

# Kinetic Theory of Condensation on Insoluble Wettable Nuclei

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**Abstract**—A kinetic theory of vapor nucleation on insoluble wettable condensation nuclei is constructed. Depending on the initial parameters of a theory that determines the properties of a liquid, vapor, substance comprising the solid wettable nucleus, and boundary layers and characterizes the sizes of condensation nuclei; their initial number in the vapor–gas medium; and the rate of the external creation of a metastable state in vapor, all basic kinetic characteristics of nucleation (such as the number of supercritical droplets emerging in nucleation, the time of the beginning and the duration of the emergence of supercritical droplets, and the width of the spectrum of supercritical droplet sizes) are determined in the analytical form. Characteristic cases of free-molecular and diffusion regimes of the growth of supercritical droplets are analyzed. The quantitative criterion indicating the nature of the termination of the nucleation of supercritical droplets is disclosed: whether it is caused by the absorption of vapor by supercritical droplets or by the depletion of the supply of condensation nuclei due to the formation of supercritical droplets on these nuclei. Data of numerical calculation are reported which demonstrate the ability of the kinetic theory to draw interesting practical predictions within a wide range of the values of the initial parameters of the theory. It is shown how the polydispersity of insoluble wettable condensation nuclei can be taken into account in the theory.

## INTRODUCTION

The aim of this work is to construct the kinetic theory of vapor nucleation on insoluble wettable condensation nuclei with a homogeneous surface under the gradual external creation of a metastable state.

Difficulties in constructing this theory are associated with the fact that droplets arising from vapor on insoluble wettable nuclei represent complex formations having two interfaces: internal (between the nucleus and the liquid film surrounding this droplet) and external (between the liquid film and surrounding vapor). Numerous macroscopic characteristics of surface forces—surface tension of a droplet at the boundary with the vapor, the condensation coefficient of vapor molecules, the correlation length in a liquid film formed around the nucleus, and the work of nucleus wetting—are exhibited simultaneously in the nucleation on insoluble wettable nuclei.

With regard to nucleation, we mean both the overcoming of the activation barrier by the nuclei resulting in the formation of supercritical droplets and the entire complex process occurring in the nucleating system from the beginning and to the termination of the effective nucleation of supercritical droplets. All basic kinetic characteristics of nucleation, such as the number of nucleating droplets, the time of the beginning and the duration of the droplet nucleation, as well as the width of the spectrum of droplet sizes, are displayed in this process.

The process of nucleation is nontrivial for the theoretical description and is the most sensitive to the sur-

face forces in the situation where this process is accompanied by the overcoming of the noticeable activation barrier by the droplets. However, this barrier is not too high; otherwise, the process intensity will be negligible. Due to the extremely sharp dependence of the height of the activation barrier on vapor supersaturation under the macroscopicity of condensation nuclei, this situation can be accomplished only when the metastable state in vapor is not created instantaneously, i.e., prior to the onset of nucleation, but gradually in the course of the nucleation process. This situation is interesting and the gradual external creation of the metastable state in vapor needed to implement such a situation will be studied in this work.

Under the condition of the gradual creation of the metastable state, the current values of vapor supersaturation and the concentrations of condensation nuclei are not known in advance. The problem of the consistency of vapor absorption and the consumption of condensation nuclei by droplets with the velocity of the external creation of the metastable state in vapor is essentially nonlinear and nonlocal in time. The intensity of the creation of new droplets at each current time moment depends in a complex nonlinear manner both on the velocity of the external creation of the metastable state in vapor at all the preceding moments and on the amount of vapor and condensation nuclei that is absorbed or consumed during this time by droplets already nucleated.

In principle, this kinetic problem of consistency was solved in [1, 2], regardless of what the condensation nuclei specifically are. However, we failed to obtain in

analytical form the final formulas from the results [1, 2] due to the complex dependence of the activation energy on vapor supersaturation in the general case of arbitrary condensation nuclei.

This solution is to be performed in this work using the thermodynamics of nucleation on insoluble wettable condensation nuclei developed in [3]. Macroscopic sizes of these nuclei allow us to analytically develop the kinetic theory of nucleation within a wide range of the values of the initial parameters of the theory.

In this work, we report the results which were not represented either in the general kinetic theory of heterogeneous nucleation [1, 2] nor in the kinetic theory of nucleation on soluble nuclei [4–7]. The results of this work are the generalization of the theory for the case of the diffusion regime of the growth of supercritical droplets, the analysis of the conditions of the applicability of the theory, the formulation of the equation for the derivation of the degree of vapor metastability at which half the supercritical droplets emerge during the gradual creation of the metastable state, and the development of the effective method of the calculation of the kinetic characteristics of nucleation on insoluble wettable nuclei covering the whole domain of the applicability of the theory.

As in [1–3], it is assumed that all the condensation nuclei are identical. The possibility of accounting for the polydispersity of insoluble wettable condensation nuclei in the kinetic theory will be demonstrated at the end of this work.

## 1. IDEAL VAPOR SUPERSATURATION AND ITS REFERENCE VALUE

Let us introduce the vapor supersaturation  $\zeta$  via the relation

$$\zeta = (n/n_\infty) - 1, \quad (1.1)$$

where  $n$  and  $n_\infty$  are the number densities of molecules of vapor and supersaturated vapor, respectively. Let us denote the radius of a droplet formed in the vapor–gas medium on one of the condensation nucleus presented in the medium by  $R$ . To describe the droplet, we use, as a variable, the parameter  $v$  determined by the equality

$$v = 4\pi R^3/3v_\alpha, \quad (1.2)$$

where  $v_\alpha$  is the molecular volume of condensing liquid. In the case of insoluble macroscopic condensation nuclei considered in this work,  $v$  represents the number of liquid molecules which would be in a droplet provided it does not contain condensation nuclei at all. For further use of results in [1, 2], it is necessary that, at the stage that is of interest to us, the characteristic droplet radius markedly exceed the radius of condensation nucleus and, hence, that the value of  $v$  determined by the equality (1.2) almost coincide with the true number of vapor molecules condensed by the droplet. The

validity of this statement will be demonstrated in Section 6.

The creation of the metastable state in vapor is described by the law of growth (in time) of the ideal supersaturation  $\Phi$  defined by the equality

$$\Phi = (n_{\text{tot}}/n_\infty) - 1, \quad (1.3)$$

where  $n_{\text{tot}}$  is the total number of molecules of a condensing substance in a unit volume of the vapor–gas medium also including the molecules condensed by the droplet. The ideal supersaturation is only dependent on the external conditions. The development of the nucleation process is governed from outside precisely by setting the growth of the ideal supersaturation in time.

The most important of all the kinetic characteristics of the nucleation is the total number of nucleating supercritical droplets. The  $\Phi_*$  value of ideal supersaturation  $\Phi$  above which half the total number of droplets emerging in the nucleation process is formed serves as the reference parameter to find this characteristic. The  $\Phi_*$  value is not known in advance when the rate of the growth of ideal supersaturation  $\Phi$  is set from the outside.

As in [1, 2], we use the time-dependent power approximation

$$\Phi = (t/t_\infty)^m \quad (1.4)$$

to determine  $\Phi$ . This approximation involves two independent positive parameters: characteristic time  $t_\infty$  and the exponent  $m$ . In this case, time  $t$  is counted from the moment when, according to approximation (1.4),  $\Phi = 0$ . The procedure for the generalization of the kinetic theory of nucleation for the case of an arbitrary dependence of the ideal vapor supersaturation on time was shown in [5].

According to (1.4), we have for moment  $t_*$  corresponding to  $\Phi_*$  the following expression:

$$t_* = t_\infty \Phi_*^{1/m}. \quad (1.5)$$

## 2. THE MAIN PARAMETERS OF THE KINETIC THEORY OF NUCLEATION

The most important parameter in the kinetic theory of nucleation [1, 2] is the dimensionless parameter  $\Gamma$  defined by the equality

$$\Gamma = -\Phi_*(\partial\Delta F/\partial\zeta)|_{\zeta=\Phi_*}. \quad (2.1)$$

Here,  $\Delta F$  is the activation energy of nucleation set by the difference between the maximum and minimum of the work of the formation of a droplet on a condensation nucleus. The  $\Delta F$  energy is expressed in  $k_B T$  units, where  $k_B$  is Boltzmann's constant and  $T$  is the temperature of droplets and the surrounding vapor–gas medium (the existence of thermal equilibrium between droplets and the medium is secured by the suggested high con-

centration of the passive gas in a medium compared to the vapor concentration). In the situation where the nucleation is accompanied by the droplets overcoming the noticeable activation barrier, the parameter  $\Gamma$  is rather large:

$$\Gamma \gg 1. \quad (2.2)$$

Let  $R_c$  be the radius of a critical droplet, which is in unstable chemical equilibrium with the vapor. For considerably supercritical droplets (for which  $R > (3-4)R_c$  is valid), we can always pass from variable  $v$  determined by equality (1.2) to such a variable  $\rho$  that increases in time at a rate  $\dot{\rho}$  independent of  $\rho$  (as well as of  $v$ ) but is determined only by the vapor supersaturation  $\zeta$ , irrespective of the regime of the matter exchange between the droplets and the vapor. It is such a variable convenient for the theory that will be used further. Then, we have

$$\dot{\rho} = \dot{\rho}(\zeta). \quad (2.3)$$

Hereafter,  $\rho$  is defined as the droplet "size." The validity of inequality  $R > (3-4)R_c$  at the stage corresponding to the nucleation of supercritical droplets is secured by the fulfillment of condition (4.8) indicated in Section 4.

The radius  $R_c$  of the critical droplet is almost always much smaller than the mean free path of vapor molecules and, moreover, much smaller than this path divided by the condensation coefficient of vapor molecules. Then, the overcoming of the activation barrier of nucleation by the droplets almost always occurs in a free-molecular regime of the matter exchange between the droplets and the vapor.

However, once the activation barrier of nucleation is overcome by the droplets, their radii can be so large that the free molecular regime is gradually changed to the diffusion mechanism, which can become even the prevailing regime at the stage corresponding to the nucleation of supercritical droplets.

Let us first consider the characteristic case where a free molecular regime still prevails at the stage corresponding to the nucleation of supercritical droplets. It is precisely this case that was studied in [1, 2]. As follows from (1.2), the variable

$$\rho = v^{1/3} \quad (2.4)$$

provides for the fulfillment of relation (2.3).

For the rate of the growth of this variable in a free molecular regime, we have

$$\dot{\rho} = \alpha \zeta / \tau. \quad (2.5)$$

Here,  $\alpha$  is the condensation coefficient of vapor molecules and  $\tau$  is the mean free time of a molecule

in the saturated vapor. It is determined by the equality

$$\tau = 12 / [(36\pi)^{1/3} v_\alpha^{2/3} n_\infty v_T], \quad (2.6)$$

where  $v_T$  is the mean thermal velocity of vapor molecules (the cross section of the collision of molecules is estimated via  $v_\alpha^{2/3}$ ).

In addition to parameter  $\Gamma$ , other important variables in the kinetic theory of nucleation [1, 2] are the dimensionless parameters  $c$  and  $h$ , which, at a free molecular growth of supercritical droplets, are determined by the equalities

$$c = \frac{m\tau\Gamma}{\alpha t_\infty \Phi_*^{(m+1)/m}}, \quad (2.7)$$

$$h = 6 \frac{\eta(-\infty)}{n_\infty} \frac{\Gamma}{\Phi_* c^3}, \quad (2.8)$$

where  $\eta(-\infty)$  denotes the initial concentration of condensation nuclei, i.e., their number in a unit volume of the vapor-gas medium at the beginning of the stage corresponding to the nucleation of supercritical droplets.

Parameter  $h$  is important because it allows us to determine the total number  $N$  of supercritical droplets nucleating in a unit volume of the vapor-gas medium by the formula

$$N = \eta(-\infty)[1 - \exp(-1/h)] \quad (2.9)$$

(formula (28) in [2]). At  $h \gg 1$  and  $h \ll 1$ , it follows from (2.9) that

$$N = \eta(-\infty)/h \quad (h \gg 1), \quad (2.10)$$

and

$$N = \eta(-\infty) \quad (h \ll 1). \quad (2.11)$$

According to (2.10), at  $h \gg 1$ , droplets consume only a fairly small portion of the entire initial amount of condensation nuclei (each droplet consumes one nucleus). However, according to (2.11), at  $h \ll 1$ , droplets consume the whole initial amount of condensation nuclei. Hence, the value of parameter  $h$  is the quantitative criterion, which determines whether the termination of the stage corresponding to the droplet nucleation is caused by the vapor absorption by the droplets or by the depletion of the reserve condensation nuclei by the droplets formed on nuclei.

According to inequality (37) in [2], relation

$$|\zeta_* - \Phi_*| / \Phi_* < (\ln 2) / \Gamma \quad (h \gg 1 \text{ or } h \ll 1) \quad (2.12)$$

is valid. The subscript \* characterizes the values of parameters at moment  $t_*$ .

The parameter  $c$  is important because it allows us to calculate the width  $\Delta\rho$  of the size spectrum of the

supercritical droplets at the  $\rho$ -axis by the equation

$$\Delta\rho \approx 3/c \quad (h \gg 1 \text{ or } h \ll 1) \quad (2.13)$$

resulted from formulas (45) and (48) in [2]. Only at this axis at which, according to (2.3), all the supercritical droplets "move" at an identical rate at each current value of the vapor supersaturation  $\zeta$  does the spectrum of droplet sizes (to be more exact, each part of the spectrum formed by the current time moment) move as a whole with no change in its shape. Correspondingly, it is only at this axis that we can state the width of the droplet size spectrum as a time-independent value.

According to formulas (45), (47), and (49) in [2], the approximate equality

$$\Delta t/t_* \approx 3/m\Gamma \quad (h \gg 1 \text{ or } h \ll 1) \quad (2.14)$$

is valid. Here,  $\Delta t$  is the duration of the nucleation of supercritical droplets. Substituting (1.5) and (2.7) into (2.14), we have

$$\Delta t \approx 3\tau/\alpha\Phi_*c \quad (h \gg 1 \text{ or } h \ll 1). \quad (2.15)$$

Hence, parameter  $c$  is also important for determining time  $\Delta t$ .

Moments  $t_{\text{on}}$  and  $t_{\text{off}}$  of the beginning and the termination of the nucleation of supercritical droplets can be found from (1.5) and (2.15) using relations

$$t_{\text{on}} \approx t_* - \Delta t/2, \quad t_{\text{off}} \approx t_* + \Delta t/2, \quad (2.16)$$

where it is taken into account that moment  $t_*$  lies approximately in the middle of the time interval of the nucleation of supercritical droplets. It follows from (2.2) and (2.14) that (at the not so small parameter  $m$ ) inequality  $t_{\text{on}} > 0$  is true, as is expected.

Let us consider the opposite characteristic case (which was not studied in [1, 2]), where the diffusion regime of matter exchange between the supercritical droplets and the vapor prevails at the stage corresponding to the nucleation of supercritical droplets. Then, as follows from (1.2), variable

$$\rho = v^{2/3} \quad (2.17)$$

secures the fulfillment of relation (2.3).

For the rate  $\dot{\rho}$  of the growth of this variable in the diffusion regime, we have

$$\dot{\rho} = \zeta/\tau_D. \quad (2.18)$$

Here,  $\tau_D$  is the characteristic time defined by the equation

$$\tau_D = (3/8\pi)(4\pi/3v_\alpha)^{1/3}/Dn_\infty, \quad (2.19)$$

where  $D$  is the diffusion coefficient of vapor molecules in the vapor-gas medium.

Generalizing the kinetic theory developed in [1, 2] for the case of the diffusion growth of supercritical droplets, we can be assured that relations (2.9)–(2.14) and (2.16) remain valid. However, dimensionless

parameters  $c$  and  $h$  of the theory are defined by the equalities

$$c = \frac{m\tau_D\Gamma}{t_\infty\Phi_*^{(m+1)/m}}, \quad (2.20)$$

$$h = \frac{3\pi^{1/2}\eta(-\infty)\Gamma}{4n_\infty\Phi_*c^{3/2}} \quad (2.21)$$

[the definition (2.1) of parameter  $\Gamma$  remains the same]. Instead of (2.15), we now have

$$\Delta t \approx 3\tau_D/\Phi_*c \quad (h \gg 1 \text{ or } h \ll 1). \quad (2.22)$$

The value of parameter  $h$  remains the quantitative criterion of the actual termination of the nucleation of supercritical droplets.

Under the condition of the linear dependence of parameter  $h$  on  $\eta(-\infty)$  followed from equalities (2.8) and (2.21), the relatively simple and physically obvious limiting situations  $h \gg 1$  or  $h \ll 1$  are more feasible than the situation where  $h \sim 1$ . Below, we confine ourselves to the limiting situations  $h \gg 1$  and  $h \ll 1$ .

### 3. EQUATION FOR THE REFERENCE VALUE OF THE IDEAL VAPOR SUPERSATURATION

The basic parameters  $\Gamma$ ,  $c$ , and  $h$  introduced into the kinetic theory of nucleation are dependent on the reference value  $\Phi_*$  of the ideal vapor supersaturation. Correspondingly, kinetic characteristics of nucleation  $N$ ,  $\Delta\rho$ ,  $\Delta t$ ,  $t_{\text{on}}$ , and  $t_{\text{off}}$  expressed via  $\Phi_*$  with the aid of parameters  $c$  and  $h$  are also dependent on the parameter  $\Phi_*$ .

At a free molecular growth of supercritical droplets, we have for  $\Phi_*$  the following implicit equation:

$$f_s \approx \begin{cases} (c/h)\ln 2 & (h \gg 1) \\ c\ln 2 & (h \ll 1) \end{cases} \quad (3.1)$$

(Eq. (36) in [2]) where the value of  $f_s$  is determined by relation

$$f_s = \frac{3}{\pi} \left( \frac{v_c^{2/3}}{\Delta v_e \Delta v_c} \frac{1 + \zeta}{\zeta} e^{-\Delta F} \right) \Big|_{\zeta = \Phi_*} \quad (3.2)$$

([1], relations (16) and (27)). Here,  $v_c$  is the value of parameter  $v$  for the critical droplet and  $\Delta v_e$  and  $\Delta v_c$  are the "half-widths" of the potential well and the potential barrier of the work of droplet formation on condensation nuclei at the  $v$ -axis, respectively. Generalizing the kinetic theory developed in [1, 2] for the case of the dif-

fusion growth of supercritical droplets, we are assured that Eq. (3.1) is still fulfilled; however, the relation

$$f_s = \frac{3\alpha\tau_D}{\pi\tau} \left( \frac{v_c^{2/3}}{\Delta v_c \Delta v_c} \frac{1+\zeta}{\zeta} e^{-\Delta F} \right) \Big|_{\zeta=\Phi_*} \quad (3.3)$$

appears instead of (3.2).

Relations (3.1)–(3.3) form the closed equation for the reference value  $\Phi_*$  of the ideal supersaturation  $\Phi$ . This equation is responsible for the consistency between the absorption of the supersaturated vapor by supercritical droplets and the consumption of condensation nuclei by these droplets and a rate of the external increase in the ideal supersaturation  $\Phi$  in time.

Let us represent this equation in the form which is important for further discussion. We introduce time  $t_s$  using equality

$$t_s \approx [(\Delta v_c)^2 / 2W_c] \Big|_{\zeta=\Phi_*}, \quad (3.4)$$

where

$$W_c = \pi\alpha v_T n R_c^2. \quad (3.5)$$

Because the matter exchange between the critical droplet and the vapor occurs, as was already mentioned, in a free molecular regime,  $W_c$  represents, according to (3.5), the number of molecules absorbed by the critical droplet from the vapor per unit time. Then, parameter  $t_s$  introduced by (3.4) characterizes [8, 9] the time of the establishment of the quasi-steady-state regime of overcoming the activation barrier of nucleation by the droplets; however, this characteristic is approximate because in (3.4) the vapor supersaturation  $\zeta$  is taken as equal to the reference value  $\Phi_*$  of the ideal supersaturation  $\Phi$ . Time  $t_s$  is actually important in the condition (4.1) of the applicability of the kinetic theory of nucleation so that the approximation in the treatment of time  $t_s$  seems to be insignificant.

Using (1.1), (1.2), and (2.6), we specify (3.5) as

$$W_c = 3\alpha\tau^{-1}(1+\zeta)v_c^{2/3}. \quad (3.6)$$

From (3.1), (3.4), and (3.6) with the allowance for (2.15) and (3.2) at the free molecular growth of supercritical droplets and, correspondingly, with allowance for (2.22) and (3.3) at the diffusion growth of supercritical droplets, we obtain

$$\left( \frac{\Delta v_e e^{\Delta F}}{\Delta v_c} \right) \Big|_{\zeta=\Phi_*} \approx \begin{cases} (h/6\pi \ln 2) \Delta t / t_s & (h \gg 1) \\ (1/6\pi \ln 2) \Delta t / t_s & (h \ll 1). \end{cases} \quad (3.7)$$

Equation (3.7) represented in the form identical for the free molecular and the diffusion regimes of the growth of supercritical droplets is quite important for further discussion.

#### 4. CONDITIONS OF THE APPLICABILITY OF THE KINETIC THEORY OF NUCLEATION

Let us formulate the conditions of the applicability of the kinetic theory of nucleation, mentioned briefly in [1, 2].

It was assumed in the kinetic theory that the activation barrier of nucleation is overcome by droplets in the quasi-steady-state regime during the entire stage corresponding to the nucleation of supercritical droplets. Evidently, to do so, it is necessary to fulfill the condition

$$\Delta t / t_s \gg 1. \quad (4.1)$$

In view of (3.7), the fulfillment of condition (4.1) also secures the fulfillment of condition

$$\exp(\Delta F|_{\zeta=\Phi_*}) \gg 1, \quad (4.2)$$

which guarantees that the stage corresponding to the nucleation of supercritical droplets will be accompanied by the overcoming of a noticeable activation barrier of nucleation by the droplets.

In the case of the free molecular growth of supercritical droplets, it was assumed in the kinetic theory that the radii of supercritical droplets typical of the stage corresponding to their nucleation satisfy inequality  $R \ll \lambda/\alpha$ . Here,  $\lambda$  is the mean free path of vapor molecules in the vapor–gas medium estimated by the gas-kinetic relation

$$\lambda \sim (n_\infty + n_g)^{-1} v_\alpha^{-2/3}, \quad (4.3)$$

where  $n_g$  is the number of passive gas molecules in the unit volume of the vapor–gas medium ( $v_\alpha^{2/3}$  characterizes the cross section of collisions between the molecules of the vapor and the medium; it is assumed that  $n \approx n_\infty$ ). Passing from  $R$  to variable  $\rho$  with the help of (1.2) and (2.4) and using (4.3) and the estimate  $\rho \sim \Delta\rho$ , we represent inequality  $R \ll \lambda/\alpha$  as

$$\Delta\rho/\rho_\lambda \ll 1, \quad (4.4)$$

where

$$\rho_\lambda \sim \alpha^{-1} (n_\infty + n_g)^{-1} v_\alpha^{-1}. \quad (4.5)$$

In the case of the diffusion growth of supercritical droplets, the opposite inequality  $R \ll \lambda/\alpha$  should be fulfilled instead of  $R \gg \lambda/\alpha$ , which according to (1.2), (2.17), (4.3), and the estimate  $\rho \sim \Delta\rho$  is written as

$$\Delta\rho/\rho_\lambda \gg 1, \quad (4.6)$$

where

$$\rho_\lambda \sim \alpha^{-2} (n_\infty + n_g)^{-2} v_\alpha^{-2}. \quad (4.7)$$

The condition

$$\Delta\rho/\rho_c \gg 1 \quad (4.8)$$

was also suggested in the kinetic theory of nucleation, where  $\rho_c$  is the size of a supercritical droplet at the  $\rho$ -axis. According to (2.13), (2.15), (3.4), (3.6), and

equality  $\rho_c = v_c^{1/3}$ , in the case of the free molecular growth of supercritical droplets, we have

$$\frac{\Delta p}{\rho_c} \approx \frac{1}{6} \left( \frac{(\Delta v_c)^2 \zeta}{v_c (1 + \zeta)} \right) \Big|_{\zeta = \Phi_* t_s} \frac{\Delta t}{t_s} \quad (4.9)$$

$(h \gg 1 \text{ or } h \ll 1).$

As is seen from (4.9), the inequality (4.8) is satisfied in this case under the fulfillment of condition (4.1) [coefficient in (4.9) at multiple  $\Delta t/t_s$  will be estimated in Section 6]. In the case of the diffusion growth of supercritical droplets, the fulfillment of condition (4.8) follows directly from the inequality (4.6) and the relation already mentioned in Section 2, according to which the radius of a supercritical droplet is almost always much smaller than the  $\lambda/\alpha$  ratio.

## 5. FUNDAMENTALS OF THERMODYNAMICS OF THE NUCLEATION ON INSOLUBLE WETTABLE NUCLEI

The chemical potential of a liquid condensed on an insoluble wettable nucleus exhibits a maximum as a function of the droplet size [3, 10]. We denote the values of parameters corresponding to this maximum by the subscript zero. From (1.2), we have

$$v_0 = 4\pi R_0^3/3v_\alpha. \quad (5.1)$$

For the threshold value  $\zeta_{th}$  of the vapor supersaturation above which the nucleation of droplets on condensation nuclei occurs in a barrierless manner, according to formula (6.16) in [3], we have

$$\zeta_{th} = 2a/3v_0^{1/3}, \quad (5.2)$$

where

$$a = (4\pi\gamma/k_B T)(3v_\alpha/4\pi)^{2/3} \quad (5.3)$$

( $\gamma$  is the surface tension of a droplet at its boundary with the vapor). Assuming inequality

$$v_0^{1/3} \gg 2a/3, \quad (5.4)$$

we see from (5.2) that

$$\zeta_{th} \ll 1. \quad (5.5)$$

Let us represent the vapor supersaturation  $\zeta$  as

$$\zeta \equiv \zeta_{th}(1 - \varepsilon), \quad (5.6)$$

where  $\varepsilon$  is its relative deviation from the  $\zeta_{th}$  value. In the prethreshold region of the vapor metastability, inequalities  $0 < \zeta < \zeta_{th}$  are transformed into  $0 < \varepsilon < 1$ .

Let us introduce parameter  $p_0$ :

$$p_0 \equiv \frac{3^9 v_0^7}{2^3 a^3} \left( \left. \frac{\partial^2 b_v}{\partial v^2} \right|_0 \right)^3, \quad (5.7)$$

where  $b_v$  is the  $v$ -dependent chemical potential of a liquid-comprising droplet expressed in  $k_B T$  units. Accord-

ing to formulas (3.4), (3.8), and (3.13) in [3], we then have

$$v_e = v_0(1 - 2^{1/2} 3 p_0^{-1/6} \varepsilon^{1/2}), \quad (5.8)$$

$$v_c = v_0(1 + 2^{1/2} 3 p_0^{-1/6} \varepsilon^{1/2}),$$

$$\Delta F = \frac{2^{7/2}}{3} a v_0^{2/3} p_0^{-1/6} \varepsilon^{3/2}, \quad (5.9)$$

$$\Delta v_e = \Delta v_c = 2^{-1/4} 3 a^{-1/2} v_0^{2/3} p_0^{-1/12} \varepsilon^{-1/4}, \quad (5.10)$$

where  $v_e$  is the value of parameter  $v$  for the droplet in a stable equilibrium with the vapor.

In the situation where the nucleation of supercritical droplets is accompanied by the overcoming of the marked activation barrier of nucleation but occurs rather intensely, inequalities

$$2 \leq \Delta F \leq 15 \quad (5.11)$$

are true.

From (5.9) and (5.11), it follows that

$$\varepsilon^{1/2} \approx a^{-1/3} v_0^{-2/9} p_0^{1/18}, \quad (5.12)$$

where it is taken into account that the variation range of parameter  $(\Delta F)^{1/3}$  is much narrower than that of parameter  $\Delta F$ ; correspondingly, it is assumed that  $(3\Delta F/2^{7/2})^{1/3} \approx 1$ . Relation (5.12) will be refined in Section 6.

Analytical expression (6.7) for  $b_v$  was obtained in [3] at the exponential approximation of the work of wetting the solid condensation nucleus. Taking this expression into account, we arrive at

$$R_0 = R_n + l \ln(s R_n^2 / 2\gamma l^2) \quad (5.13)$$

(relation (6.10) in [3]), and using (5.7), we also have

$$p_0 = v_0/k. \quad (5.14)$$

Here,  $R_n$  is the radius of a solid condensation nucleus and  $l$  is the correlation length in a liquid film formed around the nucleus; parameters  $s$  and  $k$  are determined by relations

$$s \equiv \sigma_{\beta\gamma} - \sigma_{\alpha\gamma} - \gamma, \quad (5.15)$$

$$k \equiv 4\pi l^3 / 3v_\alpha, \quad (5.16)$$

where  $\sigma_{\beta\gamma}$  and  $\sigma_{\alpha\gamma}$  are the surface tensions at the boundaries between the nucleus and vapor and liquid, respectively. According to (5.15), the parameter  $s$  represents the initial value of the spreading coefficient of condensing liquid over the homogeneous surface of a solid wettable nucleus. It is suggested that in the case of the exponential approximation of the work of nucleus wetting, which was considered for the illustration only, condition  $s > 2\gamma l^2/R_n^2$  is true. In accordance with (5.13), this condition provides for the inequality  $R_0 > R_n$ ,

implying the existence of a threshold value of the vapor supersaturation.

Let us assume the condition of the macroscopicity of condensation nuclei as

$$R_n/l \gg 1. \quad (5.17)$$

At the relatively low logarithmic value in (5.13), we have

$$R_0 \approx R_n, \quad (5.18)$$

which is fulfilled quite accurately and even without assuming the exponential approximation of the work of nucleus wetting. As is seen from (5.1) and (5.18),  $v_0$  is approximately equal to the number of liquid molecules in the volume corresponding to that of the nucleus.

According to (5.1), (5.14), (5.16), and (5.18), we have

$$p_0 \approx (R_n/l)^3, \quad (5.19)$$

which allows us to determine  $p_0$  at the exponential approximation of the work of nucleus wetting using data on  $R_n$  and  $l$ . It follows from (5.19) and condition (5.17) that

$$p_0^{1/3} \gg 1. \quad (5.20)$$

The strong inequality (5.20) is true even without the assumption about the exponential approximation of the work of nucleus wetting.

Representing (5.12) with the help of (5.1), (5.18), and (5.19) as

$$\varepsilon^{1/2} \approx (3/4\pi)^{2/9} a^{-1/3} (v_\alpha^{1/3}/l)^{2/3} (l/R_n)^{1/2} \quad (5.21)$$

and allowing for the characteristic estimates  $a \sim 10$  and  $v_\alpha^{1/3}/l \sim 10^{-1}$ , we can see that condition (5.17) also provides for inequality

$$\varepsilon^{1/2} \ll 1. \quad (5.22)$$

It follows from (5.8), (5.20), and (5.22) that

$$v_e \approx v_0, \quad v_c \approx v_0. \quad (5.23)$$

Evidently, (5.22) and (5.23) are true, with no regard for the exponential approximation of the work of nucleus wetting.

We call the region of vapor metastability where inequalities (5.11), (5.12) and (5.22) are fulfilled, as in [3], the "prethreshold" region.

The parameters  $v_0$  and  $p_0$  are taken as the reference parameters of the kinetic theory of nucleation. The interrelation between  $v_0$  and  $R_n$  is easily established from (5.1) and (5.18). Then, using (5.19) at the exponential approximation of the work of nucleus wetting, we can establish the interrelation between  $p_0$  and  $l$ ; however, in the general case, to disclose this interrelation, it is necessary [see relation (5.7)] to find  $|\partial^2 b_v / \partial v^2|_0$ . This can be accomplished both thermodynamically using the total disjoining pressure isotherm for thin liquid films on the surface corresponding to the

nucleus and with experimental data by solving the inverse problem of the nucleation kinetics.

## 6. KINETIC CHARACTERISTICS OF THE NUCLEATION ON INSOLUBLE WETTABLE NUCLEI

According to (5.6) and (5.22), we have at a high degree of accuracy

$$\zeta \approx \zeta_{th}. \quad (6.1)$$

Because (6.1) is also true at  $\zeta = \zeta_*$ , from (2.2), (2.12), and (6.1), at the same high degree of accuracy, we have

$$\Phi_* \approx \zeta_{th}. \quad (6.2)$$

Expression (6.2) for the reference value  $\Phi_*$  derived for macroscopic condensation nuclei, which has in its right-hand side the  $\zeta_{th}$  parameter known from thermodynamic relation (5.2), greatly simplifies the kinetic theory of nucleation.

Expression (6.2) is accurate enough to determine the  $\Phi_*$  power-dependent values. However, the values dependent on  $\Phi_*$  via the small deviation  $\zeta_{th} - \Phi_*$  also seem to be important in the kinetic theory. The refinement of relation (5.12) and expression (6.2), which are needed to determine such values, will be our next goal.

From (3.7) with the allowance for equality  $\Delta v_e = \Delta v_c$  followed from (5.10), we arrive at

$$\Delta F|_{\zeta = \Phi_*} \approx \begin{cases} \ln(\kappa h / 6\pi \ln 2) & (h \gg 1) \\ \ln(\kappa / 6\pi \ln 2) & (h \ll 1), \end{cases} \quad (6.3)$$

where it is taken that

$$\kappa \equiv \Delta t / t_s. \quad (6.4)$$

Let us denote the value of  $\tilde{\varepsilon}$  determined according to (5.6) at  $\zeta = \Phi_*$  via  $\varepsilon$ . Then, we have

$$\tilde{\varepsilon} \equiv (\zeta_{th} - \Phi_*) / \zeta_{th}. \quad (6.5)$$

Using (5.9) in (6.3) and allowing for (6.5), we obtain

$$\tilde{\varepsilon}^{1/2} \approx q a^{-1/3} v_0^{-2/9} p_0^{1/18}, \quad (6.6)$$

where

$$q = \begin{cases} [(3/2^{7/2}) \ln(\kappa h / 6\pi \ln 2)]^{1/3} & (h \gg 1) \\ [(3/2^{7/2}) \ln(\kappa / 6\pi \ln 2)]^{1/3} & (h \ll 1). \end{cases} \quad (6.7)$$

The parameter  $\tilde{\varepsilon}$  introduced according to (6.5) is of importance because we can use it and equality (5.9) to express parameter  $\Gamma$

$$\Gamma \approx (\partial \Delta F / \partial \varepsilon)|_{\varepsilon = \tilde{\varepsilon}} \quad (6.8)$$

followed from eqs. (2.1), (5.6), and (6.2). The value of  $\tilde{\varepsilon}$  is also important because the time  $t_s$  can be expressed via this value using (3.4) and (5.10). The parameter  $\Gamma$  and

the time  $t_s$  serve as examples of values that depend quite heavily on  $\Phi_*$  via the small deviation  $\zeta_{th} - \Phi_*$ .

Relation (6.6) refines expression (5.12) determining the value of  $\epsilon^{1/2}$ , which is typical of interval (5.11), i.e., of the prethreshold region of vapor metastability. This refinement can be represented in the following form:

$$\tilde{\epsilon}^{1/2} \approx q\epsilon^{1/2}. \quad (6.9)$$

As will be shown in Sections 8 and 9, the approximate equality

$$q \approx 1 \quad (6.10)$$

is true.

Then, from (5.22) and (6.9), it follows that

$$\tilde{\epsilon}^{1/2} \ll 1. \quad (6.11)$$

Relation (6.6), together with (6.5), also permits us to easily refine expression (6.2) for  $\Phi_*$ . In view of (6.11), this refinement is insignificant. It is not so important when the dependence on  $\Phi_*$  becomes power-dependent. Therefore, expression (6.2) will not be refined.

Let us now pass to the main goal of this section. To simplify the expression, we will drop the bounds on either  $h \gg 1$  or  $h \ll 1$  in the formulas.

Substituting (5.9) into (6.8) and using (6.6), we obtain

$$\Gamma \approx 2^{5/2} q a^{2/3} v_0^{4/9} p_0^{-1/9}. \quad (6.12)$$

From (3.4) and (3.6) with the allowance for (5.5), (5.10), (6.2), and (6.6), we have

$$t_s \approx \frac{3}{2^{3/2}} \frac{\tau}{q \alpha} \frac{v_0^{8/9}}{a^{2/3} p_0^{2/9}}. \quad (6.13)$$

Using (1.5), (5.2), and (6.2), we find

$$t_* \approx \left(\frac{2}{3}\right)^{1/m} t_\infty \frac{\alpha^{1/m}}{v_0^{1/3m}}. \quad (6.14)$$

We give further consideration first for the case of the free molecular growth of supercritical droplets. Substitution of (5.2), (6.2), and (6.12) into (2.7) and (2.8) yields

$$c \approx 2^{3/2} 3 \left(\frac{3}{2}\right)^{1/m} \frac{q m \tau}{\alpha t_\infty} \frac{v_0^{(7m+3)/9m}}{a^{(m+3)/3m} p_0^{1/9}}, \quad (6.15)$$

$$h \approx \frac{1}{12} \left(\frac{2}{3}\right)^{3/m} \frac{\eta(-\infty)}{q^2 n_\infty} \left(\frac{\alpha t_\infty}{m \tau}\right)^3 \frac{a^{(2m+9)/3m} p_0^{2/9}}{v_0^{(14m+9)/9m}}. \quad (6.16)$$

From (4.9) with allowance for (5.2), (5.5), (5.10),

(5.23), (6.2), and (6.6), we have

$$\frac{\Delta \rho}{\rho_c} \approx \frac{a^{1/3}}{2^{1/2} q} \left(\frac{v_0}{p_0}\right)^{2/9} \frac{\Delta t}{t_s}. \quad (6.17)$$

Representing  $(v_0/p_0)^{2/9}$  as  $(4\pi/3)^{2/9} (l/v_\alpha^{1/3})^{2/3}$  with the help of (5.14) and (5.16), taking into account (6.10) and the characteristic estimates  $a \sim 10$ ,  $l/v_\alpha^{1/3} \sim 10$ , we can see that the coefficient at multiple  $\Delta t/t_s$  in (6.17) is much larger than unity. Then, according to (6.17), condition (4.8) is readily satisfied under the fulfillment of inequality (4.1).

Because the radius  $R_c$  of the critical droplet exceeds the radius  $R_n$  of a condensation nucleus, it follows from condition (4.8) that at the stage corresponding to the nucleation of supercritical droplets, their characteristic radii are much larger than the radius  $R_n$  of a nucleus. Hence, at this stage, the parameter  $\nu$  determined by equality (1.2) accurately coincides with the true number of condensed vapor molecules in a droplet.

Let us now consider the case of the diffusion growth of supercritical droplets. Using (5.2), (6.2), and (6.12) in (2.20) and (2.21), we have

$$c \approx 2^{3/2} 3 \left(\frac{3}{2}\right)^{1/m} \frac{q m \tau_D}{t_\infty} \frac{v_0^{(7m+3)/9m}}{a^{(m+3)/3m} p_0^{1/9}}, \quad (6.18)$$

$$h \approx \frac{(3\pi)^{1/2}}{2^{11/4}} \left(\frac{2}{3}\right)^{3/2m} \frac{\eta(-\infty)}{q^{1/2} n_\infty} \left(\frac{t_\infty}{m \tau_D}\right)^{3/2} \frac{a^{(m+9)/6m} p_0^{1/18}}{v_0^{(7m+9)/18m}}. \quad (6.19)$$

As was mentioned in Section 4, condition (4.8) is always fulfilled in this case. Correspondingly, at the stage of the nucleation of supercritical droplets, the parameter  $\nu$  still practically coincides with the true number of molecules in a droplet.

Parameters  $c$  and  $h$  specified in this section determine the kinetic characteristics of the nucleation on insoluble wettable nuclei that depend on these parameters.

## 7. PARAMETRIZATION OF THE CHARACTERISTIC TIME OF THE CREATION OF METASTABLE STATE IN VAPOR

From (2.15), (2.22), (6.15), and (6.18) with allowance for (5.2), (6.2), and (6.13), we obtain for both cases of the free molecular and the diffusion growth of supercritical droplets the following relation:

$$\frac{\Delta t}{t_s} \approx \frac{1}{2} \left(\frac{2}{3}\right)^{1/m} \frac{\alpha t_\infty}{m \tau} \frac{a^{1/m} p_0^{1/3}}{v_0^{(4m+1)/3m}}. \quad (7.1)$$

Solving this expression with respect to  $t_\infty$  and using

definition (6.4), we have the relation

$$t_{\infty} \approx 2 \left( \frac{3}{2} \right)^{1/m} \frac{\kappa m \tau v_0^{(4m+1)/3m}}{\alpha a^{1/m} p_0^{1/3}}, \quad (7.2)$$

which parameterizes the characteristic time  $t_{\infty}$  of the creation of the metastable state in vapor and expresses it via parameter  $\kappa$ . Directly from (6.4) and (6.13), we obtain

$$\Delta t \approx \frac{3 \kappa \tau v_0^{8/9}}{2^{3/2} q \alpha a^{2/3} p_0^{2/9}}. \quad (7.3)$$

We perform a further treatment first for the case of the free molecular growth of supercritical droplets. Substituting (7.2) into (6.15) and (6.16), we find

$$c \approx 2^{1/3} 3 \frac{q p_0^{2/9}}{\kappa a^{1/3} v_0^{5/9}} \quad (7.4)$$

and

$$h \approx \frac{2 \eta(-\infty) \kappa^3 a^{2/3} v_0^{22/9}}{3 q^2 n_{\infty} p_0^{7/9}}. \quad (7.5)$$

From (2.10) and (2.13) with allowance for (7.4) and (7.5), we have

$$N \approx \frac{3 q^2 n_{\infty} p_0^{7/9}}{2 \kappa^3 a^{2/3} v_0^{22/9}} \quad (h \gg 1) \quad (7.6)$$

and

$$\Delta \rho \approx \frac{1 \kappa a^{1/3} v_0^{5/9}}{2^{1/2} q p_0^{2/9}}. \quad (7.7)$$

Solving (7.5) with respect to  $\eta(-\infty)$ , we obtain

$$\eta(-\infty) \approx \frac{3 q^2 n_{\infty} h p_0^{7/9}}{2 \kappa^3 a^{2/3} v_0^{22/9}}. \quad (7.8)$$

With the aid of (2.11) and (7.8) we find

$$N \approx \frac{3 q^2 n_{\infty} h p_0^{7/9}}{2 \kappa^3 a^{2/3} v_0^{22/9}} \quad (h \ll 1). \quad (7.9)$$

We assume that parameters  $\kappa$  and  $h$ , which, according to (6.7), determine the value of  $q$ , are the independent free parameters of the kinetic theory of nucleation. In this case, formulas (7.2) and (7.8) express the time  $t_{\infty}$  and the concentration  $\eta(-\infty)$  via parameters  $\kappa$  and  $h$ . However, formulas (7.3), (7.6), (7.7), and (7.9) also specify the kinetic characteristics of nucleation  $\Delta t$ ,  $N$ , and  $\Delta \rho$  via the same parameters. Parameters  $\kappa$  and  $h$  are more convenient for constructing the kinetic theory of nucleation than  $t_{\infty}$  and  $\eta(-\infty)$  and are as good as the initial parameters  $t_{\infty}$  and  $\eta(-\infty)$  of a theory for describing the kinetic scenario of nucleation.

Let us now consider the case of the diffusion growth of supercritical droplets. Substituting (7.2) into (6.18) and (6.19), we obtain

$$c \approx 2^{1/3} 3 \frac{q \alpha \tau_D p_0^{2/9}}{\kappa \tau a^{1/3} v_0^{5/9}} \quad (7.10)$$

and

$$h \approx \frac{(3\pi)^{1/2} \eta(-\infty) (\kappa \tau)^{3/2} a^{1/6} v_0^{29/18}}{2^{5/4} q^{1/2} n_{\infty} (\alpha \tau_D)} \frac{p_0^{4/9}}{p_0}. \quad (7.11)$$

From (2.10) and (2.13) with allowance for (7.10) and (7.11), we have

$$N \approx \frac{2^{5/4}}{(3\pi)^{1/2}} q^{1/2} n_{\infty} \left( \frac{\alpha \tau_D}{\kappa \tau} \right)^{3/2} \frac{p_0^{4/9}}{a^{1/6} v_0^{29/18}} \quad (h \gg 1) \quad (7.12)$$

and

$$\Delta \rho \approx \frac{1 \kappa \tau a^{1/3} v_0^{5/9}}{2^{1/2} q \alpha \tau_D p_0^{2/9}}. \quad (7.13)$$

Solving (7.11) with respect to  $\eta(-\infty)$ , we obtain

$$\eta(-\infty) \approx \frac{2^{5/4}}{(3\pi)^{1/2}} q^{1/2} n_{\infty} h \left( \frac{\alpha \tau_D}{\kappa \tau} \right)^{3/2} \frac{p_0^{4/9}}{a^{1/6} v_0^{29/18}}. \quad (7.14)$$

With the help of (2.11) and (7.14), we find

$$N \approx \frac{2^{5/4}}{(3\pi)^{1/2}} q^{1/2} n_{\infty} h \left( \frac{\alpha \tau_D}{\kappa \tau} \right)^{3/2} \frac{p_0^{4/9}}{a^{1/6} v_0^{29/18}} \quad (h \ll 1). \quad (7.15)$$

Formulas (7.2) and (7.14) express the time  $t_{\infty}$  and the concentration  $\eta(-\infty)$  via parameters  $\kappa$  and  $h$ . However, formulas (7.3), (7.12), (7.13), and (7.15) express the kinetic characteristics of nucleation  $\Delta t$ ,  $N$ , and  $\Delta \rho$  via the same parameters. It is apparent that in the case of the diffusion growth of supercritical droplets, the parameters  $\kappa$  and  $h$  are also more convenient for constructing the kinetic theory of nucleation than parameters  $t_{\infty}$  and  $\eta(-\infty)$ .

With the aid of (6.4), the main condition (4.1) of the applicability of the kinetic theory, which in particular is also responsible for fulfilling conditions (4.2) and (4.8), is specified as

$$\kappa \gg 1. \quad (7.16)$$

Using inequality (7.16), we can verify the fulfillment of condition (4.1) and, using parameter  $h$ , we can estimate the fulfillment of inequalities  $h \gg 1$  or  $h \ll 1$  employed in the theory; these two facts are indicative of yet another important advantage of parameters  $\kappa$  and  $h$  compared with parameters  $t_{\infty}$  and  $\eta(-\infty)$ .

### 8. PROCEDURE OF THE CALCULATION OF THE KINETIC CHARACTERISTICS OF NUCLEATION AT THE FREE MOLECULAR GROWTH OF SUPERCRITICAL DROPLETS

In the method proposed, we assume that parameters  $\kappa$  and  $h$  are free but are limited by condition (7.16) and inequalities  $h \gg 1$  or  $h \ll 1$ . Moreover, this method fully covers the domain of the applicability of a theory at once, thus indicating its efficiency.

In the case of the free molecular growth of supercritical droplets considered in this section, there is yet another limitation imposed by condition (4.4). Let us disclose this limitation. From (4.5) and (7.7) we have

$$\frac{\Delta\rho}{\rho_\lambda} \sim \frac{1}{2^{1/2}q} \alpha(n_\infty + n_g) v_\alpha \frac{\kappa \alpha^{1/3} v_0^{5/9}}{p_0^{2/9}} \quad (8.1)$$

(in our estimates, we do not approximate numerical multipliers in order to monitor them more easily). Using (6.10) and (8.1) in (4.4), we obtain

$$\kappa \ll \frac{2^{1/2}}{\alpha(n_\infty + n_g) v_\alpha a^{1/3} v_0^{5/9}} \frac{p_0^{2/9}}{p_0^{2/9}} \quad (8.2)$$

For the compatibility of (7.16) and (8.2) the inequality

$$\frac{2^{1/2}}{\alpha(n_\infty + n_g) v_\alpha a^{1/3} v_0^{5/9}} \frac{p_0^{2/9}}{p_0^{2/9}} \gg 1 \quad (8.3)$$

is required. If this inequality is fulfilled, formulas (7.2), (7.3), and (7.6)–(7.9) will be valid within the ranges of the variation of parameters  $\kappa$  and  $h$  admitted by constraints (7.16), (8.2) and  $h \gg 1$  or  $h \ll 1$ . Calculations were based precisely on these formulas.

Let us assign the following values of external parameters of a theory:

$$\begin{aligned} a &= 10, \quad \alpha = 10^{-1}, \quad n_\infty = 10^{17} \text{ cm}^{-3}, \\ n_g &= 10^{19} \text{ cm}^{-3}, \quad v_\alpha = 10^{-23} \text{ cm}^3, \\ \tau &= 5.4 \times 10^{-7} \text{ s}, \quad v_0^{1/3} = 90, \quad p_0 = 1.7 \times 10^3, \\ m &= 1. \end{aligned} \quad (8.4)$$

Data given in (8.4) are quite realistic for typical condensing liquid (water) and its saturated vapor at common temperatures as well as for the passive gas at pressures close to atmospheric. According to (5.3), the value of  $a$  corresponds to  $\gamma = 77 \text{ dyne cm}^{-1}$ . The values of  $v_0^{1/3}$  and  $p_0$  satisfy inequalities (5.4) and (5.20). According to (5.1) and (5.18), the value  $R_n \approx 10^{-6} \text{ cm}$  corresponds to  $v_0^{1/3}$ . At the exponential approximation of the work of nucleus wetting, according to (5.19), the value of  $p_0$  corresponds to  $l \approx 10^{-7} \text{ cm}$ , which is quite a

realistic quantity [11]. The value of  $R_n \approx 10^{-6} \text{ cm}$  is so large that the condition of nucleus macroscopicity (5.17) is already fulfilled; however, it is so small that the value of  $\zeta_{\text{th}} \approx 7.4 \times 10^{-2}$  of the threshold vapor supersaturation can still be reliably controlled during the experiment. According to (1.4), the value of  $m$  corresponds to a relatively representative (linear in time) growth of the ideal supersaturation  $\Phi$ .

Let us perform the calculations using the proposed procedure and the values of parameters from (8.4). In this case, inequality (8.3) is fulfilled. From (7.16) and (8.2) we have inequalities

$$1 \ll \kappa \ll 2 \times 10^2, \quad (8.5)$$

which determine the admissible region of the variation of parameter  $\kappa$ .

According to (7.2), (6.14), and (7.3), we obtain

$$t_\infty \approx 7.7 \times 10^2 \kappa \text{ s}, \quad (8.6)$$

$$t_* \approx 5.8 \times 10 \kappa \text{ s}, \quad (8.7)$$

$$\Delta t \approx 3.8 \times 10^{-2} q^{-1} \kappa \text{ s}. \quad (8.8)$$

The units of measurement of dimensional quantities are indicated. The dependence of parameter  $q$  on  $\kappa$  and  $h$  is given by the equality (6.7). Time moments  $t_{\text{on}}$  and  $t_{\text{off}}$  can be readily obtained with the help of (2.16).

Finally, from (7.6)–(7.9), we have

$$N \approx \begin{cases} 4.9 \times 10^4 q^2 \kappa^{-3} \text{ cm}^{-3} & (h \gg 1) \\ 4.9 \times 10^4 q^2 h \kappa^{-3} \text{ cm}^{-3} & (h \ll 1), \end{cases} \quad (8.9)$$

$$\Delta\rho \approx 5.3 \times 10^2 q^{-1} \kappa, \quad (8.10)$$

$$\eta(-\infty) \approx 4.9 \times 10^4 q^2 h \kappa^{-3} \text{ cm}^{-3}. \quad (8.11)$$

Let us find out to what extent conditions (4.2) and (6.10) are fulfilled. In the situation where  $h \gg 1$ , it is seen from (6.3) and (6.7) that inequality (4.2) is fulfilled over the entire range (8.5); the approximate equality (6.10) is also fulfilled, provided that inequality  $h \gg 1$  does not become too strong. The impossibility of the strong inequality  $h \gg 1$  follows from the fact that, according to (8.11), concentration  $\eta(-\infty)$  increases simultaneously with parameter  $h$ ; however, in practice, the concentration  $\eta(-\infty)$  usually does not exceed the values of the order of  $10^5 \text{ cm}^{-3}$ .

In the situation where  $h \ll 1$ , it is seen from (6.3) and (6.7) that (4.2) and (6.10) are fulfilled only for the limiting values and only in close proximity to the upper boundary of the region (8.5).

### 9. PROCEDURE FOR CALCULATING THE KINETIC CHARACTERISTICS OF NUCLEATION AT THE DIFFUSION GROWTH OF SUPERCRITICAL DROPLETS

Using the same procedure as in Section 8, we should take into account the additional constraint imposed by condition (4.6). Let us disclose this constraint. From (4.7) and (7.13), we obtain

$$\frac{\Delta\rho}{\rho_\lambda} \sim \frac{1}{2^{1/2}q} \frac{\kappa\tau a^{1/3}v_0^{5/9}}{\tau_D p_0^{2/9}} \alpha(n_\infty + n_g)^2 v_\alpha^2. \quad (9.1)$$

Accounting for (2.6), (2.19), and (4.3) and the gas-kinetic estimate  $D \sim \lambda v_T/3$ , we find

$$(\tau/\tau_D)(n_\infty + n_g)v_\alpha \sim 1. \quad (9.2)$$

With the aid of (9.2) let us represent (9.1) as

$$\frac{\Delta\rho}{\rho_\lambda} \sim \frac{1}{2^{1/2}q} \alpha(n_\infty + n_g)v_\alpha \frac{\kappa a^{1/3}v_0^{5/9}}{p_0^{2/9}}, \quad (9.3)$$

which visually coincides with (8.1), although  $\Delta\rho$  and  $\rho_\lambda$  have already been determined in a different manner, than in (8.1). Using (6.10) and (9.3) in (4.6), we obtain

$$\kappa \gg \frac{2^{1/2}}{\alpha(n_\infty + n_g)v_\alpha a^{1/3}v_0^{5/9}} p_0^{2/9}. \quad (9.4)$$

Within the variation ranges of parameters  $\kappa$  and  $h$  admissible by the strongest of inequalities (7.16), (9.4), and constraints  $h \gg 1$  or  $h \ll 1$ , formulas (7.2), (7.3), and (7.12)–(7.15) will be valid. These formulas were used as the basis for the calculations.

Let us set the following values of the external parameters of a theory:

$$\begin{aligned} a &= 10, \quad \alpha = 1, \quad n_\infty = 10^{17} \text{ cm}^{-3}, \quad n_g = 10^{19} \text{ cm}^{-3}, \\ v_\alpha &= 10^{-23} \text{ cm}^3, \quad \tau = 5.4 \times 10^{-7} \text{ s}, \\ D &= 1 \text{ cm}^2 \text{ s}^{-1}, \quad \tau_D = 8.9 \times 10^{-11} \text{ s}, \\ v_0^{1/3} &= 90, \quad p_0 = 1.7 \times 10^3, \quad m = 1. \end{aligned} \quad (9.5)$$

The difference between the data in (9.5) and (8.4) is only in using  $\alpha = 1$  instead of  $\alpha = 10^{-1}$ . However, this distinction is responsible for the passage from the free molecular to the diffusion growth of supercritical droplets. The fact that coefficient  $\alpha$  can be close to unity is admitted by the results of a number of experiments [12] and studies into molecular dynamics [13, 14]. For completeness, time  $\tau_D$  is included into the initial parameters, although it is the function of  $n_\infty$ ,  $v_\alpha$ , and  $D$  [see (2.19)]. The value of  $\tau_D$  was determined with the aid of (2.19).

Let us perform calculations that use the values of parameters from (9.5). In this case, inequality (9.4)

seems to be the strongest of (7.16) and (9.4). In view of the last inequality

$$\kappa \gg 2 \times 10, \quad (9.6)$$

that determines the admissible region of the variations in parameter  $\kappa$ .

According to (7.2), (6.14), and (7.3), we obtain

$$t_\infty \approx 7.7 \times 10 \kappa \text{ s}, \quad (9.7)$$

$$t_* \approx 5.8 \kappa \text{ s}, \quad (9.8)$$

and

$$\Delta t \approx 3.8 \times 10^{-3} q^{-1} \kappa \text{ s}. \quad (9.9)$$

Finally, from (7.12)–(7.15), we have

$$N \approx \begin{cases} 1.1 \times 10^3 q^{1/2} \kappa^{-3/2} \text{ cm}^{-3} & (h \gg 1) \\ 1.1 \times 10^3 q^{1/2} h \kappa^{-3/2} \text{ cm}^{-3} & (h \ll 1), \end{cases} \quad (9.10)$$

$$\Delta\rho \approx 3.2 \times 10^6 q^{-1} \kappa, \quad (9.11)$$

and

$$\eta(-\infty) \approx 1.1 \times 10^3 q^{1/2} h \kappa^{-3/2} \text{ cm}^{-3}. \quad (9.12)$$

Let us find out to what extent conditions (4.2) and (6.10) are fulfilled. At  $h \gg 1$ , it can be easily established from (6.3) and (6.7) that inequality (4.2) and approximate equality (6.10) are fulfilled within the whole region (9.6), provided that the inequalities (9.6) and  $h \gg 1$  are not too strong. If inequality (9.6) had been too strong, i.e., if parameter  $\kappa$  had been too large, time  $t_*$  would be very large, which is of not practical interest to us. However, if inequality  $h \gg 1$  had been too strong, concentration  $\eta(-\infty)$  would be rather high (at the already substantiated not excessively large parameter  $\kappa$ ), which (as was already mentioned) in practice does not usually exceed values of about  $10^5 \text{ cm}^{-3}$ .

However, at  $h \ll 1$ , it follows from (6.3) and (6.7) that inequality (4.2) and the approximate equality (6.10) are fulfilled over the entire range (9.6) except for the case of overly large values of parameter  $\kappa$  [corresponding, according to (9.8), to very large values of time  $t_*$ ].

### 10. ACCOUNT FOR THE POLYDISPERSITY OF INSOLUBLE WETTABLE NUCLEI

It was assumed in the preceding discussion that condensation nuclei are identical; i.e., they are monodisperse. Let us demonstrate how the kinetic theory of nucleation reported above can be generalized for the case of polydispersity of insoluble wettable condensation nuclei.

The polydispersity of nuclei involves the account for the distribution of initial concentration of nuclei over their radii  $R_n$ . Let us make the relatively realistic assumption that the density of this distribution is practically equal to zero at  $R_n > \bar{R}_n$  and markedly differs from zero at  $R_n < \bar{R}_n$ , where  $\bar{R}_n$  is the radius of the larg-

est of the nuclei encountered in practice. How the density of the distribution of initial nucleus concentrations depends on  $R_n$  at  $R_n < \bar{R}_n$  is insignificant for further discussion. It is only important that the density only slightly depend on  $R_n$  compared with the "jump" that occurs during the passage from  $R_n < \bar{R}_n$  to  $R_n > \bar{R}_n$ .

Having in mind the estimation character of forthcoming discussion, we will use approximate equality (6.10) and relation (5.14), which is true at the exponential approximation of the work of nucleus wetting, without mentioning this fact especially. From (5.6) and (5.12), we obtain an estimate for the width  $\Delta\zeta$  of the prethreshold region of vapor metastability at the  $\zeta$ -axis:

$$\Delta\zeta \sim a^{-2/3} v_0^{-4/9} (v_0/k)^{1/9} \zeta_{th}. \quad (10.1)$$

As is seen from (5.6) and (5.22), as the radius  $R_n$  varies, this region moves along the  $\zeta$ -axis approximately at a rate  $\partial\zeta_{th}/\partial R_n$  estimated, according to (5.1), (5.2), and (5.18), by the relation

$$\partial\zeta_{th}/\partial R_n \sim -\zeta_{th}/R_n. \quad (10.2)$$

As the metastable state in vapor is developed, its supersaturation  $\zeta$  evidently fits the range which is the prethreshold region compared both with nuclei for which  $R_n \approx \bar{R}_n$  and with all the nuclei within the range  $\bar{R}_n - \Delta R_n < R_n < \bar{R}_n$  whose width  $\Delta R_n$  is estimated as

$$\Delta\zeta|_{R_n=\bar{R}_n} \sim |\partial\zeta_{th}/\partial R_n|_{R_n=\bar{R}_n} \Delta R_n. \quad (10.3)$$

All these nuclei are the possible centers of the nucleation of supercritical droplets.

From (10.1)–(10.3), we have

$$\Delta R_n/\bar{R}_n \sim a^{-2/3} v_0^{-4/9} (v_0/k)^{1/9}, \quad (10.4)$$

where, for simplicity, it is not indicated that  $v_0$  refers to  $\bar{R}_n$ . It is the relation (10.4) that estimates the width  $\Delta R_n$  of the range where the nucleation of supercritical droplets actually occurs. According to (10.4), the inequality

$$\Delta R_n/\bar{R}_n \ll 1 \quad (10.5)$$

is valid for macroscopic nuclei.

Because the total number of supercritical droplets formed during nucleation serves as the most important kinetic characteristic of this process, the condition

$$\left| \frac{1}{N} \frac{\partial N}{\partial R_n} \right|_{R_n=\bar{R}_n} \Delta R_n \ll 1 \quad (10.6)$$

should be fulfilled in order to use the kinetic theory of nucleation discussed above. This condition guarantees the smallness of the relative variation in the number of droplets  $N$  with the variation in  $R_n$  over the range  $\bar{R}_n - \Delta R_n < R_n < \bar{R}_n$ .

According to (2.9), the dependence of  $N$  on  $R_n$  (at the preset concentration  $\eta(-\infty)$ ) is strongest at  $h \gg 1$ . In this case, this dependence turns out to be the strongest

of all dependences of the kinetic characteristics of nucleation on  $R_n$ , and, hence, it is the crucial one in the discussion of the deviation of condensation nuclei from monodispersity within the range  $\bar{R}_n - \Delta R_n < R_n < \bar{R}_n$ .

In the case of  $h \gg 1$ , from (2.10) and (6.16) with allowance for (5.1) and (5.18) at the free molecular growth of supercritical droplets we have

$$\frac{\partial N}{\partial R_n} \sim \frac{4m+3}{m} \frac{N}{R_n}. \quad (10.7)$$

Using (10.4) and (10.7), we reduce condition (10.6) to the inequality

$$\frac{4m+3}{m} a^{-2/3} v_0^{-4/9} (v_0/k)^{1/9} \ll 1 \quad (10.8)$$

(it is not indicated whether  $v_0$  refers to the value of  $\bar{R}_n$ ). The macroscopicity of nuclei secures the fulfillment of inequality (10.8) (provided that the  $m$  value is not too small).

At the diffusion growth of supercritical droplets in the case of  $h \gg 1$ , from (2.10) and (6.19) with allowance for (5.1) and (5.18), we have

$$\frac{\partial N}{\partial R_n} \sim \frac{2m+3}{2m} \frac{N}{R_n}. \quad (10.9)$$

Using (10.4) and (10.9), we reduce condition (10.6) to the inequality

$$\frac{2m+3}{2m} a^{-2/3} v_0^{-4/9} (v_0/k)^{1/9} \ll 1. \quad (10.10)$$

The macroscopicity of condensation nuclei secures the fulfillment of inequality (10.10), provided that  $m$  value is not too small.

Hence, it is seen that to account for the polydispersity of insoluble wettable condensation nuclei, it is sufficient to perceive the  $R_n$  value as  $\bar{R}_n$ , and  $\eta(-\infty)$  as the total initial concentration of condensation nuclei whose radii  $R_n$  fit the range  $\bar{R}_n - \Delta R_n < R_n < \bar{R}_n$ , which is responsible for the nucleation of supercritical droplets. The width of this range  $\Delta R_n$  is given by relation (10.4).

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