

# Kinetics of the Establishment of Quasi-Steady-State Regime of Overcoming Activation Barrier of Nucleation on the Macroscopic Wettable Nuclei

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**Abstract**—The solution of the kinetic equation of nucleation on macroscopic wettable condensation nuclei was constructed for the initial (incubation) stage. The solution thus constructed determines the times of relaxation to quasi-steady-state distribution of droplets generating on droplet nuclei in the vicinity of maximum of the work of droplet heterogeneous formation as well as the relaxation to quasi-equilibrium droplet distribution throughout the entire region located to the left of this vicinity at the droplet size axis. The dependence of relaxation times on the height of activation barrier of nucleation, size of nuclei, their nature, and characteristics of matter comprising condensate was elucidated. It was shown when the non-steady-state rate of nucleation becomes actually equal to the quasi-steady-state rate of nucleation.

## INTRODUCTION

The steady-state rate of nucleation is the regular frequency at which significantly overcritical droplets appear after the completion of the incubation period, the droplets further growing irreversibly; this rate is established in the course of overcoming the activation barrier of nucleation by the droplets. The height of this barrier is the activation energy of nucleation depends on the vapor supersaturation and, at the heterogeneous nucleation of a droplet on wettable condensation nucleus, is set by the difference in the height of potential barrier and the depth of potential well of the work of droplet formation on a nucleus. If, in the process of nucleation, the vapor supersaturation varies rather slowly as compared with the establishment of the steady-state regime of overcoming the activation barrier of nucleation at a current vapor supersaturation, the nucleation rate can be approximately considered as the steady-state value characterizing the quasi-steady-state regime of barrier overcoming. In order to answer more definitely when this approximation is valid, we should find the characteristic times of the incubation stage of nucleation, in particular, the time of the establishment of steady-state droplet distribution in the vicinity of the maximum of the work of droplet formation with allowance for the presence of preceding minimum of the formation work. These times will be determined in this work and it will be shown when the non-steady-state rate of nucleation becomes practically equal to the steady-state rate of nucleation.

In a final section of this work, the characteristic times thus determined will be compared with the earlier obtained times of the establishment of quasi-steady-state regime of overcoming the activation barrier in the

kinetics of homogeneous and heterogeneous nucleation [1–8], as well as in the kinetics of the initial stages of micellization [9]. Speaking of macroscopic wettable nuclei, we will have in mind the aerosol particles composed of substance both soluble and insoluble in a liquid condensing from vapor.

## 1. BASIC THERMODYNAMIC RELATIONS

We denote the chemical potential of condensate in the droplet by  $b_v$  considering it as a function of the number  $v$  of condensate molecules, and the chemical potential of vapor, by  $b$ . Chemical potentials  $b_v$  and  $b$  are expressed in thermal energy units  $kT$  (where  $k$  is Boltzmann's constant and  $T$  is the temperature of vapor and droplet) and measured from the level corresponding to the equilibrium between the vapor and the condensed liquid at a flat contact surface. The work of droplet heterogeneous formation in vapor on the aerosol particle expressed in energy units  $kT$  is denoted by  $F_v$ .

For work  $F_v$  we have general thermodynamic relation

$$\partial F_v / \partial v = b_v - b. \quad (1.1)$$

The dependence of work  $F_v$  of droplet heterogeneous formation on the number  $v$  of condensate molecules in the droplet is qualitatively shown in Fig. 1. The values of  $v$  corresponding to the equilibrium and critical droplets, that is to the minimum and maximum of the work  $F_v$ , we denote by  $v_e$  and  $v_c$ , respectively. The values of  $v_e$  and  $v_c$  are determined from the equality of the right-hand side of expression (1.1) to zero. The value of  $v$  corresponding to the threshold value of the chemical potential of vapor  $b_{th}$  (i.e., to the largest maxima of the

condensate chemical potential  $b_v$ , provided that there are several maxima) is denoted by  $v_{th}$ ; this value is found from the solution of equation

$$\partial b_v / \partial v|_{th} = 0. \quad (1.2)$$

In the following, subscripts  $th$ ,  $e$ , and  $c$  at the values will indicate that these values are determined at  $v = v_{th}$ ,  $v = v_e$ , and  $v = v_c$ , respectively.

In the case of macroscopic condensation nuclei, the intense process of nucleation proceeds at the values of the chemical potential of vapor  $b$  located in the sub-threshold region, i.e., at

$$b = b_{th}(1 - \varepsilon) \quad (\varepsilon > 0, \varepsilon \ll 1) \quad (1.3)$$

(see [1, 10–12] for more detail). For the condensate chemical potential  $b_v$ , we can use the parabolic approximation in the vicinity of point  $v_{th}$

$$b_v = b_{th} - \frac{1}{2} \left| \frac{\partial^2 b_v}{\partial v^2} \right|_{th} (v - v_{th})^2. \quad (1.4)$$

At the parabolic approximation (1.4), the activation energy of nucleation  $\Delta F$  and the coordinates of  $v_e$ , and  $v_c$  depend on  $\varepsilon$  as [10–12]

$$\Delta F = \frac{4}{3} \varepsilon^{3/2} b_{th}^{3/2} [2 \left| \partial^2 b_v / \partial v^2 \right|_{th}]^{1/2}, \quad (1.5)$$

$$v_e = v_{th} - [2 \varepsilon b_{th} / \left| \partial^2 b_v / \partial v^2 \right|_{th}]^{1/2}, \quad (1.6)$$

$$v_c = v_{th} + [2 \varepsilon b_{th} / \left| \partial^2 b_v / \partial v^2 \right|_{th}]^{1/2}. \quad (1.7)$$

In the subthreshold region of vapor supersaturation, we can confine ourselves to the values of  $\Delta F \leq 15$ . At larger heights of activation barrier, the intensity of heterogeneous nucleation becomes negligible.

As supplementary characteristics, we determine the half-width  $\Delta v_e$  of the potential well in the vicinity of the minimum of the work of droplet formation and the half-width  $\Delta v_c$  of the potential barrier in the vicinity the maximum of this work at the  $v$ -axis. With allowance for Eqs. (1.1), (1.4), (1.6), and (1.7), we have [10–12]

$$\Delta v_e = \Delta v_c = (2 / \varepsilon b_{th} \left| \partial^2 b_v / \partial v^2 \right|_{th})^{1/4}. \quad (1.8)$$

It follows from Eqs. (1.5)–(1.8) that values  $\Delta F$ ,  $v_e$ ,  $v_c$ ,  $\Delta v_e$ , and  $\Delta v_c$  are interrelated by the simple expressions

$$(v_c - v_e)^2 / 3 \Delta v_e^2 = (v_c - v_e)^2 / 3 \Delta v_c^2 = \Delta F. \quad (1.9)$$

In the following, the vicinities of minimum and maximum of the work of droplet formation will be understood as the near-equilibrium  $|v - v_e| \leq \Delta v_e$  and near-critical  $|v - v_c| \leq \Delta v_c$  regions, respectively. We assume that these regions are not intersected at the  $v$ -axis; however, strong inequalities  $(v_c - v_e) / \Delta v_c \gg 1$  or  $(v_c - v_e) / \Delta v_e \gg 1$  sometimes cannot be fulfilled. It follows from Eq. (1.9) that  $\Delta F \approx 2$  can be considered as a lower limit of the values of activation energy. The vicinity of

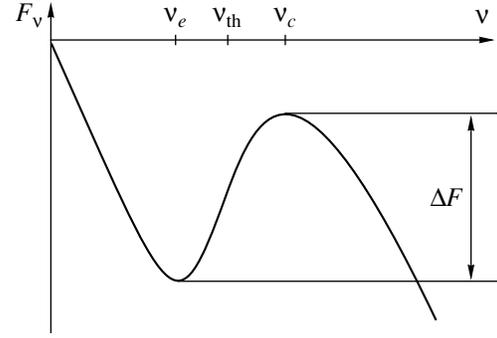


Fig. 1. The work of droplet formation versus the number of condensate molecules  $v$ .

intersection point  $v = v_{th}$  is taken as the entire  $v_e - \Delta v_e \leq v \leq v_c + \Delta v_c$  region.

## 2. THE KINETIC EQUATION OF NUCLEATION

We denote the number of droplets with size  $v$  per unit volume of the vapor–gas medium at time  $t$  by  $n_v(t)$ . Droplet size distribution  $n_v(t)$  increases in time according to the kinetic balance equation [5, 13, 14]

$$\partial n_v(t) / \partial t = J_{v-1} - J_v, \quad (2.1)$$

where the droplet flux  $J_v$  at the transition unit  $\{v \rightarrow v + 1\}$  is determined as

$$J_v = W_v^+ n_v - W_{v+1}^- n_{v+1}. \quad (2.2)$$

Here,  $W_v^+$  and  $W_{v+1}^-$  are the numbers of vapor molecules absorbed by the droplet of  $v$  molecules and, correspondingly, emitted by the droplet of  $v + 1$  molecules per unit time. In a free molecular regime of the absorption of vapor molecules, we have

$$W_v^+ = \alpha_c (v_T / 4) n_1 S_v, \quad (2.3)$$

where  $\alpha_c$  is the coefficient of vapor molecule condensation at the droplet surface,  $n_1$  is the concentration of vapor molecules,  $v_T$  is the average thermal velocity of vapor molecules, and  $S_v$  is the droplet surface area.

It is convenient to pass to a new distribution function, using relation

$$f(v, t) = (n_v - n_v^{(s)}) / n_v^{(0)}, \quad (2.4)$$

where  $n_v^{(0)}$  and  $n_v^{(s)}$  are the equilibrium and steady-state droplet size distributions, respectively. For the equilibrium and steady-state distributions, we have

$$J_v|_{n_v = n_v^{(0)}} = 0, \quad (2.5)$$

$$J_v|_{n_v = n_v^{(s)}} = J_s, \quad (2.6)$$

where  $J_s$  is  $v$ -independent steady-state nucleation velocity at given vapor supersaturation.

Substituting Eq. (2.4) into Eq. (2.1) with allowance for Eqs. (2.2), (2.5), and (2.6), assuming the sufficient flatness of  $f(v, t)$  as a function of  $v$ , and retaining only two first terms in expansions  $f(v, t) - f(v - 1, t)$  and  $f(v + 1, t) - f(v, t)$  in powers of  $v$  at  $v \gg 1$ , we rewrite Eq. (2.1) as

$$\begin{aligned} \partial f(v, t)/\partial t &= (W_v^+ - W_v^-) \partial f(v, t)/\partial v \\ &+ \frac{1}{2}(W_v^+ + W_v^-) \partial^2 f(v, t)/\partial v^2. \end{aligned} \quad (2.7)$$

If the inequality  $|\partial F_v/\partial v| \ll 1$  is additionally fulfilled, Eq. (2.7) can be, with the aid of equality  $W_{v+1}^- = W_v^+ \exp(F_{v+1} - F_v)$ , presented in the form

$$\begin{aligned} \partial f(v, t)/\partial t &= -(W_v^+ \partial F_v/\partial v - \partial W_v^+/\partial v) \\ &\times \partial f(v, t)/\partial v + W_v^+ \partial^2 f(v, t)/\partial v^2. \end{aligned} \quad (2.8)$$

At the macroscopicity of condensation nuclei, inequalities  $v \gg 1$  and  $|\partial F_v/\partial v| \ll 1$  are readily fulfilled in the vicinities of extrema of the formation work  $F_v$  at the droplet size axis. As follows from Eqs. (1.1) and (1.4), derivative  $\partial F_v/\partial v$  in the vicinity of extrema of  $F_v$  and in the region between the extrema is maximal in the inflection point  $v = v_{th}$ . With allowance for Eqs. (1.1) and (1.3), equality  $\partial F_v/\partial v|_{th} = b_{th}\epsilon$  is fulfilled in the inflection point; because strong inequalities  $b_{th} \ll 1$  and  $\epsilon \ll 1$  take place for macroscopic nuclei [1, 10–12], inequality  $\partial F_v/\partial v|_{th} \ll 1$  is valid. Thereby, we are convinced that inequality  $|\partial F_v/\partial v| \ll 1$  is fulfilled within the entire vicinity  $v_e - \Delta v_e \leq v \leq v_c + \Delta v_c$  of the inflection point  $v = v_{th}$ . Equation (2.8) will be solved in the next section.

Let us cite the explicit relations for  $n_v^{(0)}$ ,  $n_v^{(s)}$ , and  $J_s$ . They can be found, if one takes into account that Eq. (2.1) for distribution  $n_v(t)$  at  $v \gg 1$  and  $|\partial F_v/\partial v| \ll 1$  can be written in the form of the Fokker–Planck equation [15]

$$\partial n_v(t)/\partial t = -\partial J_v/\partial v, \quad (2.9)$$

where, with allowance for Eq. (2.2) and flatness of  $W_v^+$  followed from Eq. (2.3) and expression for  $W_v^-$ , we have

$$J_v = -W_v^+ \partial F_v/\partial v n_v - W_v^+ \partial n_v/\partial v. \quad (2.10)$$

Let us assume that  $n_v$ ,  $n_v^{(s)}$ , and  $n_v^{(0)}$  tend to zero and virtually coincide while moving to the left of the left boundary of the vicinity of the minimum of work  $F_v$  at the  $v$ -axis. We also take into account that  $n_v$  and  $n_v^{(s)}$  become much smaller than  $n_v^{(0)}$  when moving along the  $v$ -axis to the right of the right boundary of the vicinity of the maximum of work  $F_v$ . This implies that  $n_v^{(0)} f(v,$

$t) \rightarrow 0$  takes place on the left and  $f(v, t) \rightarrow 0$ , on the right of the vicinity of the inflection point of work  $F_v$ .

The aforementioned boundary conditions to  $n_v^{(s)}$  allow us to write explicit expressions for the steady-state distribution and nucleation velocity. From Eqs. (2.6) and (2.10), we find

$$\begin{aligned} n_v^{(s)} &= J_s \int_v^{(v_c + \Delta v_c)} dv' \exp(F_{v'} - F_v)/W_{v'}^+ \\ &(v_e - \Delta v_e \leq v \leq v_c + \Delta v_c), \end{aligned} \quad (2.11)$$

$$J_s = n_v^{(0)} \int_{(v_e - \Delta v_e)}^{(v_c + \Delta v_c)} dv' \exp(F_{v'} - F_v)/W_{v'}^+, \quad (2.12)$$

where the upper limit in Eq. (2.11) and both limits of integration in Eq. (2.12) are taken arbitrarily. As is seen, at  $\Delta F \geq 2$ , the main contribution to the integrals in Eqs. (2.11) and (2.12) is introduced by the near-critical region, and the steady-state distribution  $n_v^{(s)}$  virtually coincides with the equilibrium distribution  $n_v^{(0)}$  at  $v < v_e - \Delta v_e$ . Indeed, representing the equilibrium distribution  $n_v^{(0)}$  as [1]

$$n_v^{(0)} = (n_n/\pi^{1/2} \Delta v_e) \exp(F_e - F_v), \quad (2.13)$$

where  $n_n$  is the concentration of nuclei per unit volume, with a good accuracy we obtain from Eqs. (2.11) and (2.12), the well-known relations

$$\begin{aligned} n_v^{(s)} &= \begin{cases} n_v^{(0)} & \text{at } v \leq v_e - \Delta v_e \\ n_v^{(0)} \left[ 1 - \frac{1}{\pi^{1/2} \Delta v_e} \int_{v_e - \Delta v_e}^v dv' \frac{W_c^+}{W_{v'}^+} \exp(F_{v'} - F_c) \right] & \text{at } v_e - \Delta v_e < v < v_c + \Delta v_c \\ n_v^{(0)} & \text{at } v \geq v_c + \Delta v_c \end{cases} \end{aligned} \quad (2.14)$$

$$J_s = n_n \frac{W_c^+}{\pi \Delta v_e \Delta v_c} \exp(-\Delta F). \quad (2.15)$$

### 3. SOLUTION OF THE KINETIC EQUATION IN THE VICINITY OF THE INFLECTION POINT OF THE WORK OF NUCLEUS FORMATION

Assuming, on the basis of equality (2.3), that  $W_v^+$  is a sufficiently smooth function of  $v$  throughout the entire vicinity of the inflection point of the work of droplet formation (which is of interest to us), ignoring (at  $v \gg 1$ ) corrections of the order of  $1/v$  and  $(v_c - v_e)/v_{th}$ , with adequate accuracy we can write the kinetic equation (2.8) in the following form:

$$\begin{aligned} \frac{\partial f(v, t)}{\partial t} = & -W_{th}^+ \frac{\partial F_v}{\partial v} \frac{\partial f(v, t)}{\partial v} \\ & + W_{th}^+ \frac{\partial^2 f(v, t)}{\partial v^2} \end{aligned} \quad (3.1)$$

(that will be confirmed at the end of this section). Let us introduce new variables

$$x = \frac{v - v_{th}}{v_c - v_e}, \quad (3.2)$$

$$\tau = \frac{W_{th}^+}{(v_c - v_e)^2} t. \quad (3.3)$$

Evidently, value  $v = v_e$  corresponds to  $x = -1/2$  and  $v = v_c$ , to  $x = 1/2$ . Equation (3.1) in variables of Eqs. (3.2) and (3.3) and with allowance for Eqs. (1.1), (1.3)–(1.7) is written as

$$\frac{\partial f(x, \tau)}{\partial \tau} = \frac{\partial^2 f(x, \tau)}{\partial x^2} - \frac{3}{2} \Delta F (1 - 4x^2) \frac{\partial f(x, \tau)}{\partial x}. \quad (3.4)$$

We assume

$$f = \phi z \quad (3.5)$$

and choose the  $\phi$  function such that, after substituting Eq. (3.5) into Eq. (3.4), the coefficient at the first derivative with respect to  $z$  over  $x$  in the right-hand side of Eq. (3.4) vanishes. Then, we have

$$\phi = \exp\left[\frac{3\Delta F}{4}\left(x - \frac{4}{3}x^3\right)\right]. \quad (3.6)$$

In this case, Eq. (3.4) is reduced to the Schrödinger non-steady-state equation

$$\frac{\partial z}{\partial \tau} = \frac{\partial^2 z}{\partial x^2} - \left[6\Delta F x + \frac{9\Delta F^2}{16}(1 - 4x^2)^2\right] z \quad (3.7)$$

for the motion in potential

$$V(x) = 6\Delta F x + \frac{9\Delta F^2}{16}(1 - 4x^2)^2. \quad (3.8)$$

Taking into account relations (3.2), (1.1), (1.3)–(1.7), and (2.13), it is easy to see that

$$1/\phi \propto \sqrt{n_v^{(0)}}. \quad (3.9)$$

Then, from Eqs. (2.4), (3.5), and (3.9) it follows

$$z \propto (n_v - n_v^{(s)})/\sqrt{n_v^{(0)}}. \quad (3.10)$$

From Eqs. (3.2) and (3.10) with allowance for what have been said in the preceding section, we arrive at the following boundary conditions to Eq. (3.7)

$$\begin{aligned} z & \longrightarrow 0 \quad \text{at} \quad x \longrightarrow -\infty; \\ z & \longrightarrow 0 \quad \text{at} \quad x \longrightarrow \infty. \end{aligned} \quad (3.11)$$

Potential  $V$  is shown in Fig. 2 as a function of  $x$  at two values of activation energy  $\Delta F = 3$  (curve 1) and  $\Delta F = 10$  (curve 2). It is seen that the potential has two

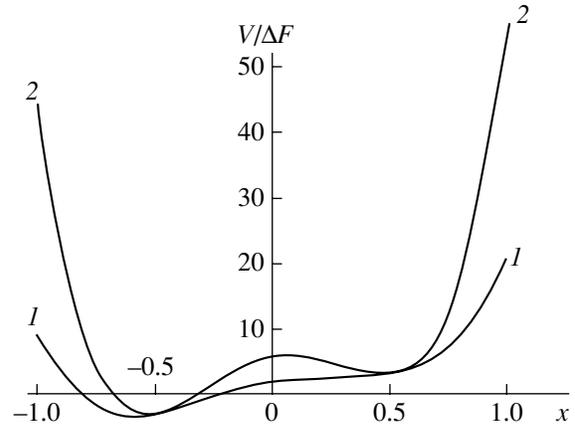


Fig. 2. Dependences of value  $V/\Delta F$  on  $x$  at  $\Delta F$ : (1) 3 and (2) 10.

minima at large  $\Delta F$  values. As the activation energy increases, the plot of the  $V(x)$  function becomes more symmetric with respect to the ordinate and the coordinates of minima approach the values of  $x = -1/2$  and  $x = 1/2$ . As  $\Delta F$  decreases, the right minimum (in the vicinity of the maximum of work  $F_v$  at the droplet size axis) vanishes. With a large margin at  $-1 < x < 1$ , the particle motion in potential  $V(x)$  is restricted that is confirmed by the boundary condition (3.11). The spectrum of eigenvalues of Hermitian [at boundary conditions (3.11)] operator in the right-hand side of Eq. (3.7) is real and discrete.

All what have been said above allow us to seek for the solution of Eq. (3.7) by the method of separation of variables in the following form

$$z = \sum_{i=0}^{\infty} C_i \phi_i(x) \exp(-E_i \tau). \quad (3.12)$$

Here,  $C_i$  are the constants determined by the initial condition;  $E_i$  are the eigenvalues numerated in ascending order; and  $\phi_i$  are eigenfunctions of equation

$$\hat{H} \phi_i = E_i \phi_i \quad i = 0, 1, 2, \dots, \quad (3.13)$$

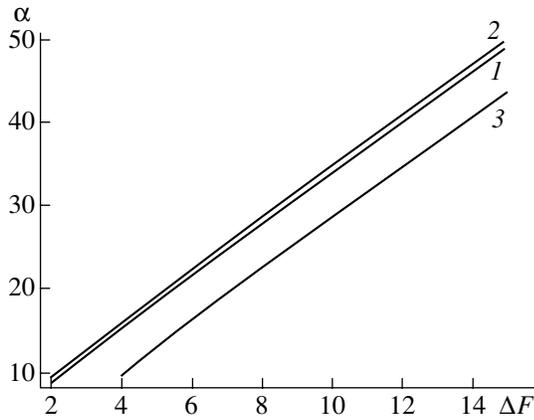
where operator  $\hat{H}$  is set by expression

$$\hat{H} = -\frac{d^2}{dx^2} + 6\Delta F x + \frac{9\Delta F^2}{16}(1 - 4x^2)^2. \quad (3.14)$$

To find lower eigenvalues of operator  $\hat{H}$  that determine the largest relaxation times, we use the Ritz method. We take trial functions  $\psi_0$  and  $\psi_1$  in the form

$$\psi_0(x, \alpha, x') = (\alpha/\pi)^{1/4} \exp\left(-\frac{1}{2}\alpha(x - x')^2\right), \quad (3.15)$$

$$\begin{aligned} \psi_1(x, \alpha, x_l) = & (4\alpha^3/\pi)^{1/4} (x - x_l) \\ & \times \exp\left(-\frac{1}{2}\alpha(x - x_l)^2\right), \end{aligned} \quad (3.16)$$



**Fig. 3.** Dependences of the optimal values of parameters (1)  $\alpha_0$ , (2)  $\alpha_l$ , and (3)  $\alpha_r$ , on  $\Delta F$ .

where the  $x'$  value can take the values of  $x_l$ , coordinate of the left (smaller), and  $x_r$ , coordinate of the right (larger) minima of potential  $V$  at the  $x$ -axis, parameter  $\alpha$  being adjustment parameter. Let us define mean values  $E_0(\alpha, x')$  and  $E_1(\alpha, x_l)$  by relations  $E_0(\alpha, x') \equiv \int_{-\infty}^{\infty} \psi_0 \hat{H} \psi_0 dx$  and  $E_1(\alpha, x_l) \equiv \int_{-\infty}^{\infty} \psi_1 \hat{H} \psi_1 dx$ . In view of Eqs. (3.14)–(3.16), we have

$$E_0(\alpha, x') = \frac{\alpha}{2} + 6\Delta F x' + \frac{9\Delta F^2}{16} \left[ (1 - 4x'^2)^2 + 4 \frac{12x'^2 - 1}{\alpha} + \frac{12}{\alpha^2} \right], \quad (3.17)$$

$$E_1(\alpha, x_l) = \frac{3\alpha}{2} + 6\Delta F x_l + \frac{9\Delta F^2}{16} \left[ (1 - 4x_l^2)^2 + 12 \frac{12x_l^2 - 1}{\alpha} + \frac{60}{\alpha^2} \right]. \quad (3.18)$$

We seek for the optimal values of parameter  $\alpha$  (denoted as  $\alpha_0$ ,  $\alpha_l$ , and  $\alpha_r$ ) from the condition imposed on extrema for  $E_0(\alpha, x_l)$ ,  $E_0(\alpha, x_r)$ , and  $E_1(\alpha, x_l)$ , respectively. In this case, minimal values of  $E_0(\alpha, x_l)$ ,  $E_0(\alpha, x_r)$ , and  $E_1(\alpha, x_l)$  determine actual eigenvalues  $E_0$ ,  $E_1$ , and  $E_2$  of operator (3.14).

For the further discussion, we need to know coordinates  $x_l$  and  $x_r$ . From equations for extrema of potential  $V$ , we find  $x_l$  and  $x_r$  in the form of asymptotic expansions in powers of  $1/\Delta F$

$$x_l = -\frac{1}{2} - \frac{1}{3\Delta F} + \frac{1}{3\Delta F^2} + O\left(\frac{1}{\Delta F^3}\right), \quad (3.19)$$

$$x_r = \frac{1}{2} - \frac{1}{3\Delta F} - \frac{1}{3\Delta F^2} + O\left(\frac{1}{\Delta F^3}\right). \quad (3.20)$$

Substituting expressions (3.19) and (3.20) into (3.17) and (3.18), from condition to extrema for  $E_0(\alpha, x_l)$ ,  $E_0(\alpha, x_r)$ , and  $E_1(\alpha, x_l)$ , we obtain

$$\alpha_0 = 3\Delta F + \frac{9}{2} + O\left(\frac{1}{\Delta F}\right), \quad (3.21)$$

$$\alpha_r = 3\Delta F - \frac{3}{2} + O\left(\frac{1}{\Delta F}\right), \quad (3.22)$$

$$\alpha_l = 3\Delta F + \frac{11}{2} + O\left(\frac{1}{\Delta F}\right), \quad (3.23)$$

respectively.

The plots of the dependences of optimal values of parameters  $\alpha_0$ ,  $\alpha_l$ , and  $\alpha_r$  on  $\Delta F$  with exact solution of equations with respect to extrema  $E_0(\alpha, x_l)$ ,  $E_0(\alpha, x_r)$ , and  $E_1(\alpha, x_l)$  are shown in Fig. 3. As is seen, the values of  $\alpha_0$ ,  $\alpha_l$ , and  $\alpha_r$  increase almost linearly with  $\Delta F$ ; i.e., asymptotics (3.21)–(3.23) are good approximations for these values.

Substituting expressions (3.19)–(3.23) into (3.17) and (3.18), we find the asymptotic representations for the desired eigenvalues

$$E_0 \equiv E_0(\alpha_0, x_l) = \frac{11}{4} - \frac{113}{24\Delta F} + O\left(\frac{1}{\Delta F^2}\right), \quad (3.24)$$

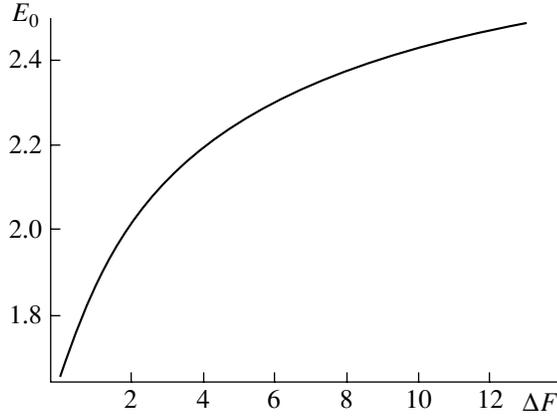
$$E_1 \equiv E_0(\alpha_r, x_r) = 6\Delta F - \frac{13}{4} + O\left(\frac{1}{\Delta F}\right), \quad (3.25)$$

$$E_2 \equiv E_1(\alpha_l, x_l) = 6\Delta F + \frac{47}{4} + O\left(\frac{1}{\Delta F}\right). \quad (3.26)$$

Eigenfunctions  $\phi_i$  corresponding to these eigenvalues can be represented, with allowance for Eqs. (3.15) and (3.16), as  $\phi_0 = \psi_0(x, \alpha_0, x_l)$ ,  $\phi_1 = \psi_0(x, \alpha_r, x_r)$ , and  $\phi_2 = \psi_1(x, \alpha_l, x_l)$ . Figures 4 and 5 show the plots of dependences of  $E_0$ ,  $E_1$ , and  $E_2$  on  $\Delta F$ , using exact relations for  $x_l$ ,  $x_r$ ,  $\alpha_0$ ,  $\alpha_l$ , and  $\alpha_r$  (without requirement for the smallness of  $1/\Delta F$ ). In view of evident linearity of dependences for  $E_1$  and  $E_2$ , we conclude that asymptotics (3.25) and (3.26) result in good approximation of these values.

It is reasonable to question the effect of approximations made when passing from Eq. (2.8) to Eq. (3.1) on the found value of  $E_0$  [as the smallest eigenvalue of operator (3.14)]. If we did not do this passage, we could demonstrate that relation (3.24) would be transformed into relation  $E_0 = \frac{11}{4} - \frac{11(v_c - v_e)}{12 v_{th}} - \frac{113}{24\Delta F} +$

$\frac{157}{72\Delta F} \frac{(v_c - v_e)}{v_{th}}$ . Evidently, while fulfilling strong inequality  $(v_c - v_e)/v_{th} \ll 1$ , the effect of approximations made during passage from Eq. (2.8) to Eq. (3.1) is insignificant even for the smallest eigenvalue of  $E_0$ .


 Fig. 4. Dependence of eigenvalue  $E_0$  on  $\Delta F$ .

Note now that eigenvalue  $E_1$  exists actually only at  $\Delta F > 4$  when the right-hand minimum and maximum of potential  $V(x)$  set by relation (3.8) are sufficiently far apart at the  $x$ -axis. At  $\Delta F < 4$ , the right-hand minimum and maximum of potential  $V(x)$  first converge to an inflection point and then vanish; correspondingly, eigenvalue  $E_1$  also vanishes. Thus, at  $2 \leq \Delta F < 4$ , the main relaxation contribution to Eq. (3.12) is made only by the terms in Eq. (3.12) with eigenfunctions  $\varphi_0$  and  $\varphi_2$  corresponding to eigenvalues  $E_0$  and  $E_2$ .

#### 4. CHARACTERISTIC TIMES OF HETEROGENEOUS NUCLEATION

Taking into account relations (2.4), (3.3), (3.12), (3.5), and (3.24)–(3.26), we arrive at the following expressions for characteristic times  $\Delta t_0 > \Delta t_1 > \Delta t_2$  of the heterogeneous nucleation at the incubation stage:

$$\Delta t_0 = \frac{(v_c - v_e)^2}{W_{\text{th}}^+} \frac{1}{E_0} = \frac{4(v_c - v_e)^2}{11 W_{\text{th}}^+ (1 - 113/66 \Delta F)}, \quad (4.1)$$

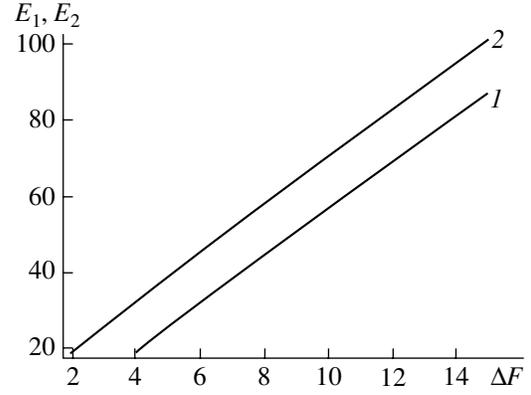
$$\Delta t_1 = \frac{(v_c - v_e)^2}{W_{\text{th}}^+} \frac{1}{E_1} = \frac{(v_c - v_e)^2}{6 W_{\text{th}}^+ \Delta F (1 - 13/24 \Delta F)}, \quad (4.2)$$

$$\Delta t_2 = \frac{(v_c - v_e)^2}{W_{\text{th}}^+} \frac{1}{E_2} = \frac{(v_c - v_e)^2}{6 W_{\text{th}}^+ \Delta F (1 + 47/24 \Delta F)}. \quad (4.3)$$

There are two independent external parameters of a problem affecting characteristic times (4.1)–(4.3). One of these parameters is related to the size of condensation nucleus, while the other one, to the chemical potential (or supersaturation) of vapor. The nucleus size manifest itself in Eqs. (4.1)–(4.3) via values  $v_{\text{th}}$ ,  $b_{\text{th}}$ , and  $|\partial^2 b_v / \partial v^2|_{\text{th}}$ . For example, in the case of macroscopic nuclei of well-soluble surfactant, we have [11, 12]

$$v_{\text{th}} = (9v_n/2a)^{3/2}, \quad (4.4)$$

$$b_{\text{th}} = 2(2a)^{3/2}/27v_n^{1/2}, \quad (4.5)$$


 Fig. 5. Dependences of eigenvalues (1)  $E_1$  and (2)  $E_2$  on  $\Delta F$ .

$$|\partial^2 b_v / \partial v^2|_{\text{th}} = 2^{11/2} a^{9/2} / 3^{10} v_n^{7/2}, \quad (4.6)$$

where the size of condensation nucleus dissolved in a droplet is characterized by the number  $v_n$  of its molecules or ions;  $a = (4\pi\gamma/kT)(3v_\alpha/4\pi)^{2/3}$ ,  $\gamma$  is the droplet surface tension; and  $v_\alpha$  is the molecular volume of condensate in the liquid phase.

According to Eqs. (1.3) and (1.5)–(1.7), the chemical potential of vapor enters into Eqs. (4.1)–(4.3) via values  $v_c - v_e$  and  $\Delta F$ . In this case, it is convenient to choose directly the height  $\Delta F$  of activation barrier of nucleation, instead of the relative chemical potential of vapor  $\varepsilon$ , as a second independent parameter of a problem for the analysis of characteristic kinetic times. This is due to the fact that, as the size of condensation nucleus varies, we should remain in the subthreshold region of vapor metastability whose boundaries with respect to vapor supersaturation depend on the nucleus size. However, setting  $\Delta F$ , we can satisfy this condition in the simplest manner.

From Eqs. (4.1)–(4.3) and in view of Eqs. (1.5)–(1.7), we arrive at the following general estimates of times  $\Delta t_0$ ,  $\Delta t_1$ , and  $\Delta t_2$ :

$$\Delta t_0 > (16/11 W_{\text{th}}^+) (\cdot |\partial^2 b_v / \partial v^2|_{\text{th}})^{2/3} \Delta F^{2/3}, \quad (4.7)$$

$$\Delta t_1 > (2/3 W_{\text{th}}^+) (3/2 |\partial^2 b_v / \partial v^2|_{\text{th}})^{2/3} \Delta F^{-1/3}, \quad (4.8)$$

$$\Delta t_2 < (2/3 W_{\text{th}}^+) (3/2 |\partial^2 b_v / \partial v^2|_{\text{th}})^{2/3} \Delta F^{-1/3}, \quad (4.9)$$

respectively.

In the limit of large activation energies  $\Delta F$ , inequalities (4.7)–(4.9) are transformed into equalities. It is seen that, as  $\Delta F$  increases, time  $\Delta t_0$  increases, while times  $\Delta t_1$  and  $\Delta t_2$  diminish.

It was shown earlier [2, 3, 9], that, at  $\Delta F \gg 1$ , time required to establish the steady state in the vicinity of the maximum of the work of droplet formation is equal to  $\Delta t_c = (\Delta v_c)^2 / 2 W_{\text{th}}^+$ , whereas the time required to establish the equilibrium distribution in the vicinity of

the minimum of formation work is equal to  $\Delta t_e = (\Delta v_e)^2/2W_{th}^+$ . When equality  $\Delta v_e = \Delta v_c$  is fulfilled within the framework of approximation (1.4), characteristic times  $\Delta t_e$  and  $\Delta t_c$  coincide with each other. It is seen from relations (1.5) and (1.8) that times  $\Delta t_c$  and  $\Delta t_e$  are equal to the right-hand side of Eq. (4.8); i.e., they coincide with times  $\Delta t_1$  and  $\Delta t_2$  in the principal order with respect to small parameter  $1/\Delta F$ . A large number of works are available (for example, see [6–8]) on the study of times required to establish the steady state in the vicinity of the maximum of the work of droplet formation in the theory of homogeneous nucleation, which are reviewed in a monograph [5]. Times obtained in [5–8] are characterized by the same functional dependence on the half-width  $\Delta v_c$  and value  $W_{th}^+$  as the principal term of expression (4.2) for time  $\Delta t_1$  in the principal order with respect to small parameter  $1/\Delta F$  [with allowance for Eq. (1.9)] and only slightly differ in the numerical coefficient.

Based on relations (3.10), (3.12), (3.15), (3.16), and (3.19)–(3.26) and taking into account equalities (4.1)–(4.3), we interpret relaxation times  $\Delta t_0$ ,  $\Delta t_1$ , and  $\Delta t_2$ . It is seen that time  $\Delta t_0$ , which is the longest of all relaxation times, actually determines the establishment of equilibrium droplet distribution over the entire region  $v_e - \Delta v_e \leq v \leq v_c - \Delta v_c$  where the  $\phi_0(x)$  function is non-zero. The establishment of steady-state droplet distribution in the near-critical region  $|v - v_c| \leq \Delta v_c$  depends on the value of  $\Delta F$ . If  $\Delta F > 4$ , the eigenvalue  $E_1$  and eigenfunction  $\phi_1(x)$  exist. Since eigenfunctions  $\phi_0(x)$  and  $\phi_2(x)$  in the near-critical region are exponentially small as compared with this function, time  $\Delta t_1$  determines, in accordance with [2–4], the establishment of steady-state droplet distribution in this region. However, if  $2 \leq \Delta F \leq 4$ , the eigenvalue  $E_1$  and eigenfunction  $\phi_1(x)$  do not exist. Then, the establishment of droplet steady-state distribution in the near-critical region is determined by times  $\Delta t_0$  and  $\Delta t_2$ . In this case, this establishment occurs slower in view of inequality  $\Delta t_0 > \Delta t_1$ . Note, however, that, at all  $t > 0$  in the near-critical region, deviation  $n_v - n_v^{(s)}$  is small due to the exponential smallness of eigenfunctions  $\phi_0(x)$  and  $\phi_2(x)$ .

Let us find now how the nucleation rate varies in time. For the non-steady-state nucleation rate  $J_c$  (equal to droplet flux  $J_v$  along the size axis at  $v = v_c$ ), from Eqs. (2.4)–(2.6) and (2.10), we find

$$J_c = J_s - W_{v_c}^+ n_v^{(0)} \left. \frac{\partial f}{\partial v} \right|_{v=v_c}. \quad (4.10)$$

Allowing for relations (3.2), (3.5), (3.6), and (3.12), we transform Eq. (4.10) into:

$$J_c = J_s - \frac{W_c^+ n_c^{(0)}}{v_c - v_e} \sum_{i=0}^{\infty} C_i \phi_i \left. \frac{\partial \phi_i}{\partial x} \right|_{x=\frac{1}{2}} e^{-E_i \tau}. \quad (4.11)$$

Taking into account equalities (2.13), (2.15), and (1.9) and considering only the contributions with the longest relaxation times, we rewrite expression (4.11) with allowance for (3.15), (3.16), (3.19)–(3.26), (3.3), and (4.1)–(4.3) as

$$\begin{aligned} \frac{J_c}{J_s} = & 1 + \pi^{1/4} (3\Delta F)^{3/4} e^{-5\Delta F/4 - 13/4} C_0 e^{-t/\Delta t_0} \\ & + \frac{\pi^{1/4}}{(3\Delta F)^{1/4}} e^{\Delta F/4} C_1 e^{-t/\Delta t_1} \\ & + (4\pi)^{1/4} (3\Delta F)^{5/4} e^{-5\Delta F/4 - 15/4} C_2 e^{-t/\Delta t_2}, \end{aligned} \quad (4.12)$$

where only the principal orders with respect to  $\Delta F$  are accounted for in pre-exponential factors, whereas the first corrections with respect to small parameter  $1/\Delta F$  are additionally taken into account in the powers of exponents. Let us suggest that the values of coefficients  $C_0$ ,  $C_1$ , and  $C_2$  that are determined by the initial condition to the droplet size distribution are of the order of unity. At  $\Delta F \geq 2$ , the second and fourth summands in the right-side of Eq. (4.12) will be at least by two orders of magnitude smaller than unity at all  $t > 0$ . Then, it is seen from Eq. (4.12) that these summands cannot cause any noticeable deviations in the non-steady-state nucleation rate  $J_c$  from the steady-state rate  $J_s$ . This is explained by the fact that eigenfunctions  $\phi_0$  and  $\phi_2$  corresponding to eigenvalues  $E_0$  and  $E_2$  are exponentially small near the value  $v = v_c$  in Eq. (4.10). The third term in the right-hand side of Eq. (4.12) appearing only at  $\Delta F > 4$  (when eigenvalue  $E_1$  exists) becomes exponentially smaller than unity at  $t \geq t_1$ . Thus, at  $\Delta F > 4$ , time  $\Delta t_1$  is the time of the relaxation of non-steady-state nucleation rate  $J_c$  to the steady-state value  $J_s$ . As was already noted, in the principal order with respect to small parameter  $1/\Delta F$ , this time coincides with time  $\Delta t_c$  found in [2–4].

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