.

Below the prethreshold region of vapour metastability, the characteristic v_e of an equilibrium drop would be closer to v_n than in the prethreshold region. Here the solvation of a nucleus in the equilibrium drop could be of a more complex character, occurring via discrete "islands" instead of by formation of a uniform film. The theory would then need all the information about the behaviour of the work of heterogeneous formation of a drop in the region of molecular dimensions for the thickness of a liquid film around the nucleus. Only the prethreshold region of vapour metastability is of interest for the theory and, in addition, only this region is accessible for analytical description. This region is also remarkable in that the information referred to above as all being needed may be reduced to the knowledge of the three first derivatives for the work f of wetting of the nucleus at the point $v = v_0$. The second derivative $\partial^2 f / \partial v^2 |_{v=v_0}$ allows us to determine the point $v = v_0$ itself, the first derivative $\partial f / \partial v |_{v=v_0}$ is needed for finding the threshold value, b_{th}, for the vapour chemical potential, and the third derivative $\partial^3 f / \partial v^3 |_{v=v_0}$ is necessary for the calculation of v_e, v_c, Δv_e, Δv_c, ΔF, and t_s.

The threshold value of the vapour chemical potential for heterogeneous nucleation on macroscopic insoluble nuclei depends not only on the nucleus size, i.e. on the purely geometrical factor, but also on the physical–chemical properties of the nucleus surface and the drop surface.

The experimental data on nucleation on macroscopic insoluble nuclei present in the literature [47–49] do not allow a sufficiently complete comparison between theory and experiment. The problem is that only the data on the dependence of "critical" vapour supersaturation on the size of "dry" condensation nuclei are given in Refs. [47–49]. The "critical" supersaturation ζ_{crit} is understood as such a vapour supersaturation, created sufficiently rapidly in the vapour–gas-medium under investigation, at which the condensation process proceeds rapidly. As is clear from the considerations in this article, this supersaturation for heterogeneous nucleation will be close to the threshold value of vapour supersaturation. With enough accuracy, we may set $\zeta_{crit} \approx \zeta_{th}$, and also $\zeta_{crit} \approx b_{th}$, recognizing Eq. (1.8) and the smallness b_{th} with respect to unity. The experimental dependence of ζ_{crit} on $\lg R_n$ given in Refs. [47–49] coincides with the dependence of b_{th} on $\lg R_0$ implied by Eq. (6.16) [or by Eq. (7.10)]. However, in order to determine the peculiarities in behaviour of the condensate chemical potential at small thickness of a liquid film between a nucleus and vapour, we need more detailed information about the size of equilibrium drops arising heterogeneously in undersaturated vapour and about the dependence of the number of such drops on the initial value of the vapour supersaturation and on the initial number of condensation nuclei.

Acknowledgements

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