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The Stage of Nonisothermal Nucleation of Supercritical Particles of a New Phase under Nonstationary Conditions of Particle Diffusion Growth and Heat Transfer to a Medium

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Abstract—An analytical theory has been formulated for the stage of nonisothermal nucleation of supercritical particles in a metastable medium with instantaneously generated initial supersaturation. The theory takes into account the nonuniformities of metastable substance concentration and temperature, which result from the nonstationary diffusion of the substance to growing particles and the nonstationary transfer of the heat of the phase transition from the particles to the medium. The formulated theory extends the approach based on the concept of excluded volume that has recently been used in the theory of the stage of nucleation under isothermal conditions. This approach implies that the nucleation intensity of new particles is suppressed in spherical diffusion regions with certain sizes that surround previously nucleated supercritical particles and remaining unchanged in the rest of the medium. It has been shown that, when self-similar solutions are used for nonstationary equations of substance diffusion to particles and heat transfer from the particles, the ratio between the excluded volume and the particle volume is independent of particle size, thereby enabling one to analytically solve the integral equation for the excluded volume throughout a system as a time function at the stage of nucleation. The main characteristics of the phase transition have been found for the end of the stage of nucleation. Comparison has been carried out with the characteristics obtained in terms of the isothermal and nonisothermal nucleation theory upon uniform vapor consumption and heat dissipation (the mean-field approximation of vapor supersaturation and temperature).

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INTRODUCTION

This article generalizes and develops the approach to the description of the kinetics of a new phase formation in a metastable medium with instantaneously generated supersaturation at the stage of nucleation (i.e., the stage of formation of stably growing supercritical nuclei of a new phase). The approach takes into account that the intensity of the nucleation of new supercritical particles is suppressed in spherical diffusion regions of a certain size, which surround previously nucleated particles and remaining at the initial level in the rest of the metastable medium. In this way, the volume excluded from the nucleation is formed around particles growing in a diffusion regime [1–7]. At the stage of nucleation, the effects of the excluded volume play a fundamental role in the separation of highly supersaturated gas solutions, substantially (by several times) increasing solution volume [6, 7]. Recently, we have considered [8] the application of this approach to the stage of nucleation in a supersaturated vapor under isothermal conditions and compared the results obtained with the more traditional description in terms of the mean-field approximation of vapor supersaturation, which implies that vapor consumption by growing droplets results in a simultaneous and uniform decrease in vapor supersaturation throughout the system volume [9–12]. In this article, we supplement the excluded-volume approach with taking into account the thermal effects of nonisothermal nucleation and the nonstationary transfer of heat releasing upon the transition of metastable substance molecules to particles. The existence of the nonstationary heat flux provides the metastable medium with additional nonuniformity and substantially contributes to the formation of an excluded volume in the course of nonisothermal nucleation. This problem is rather complex to solve even under the mean-field approximation of the supersaturation of a metastable substance in a medium and the temperature of the latter [13–16]. Since not all effects relevant to the nonisothermal mean-field theory have been previously considered for the stage of nucleation, we briefly discuss the results obtained in terms of this theory in Section 1 mainly following the approach described in [13–16]. Detailed consideration of the results obtained in terms of the mean-field theory is also necessary to consistently compare them with corresponding results of the excluded-volume approach; this comparison is carried out in Section 3. The excluded-volume approach per se is considered in Section 2.

1. MEAN-FIELD APPROXIMATION OF SUPERSATURATION AND TEMPERATURE

1.1. Nucleation Rate of Supercritical Particles

As has been known [12], the intensity of the generation of supercritical nuclei in a supersaturated homogeneous metastable medium with molecular concentration n and absolute temperature T is determined by nucleation rate $\bar{I}$, which may be represented as follows:

$$\bar{I} = \sqrt{\frac{\left|d^2F_\nu/d\nu^2\right|_{\nu_c}}{2\pi}}\, n W_{\nu_c}(n)\exp\left(-F_{\nu_c}\right). \qquad (1)$$

Here, F_ν is the formation work of a nucleus composed of number ν of molecules expressed in the k_BT, units, where k_B is Boltzmann's constant; ν_c is the number of molecules in the critical nucleus that corresponds to the maximum of work F_{ν_c}, $W_{\nu_c}(n)$ is the rate of attachment of molecules to the critical nucleus. In terms of the classical theory of nucleation, the formation work of a spherical nucleus with radius $R = \left(3\nu/4\pi n_l\right)^{1/3}$ ($n_l(T)$ is the number density of molecules in a new phase) may be written as

$$F_\nu = \frac{4\pi R^2\sigma(T)}{k_BT} - \nu\ln(1+\zeta),$$

where $\sigma(T)$ is the surface tension of the nucleus and ζ is the supersaturation of a metastable substance. Accordingly, the activation barrier of nucleation $\Delta F(\zeta, T)$, which is equal to the maximum of work F_{ν_c}, may be represented in the following form:

$$\Delta F(\zeta, T) = F_{\nu_c} = \frac{4}{27}\left(\frac{4\pi\sigma(T)}{k_BT}\right)^3\left(\frac{3}{4\pi n_l(T)}\right)^2\frac{1}{\ln^2(1+\zeta)}. \qquad (2)$$

In the free-molecular regime of substance exchange between a nucleus and a medium, which is typical of the initial stage of nucleation (incubation), at which the stationary state is established in the near-critical range of nucleus sizes, we have $W_\nu(n) = \alpha_C\pi R^2 v_T n$, where α_C is the capture coefficient of metastable substance molecules on the nucleus surface and v_T is the average thermal velocity of metastable substance molecules. The development of a stationary state in the near critical range of nucleus sizes under the conditions of nonisothermal homogeneous nucleation was described in [13, 14], where it was shown that rate I is renormalized by the thermal effects as compared with rate $\bar{I}$ upon the isothermal homogeneous nucleation as follows:

$$I = (1+k)^{-1}\bar{I},$$
$$k \equiv k(n,T) \equiv \alpha_C\left(\frac{q}{k_BT}\right)^2\frac{v_T n}{c_g n_g v_T^g + c n v_T}, \qquad (3)$$

where $q \equiv q(T)$ is the latent heat of transition of a metastable substance molecule to the new phase at temperature T; v_T^g is the average thermal velocity of carrier medium molecules; n_g is the molecular concentration of the carrier medium; and c and c_g are the molecular heat capacities of the substance and the carrier medium in the units of Boltzmann's constant k_B, respectively.

In the case of nonisothermal generation of supercritical particles, ignoring a change in the preexponential factors of expression (1), current intensity $I(t) = I\left(\zeta(t), T(t)\right)$ (for time moment t) is related to initial intensity $I_0 \equiv I(\zeta_0, T_0)$ (for some initial time moment $t = 0$) via the following relation:

$$I(t) \approx I_0\exp\left[-\left(\Delta F\left(\zeta(t), T(t)\right) - \Delta F\left(\zeta_0, T_0\right)\right)\right]. \qquad (4)$$

Let us define the initial ζ_0 and current $\zeta(t)$ average supersaturations of the metastable substance in the system as

$$\zeta_0 = \frac{n_0 - n_\infty(T_0)}{n_\infty(T_0)}, \quad \zeta(t) = \frac{n(t) - n_\infty(T(t))}{n_\infty(T(t))}, \qquad (5)$$

where $n(t)$ is the current concentration of the metastable substance, $n_0 \equiv n(t_0)$, $n_\infty(T)$ is the equilibrium concentration of the metastable substance over a planar surface of the stable phase at temperature T. With regard to the Clapeyron–Clausius formula, at $\Delta T(t)/T_0 = \left(T(t) - T_0\right)/T_0 \ll 1$, we have

$$n_\infty(T) = n_\infty(T_0)\exp\left(\frac{q_0\Delta T}{k_BT_0^2}\right). \qquad (6)$$

Let us write the $\Delta F(\zeta(t), T(t)) - \Delta F(\zeta_0, T_0)$ difference in the following form:

$$\Delta F(\zeta, T) - \Delta F(\zeta_0, T_0) \approx -\frac{\zeta_0 - \zeta}{\zeta_0}\frac{\partial\Delta F(\zeta_0, T_0)}{\partial\ln\zeta_0} + \frac{T - T_0}{T_0}\frac{\partial\Delta F(\zeta_0, T_0)}{\partial\ln T_0}. \qquad (7)$$

The second term in expression (7) was previously ignored [13, 16]; however, we shall retain it. Note that, in view of Eq. (2), the $\partial\Delta F(\zeta_0, T_0)/\partial\ln\zeta_0$ and $\partial\Delta F(\zeta_0, T_0)/\partial\ln T_0$ are expressed via $\Delta F(\zeta_0, T_0)$ as follows:

$$\frac{\partial\Delta F(\zeta_0, T_0)}{\partial\ln\zeta_0} = -\frac{2\zeta_0}{1+\zeta_0}\frac{\Delta F(\zeta_0, T_0)}{\ln(1+\zeta_0)}, \qquad (8)$$

$$\frac{\partial\Delta F(\zeta_0, T_0)}{\partial\ln T_0} = \gamma(T_0)\Delta F(\zeta_0, T_0), \qquad (9)$$

where

$$\gamma_0 \equiv \frac{\partial}{\partial \ln T_0} \ln\left(\frac{\sigma^3(T_0)}{T_0^3 n_l^2(T_0)}\right). \tag{10}$$

Let us estimate these derivatives. For example, using the thermodynamic data [17] for liquid water taken as a stable phase, at $T_0 = 298$ K and $\zeta_0 = 2$ we have

$$\begin{gathered} d\ln\sigma(T_0)/d\ln T_0 = -0.63, \\ d\ln n_l(T_0)/d\ln T_0 = -0.08, \quad \gamma_0 = -4.74, \\ \Delta F(\zeta_0, T_0) = 66.5, \quad \partial\Delta F(\zeta_0, T_0)/\partial \ln\zeta_0 = -80.5, \\ \partial\Delta F(\zeta_0, T_0)/\partial \ln T_0 = -316. \end{gathered} \tag{11}$$

Since, according to parameters (11), $|\partial\Delta F(\zeta_0, T_0)/\partial\ln\zeta_0| \gg 1$ and $|\partial\Delta F(\zeta_0, T_0)/\partial\ln T_0| \gg 1$, the relative deviations of the supersaturation and temperature in expression (7) must be small.

Let us, in accordance with [13, 16], introduce the denotation

$$\Gamma_0 \equiv -\frac{\partial\Delta F(\zeta_0, T_0)}{\partial\ln\zeta_0} \tag{12}$$

and define the current value of the relative decrease in the supersaturation of the metastable substance $\varphi(t)$ as

$$\varphi(t) \equiv \frac{\zeta_0 - \zeta(t)}{\zeta_0}. \tag{13}$$

With allowance for relations (7)–(10) and definitions (12), (13), expression (4) for the intensity of the nonisothermal generation of supercritical particles is transformed as follows:

$$\begin{aligned} I(t) &\approx I_0 \\ &\times \exp\left[-\Gamma_0\left(1 + \gamma_0 \frac{(1+\zeta_0)\ln(1+\zeta_0)}{2\zeta_0}\frac{\Delta T(t)}{\varphi(t) T_0}\right)\varphi(t)\right]. \end{aligned} \tag{14}$$

The heating of the medium due to the heat of the phase transition upon the formation and growth of supercritical particles may be determined in terms of the mean-field approximation with the help of the heat balance equation. Assuming that the heat resulting from the transition of the metastable substance to particles has entirely been consumed for medium heating, we obtain

$$q_0(n_0 - n(t)) \approx (c_g n_g + c n_0) k_B \Delta T(t). \tag{15}$$

From this, we derive the following:

$$\frac{\Delta T(t)}{T_0} = \frac{q_0}{k_B T_0}\frac{(n_0 - n(t))}{(c_g n_g + c n_0)}. \tag{16}$$

Substitution of Eq. (16) into identity (13) with allowance for relations (5) and (6) yields

$$\begin{aligned} \varphi(t) &= \left(1 + \frac{n(t)}{n_0 - n(t)}\right. \\ &\times \left.\left(1 - \exp\left(-\left(\frac{q_0}{k_B T_0}\right)^2 \frac{n_0 - n(t)}{c_g n_g + c n_0}\right)\right)\right)\frac{n_0 - n(t)}{\zeta_0 n_\infty(T_0)}. \end{aligned} \tag{17}$$

At the smallness of the argument in the exponent, this implies [13, 16] that

$$\varphi(t) = \left(1 + k_0'\right)\psi(t), \quad \frac{\zeta_0}{\zeta_0 + 1} k_0'\psi(t) \ll 1, \tag{18}$$

where

$$k_0' \equiv \beta_0^2 \frac{n_0}{c_g n_g + c n_0}, \quad \beta_0 \equiv \frac{q_0}{k_B T_0}, \tag{19}$$

$$\psi(t) \equiv \frac{n_0 - n(t)}{\zeta_0 n_\infty(T_0)}. \tag{20}$$

Using relations (18)–(20) in Eq. (16), we obtain

$$\frac{\Delta T(t)}{T_0} = \frac{\zeta_0}{\zeta_0 + 1}\frac{k_0'}{1 + k_0'}\frac{\varphi(t)}{\beta_0}, \tag{21}$$

Substitution of Eq. (21) into expression (14) yields

$$I(t) \approx I_0 \exp\left(-\Gamma_0'\psi(t)\right), \tag{22}$$

$$\Gamma_0' = \Gamma_0\left(1 + k_0'\right)\left(1 + \frac{k_0'}{1 + k_0'}\frac{\ln(1+\zeta_0)}{2\beta_0}\gamma_0\right). \tag{23}$$

As follows from relation (22), under the mean-field approximation of supersaturation, duration t_1^{mf} of the stage of nucleation is determined by the following condition:

$$\Gamma_0'\psi\left(t_1^{\mathrm{mf}}\right) = 1. \tag{24}$$

1.2. Balance of Metastable Substance, Heat Balance of Particles, and Particle-Size Distribution

Squared radius distribution function for supercritical new-phase particles growing in the stationary nonisothermal diffusion regime is determined at time moment t as follows [8]:

$$f(R^2, t) = \int_0^t d\tau I(\tau)\delta(R^2 - R^2(t, \tau)), \tag{25}$$

where

$$R^2(t, \tau) = \int_\tau^t \frac{dR^2}{d\tilde{t}} d\tilde{t} = 2D\int_\tau^t \frac{n(\tilde{t}) - n_\infty(T_d(\tilde{t}))}{n_l(T_d(\tilde{t}))} d\tilde{t}, \tag{26}$$

T_d is droplet temperature, D is the diffusion coefficient of a metastable substance molecule in a medium, and $n_\infty(T_d)$ is determined by formula (6) at $T = T_d$.

Droplet temperature T_d may be found from the condition of heat balance between a new-phase particle and a medium due to thermal conductivity. Assuming that the diffusion to a particle and the heat transfer from the particle occur in the stationary regime, at metastable substance concentration $n(t)$ and temperature $T(t)$ at a large distance from the particle (time variations $n(t)$ and $T(t)$ result from the collective effect of all supercritical particles that have been nucleated on the medium), we have

$$D\left(n(t)-n_\infty\left(T_d(t)\right)\right)q_0=\kappa\left(T_d(t)-T(t)\right), \qquad (27)$$

where $\kappa=\chi k_B\left(c_g n_g+c n_0\right)$ is the thermal-conductivity coefficient of the medium and χ is the corresponding thermal diffusivity. Keeping in mind that, according to formulas (24), (18), and (21),

$$\frac{n_0-n(t)}{n_0-n_\infty(T_0)}=\psi(t)\le\frac{1}{\Gamma'_0}\ll 1, \qquad (28)$$

$$\frac{\Delta T(t)}{T_0}=\frac{\zeta_0}{\zeta_0+1}\frac{k'_0\psi(t)}{\beta_0}\ll 1, \qquad (29)$$

it may, with a sufficient accuracy, be taken that, in the equation of heat balance between a particle and a medium, $n(t)\approx n_0$ and $T(t)\approx T_0$:

$$\begin{gathered}D\left(n_0-n_\infty\left(T_0\right)\exp\left(\beta_0\frac{T_d(t)-T_0}{T_0}\right)\right)q_0\\=\kappa\left(T_d(t)-T_0\right).\end{gathered} \qquad (30)$$

As a consequence, the solution of Eq. (30) for particle temperature $T_d(t)\equiv T_d$ is time-independent. As in the case of the growth of a single particle [13, 15], Eq. (30) may be transformed into the following form:

$$\begin{gathered}1-\frac{\beta_0}{k_D}\frac{T_d-T_0}{T_0}=\frac{1}{\zeta_0+1}\exp\left(\beta_0\frac{T_d-T_0}{T_0}\right),\\k_D\equiv\frac{Dn_0k_B}{\kappa}\beta_0^2.\end{gathered} \qquad (31)$$

Analogously, assuming that, in Eq. (26), $n(\tilde{t})\approx n_0$ and $T_d(\tilde{t})\equiv T_d$, we obtain the following relation for $R^2(t,\tau)$,:

$$R^2(t,\tau)=2Da(t-\tau),\quad a\equiv\frac{n_0-n_\infty(T_d)}{n_l(T_d)}. \qquad (32)$$

Then, using relations (32) in Eq. (25), with allowance for expression (22), the particle-size distribution function is represented as

$$f(R^2,t)=\frac{I_0}{2Da}\exp\left[-\Gamma'_0\psi\left(t-\frac{R^2}{2Da}\right)\right]. \qquad (33)$$

The amount of the metastable substance that has been transferred to supercritical particles in unit volume is related to the distribution function via the following obvious expression:

$$\begin{gathered}n_0-n(t)=\frac{4\pi}{3}n_l(T_d)\int\limits_0^{R^2(t)}R^3f(R^2,t)dR^2,\\R^2(t)=2Dat.\end{gathered} \qquad (34)$$

With regard to expressions (20) and (34), this yields the following integral equation for the $\psi(t)$ function:

$$\psi(t)=\frac{8\pi I_0D^{3/2}2^{1/2}a^{3/2}}{3a_0}\int\limits_0^t\exp\left\{-\Gamma'_0\psi(z)\right\}(t-z)^{3/2}dz, \qquad (35)$$

where $a_0=\left(n_0-n_\infty(T_0)\right)/n_l\left(T_d\right)$. The first iteration of this equation gives

$$\psi(t)\approx 2^{5/2}\frac{4\pi a^{3/2}}{15a_0}I_0D^{3/2}t^{5/2}. \qquad (36)$$

Substituting relation (36) into Eq. (33), we derive

$$\begin{gathered}f(R^2,t)=\frac{I_0}{2Da}\\\times\exp\left(-2^{5/2}\frac{4\pi a^{3/2}}{15a_0}\Gamma'_0I_0D^{3/2}\left(t-\frac{R^2}{2Da}\right)^{5/2}\right).\end{gathered} \qquad (37)$$

For the duration of the stage of nucleation t_1^{mf}, which is determined by condition (24), we have

$$t_1^{\mathrm{mf}}=\frac{1}{2}\left(\frac{15a_0}{4\pi\Gamma'_0a^{3/2}}\right)^{2/5}D^{-3/5}I_0^{-2/5}. \qquad (38)$$

Accordingly, the maximum particle size and the total number of supercritical particles nucleated by the end of the stage of nucleation are determined as follows:

$$R_{\max}^2\equiv R^2(t_1)=2Dat_1=\left(\frac{15aa_0}{4\pi\Gamma'_0}\frac{D}{I_0}\right)^{2/5}, \qquad (39)$$

$$\begin{gathered}N\left(t_1^{\mathrm{mf}}\right)=\int\limits_0^{R^2\left(t_1^{\mathrm{mf}}\right)}dR^2f(R^2,t_1^{\mathrm{mf}})\\=\frac{I_0}{2Da}\int\limits_0^{R^2\left(t_1^{\mathrm{mf}}\right)}dR^2\exp\left\{-\left(1-\frac{R^2}{R^2(t_1^{\mathrm{mf}})}\right)^{5/2}\right\}.\end{gathered} \qquad (40)$$

Finally, we arrive at

$$\begin{gathered}N\left(t_1^{\mathrm{mf}}\right)=\frac{\alpha_d}{2}\left(\frac{15a_0}{4\pi\Gamma'_0a^{3/2}}\right)^{2/5}\left(\frac{I_0}{D}\right)^{3/5},\\\alpha_d\equiv\int\limits_0^1d\xi\exp[-\xi^{5/2}]\approx 0.78.\end{gathered} \qquad (41)$$

2. THERMAL EFFECTS AT THE STAGE OF NUCLEATION ACCORDING TO THE EXCLUDED-VOLUME APPROACH

2.1. Concept of Excluded Volume and Its Calculation for Self-Similar Regime of New-Phase Particle Growth

In the real situation of nonstationary diffusion of a metastable substance to supercritical particles and heat transfer from the particles to a medium, each supercritical particle is surrounded by a diffuse layer with a finite thickness, in which the density of the metastable substance and temperature are spatially nonuniform and vary with time. It is obvious that, inside these diffuse shells, the nucleation of new supercritical particles is decelerated due to both a decrease in the concentration of the metastable substance and an increase in the temperature; the shorter the distance from the particle surface the stronger the deceleration. Outside of the diffuse shells, the nucleation rate remains at the initial level. In the course of time, the diffuse shells will start to overlap; in this case, the nucleation of new particles will actually stop, and the stage of nucleation will come to the end.

To describe the stage of nucleation with allowance for the thermal effects upon the formation of diffuse shells with time-dependent concentration fields around supercritical particles, we use the approach that we have previously developed in [8] for isothermal nucleation. Assume that, inside diffuse shells with a certain thickness, the nucleation rate of new particles is completely suppressed, while, outside of these shells, the nucleation rate is the same as it is at the initial time moment. As a consequence, some volume of the medium around existing supercritical particles can be excluded from the nucleation process. We shall refer to this volume as the excluded one.

Excluded volume $V_{\text{ex}}(t)$, surrounding a particle with radius $R(t)$ may be found from the integral condition that the total number of new particles, which are nucleated per unit time around this specific particle in sufficiently large volume V of the medium at current profiles of metastable substance supersaturation $\zeta(\mathbf{r},t)$ and temperature $T(\mathbf{r},t)$, as well as corresponding profile of nucleation rate $I(\zeta(\mathbf{r},t),T(\mathbf{r},t))$, is equal to the number of particles nucleated outside of the excluded volume at initial nucleation rate I_0. This condition may be expressed in the form of the following integral relation:

$$\int_V d\mathbf{r}I(\zeta(\mathbf{r},t),T(\mathbf{r},t)) = I_0(V - V_{\text{ex}}(t)). \qquad (42)$$

Note that, in the presence of thermal effects, initial nucleation rate I_0 is determined by the same relation (3) at $T = T_0$ and $n = n_0$, while, for the current local vapor supersaturation, instead of the second of definitions (5), we have the following:

$$\zeta(\mathbf{r},t) = \frac{n(\mathbf{r},t) - n_\infty(T(\mathbf{r},t))}{n_\infty(T(\mathbf{r},t))}. \qquad (43)$$

Taking into account the spherical symmetry of the medium around a growing spherical particle, Eq. (42) yields

$$V_{\text{ex}}(t) = 4\pi\int_{R(t)}^{\infty}\frac{I_0 - I(\zeta(r,t),T(r,t))}{I_0}r^2dr. \qquad (44)$$

It is obvious that the upper limit of the integral in Eq. (44) cannot exceed the average interparticle distance and has been specified as infinity formally, because the integrand rather rapidly tends to zero.

When considering the nonstationary profiles of metastable substance concentration and temperature around the particle, we shall be interested in the self-similar regimes of diffusion particle growth and heat transfer from the particle to the medium [18–22]. Let us introduce the following self-similar variables:

$$\rho = \frac{r}{R(t)},\quad n(r,t) = n(\rho),\quad T(r,t) = T(\rho),\quad \zeta(r,t) = \zeta(\rho). \qquad (45)$$

Being expressed in these variables, relation (44) for the excluded volume is written as follows:

$$V_{\text{ex}}(t) = 4\pi R^3(t)\int_1^\infty d\rho\rho^2\left(1 - \frac{I(\zeta(\rho),T(\rho))}{I_0}\right). \qquad (46)$$

Let us denote the particle radius- and time-independent integral in Eq. (46) as μ:

$$\mu \equiv 3\int_1^\infty d\rho\rho^2\left(1 - \frac{I(\zeta(\rho),T(\rho))}{I_0}\right). \qquad (47)$$

Then, we have

$$V_{\text{ex}}(t) = \mu V_R(t),\quad V_R(t) = \frac{4\pi}{3}R^3(t). \qquad (48)$$

Excluded volume coefficient μ may be analyzed using relation (14) derived above. The replacement of $\varphi(t)$ by $(\zeta_0 - \zeta(\rho))/\zeta_0$ and $\Delta T(t)$ by $T(\rho) - T_0$, in this relation leads to

$$\mu = 3\int_1^\infty d\rho\rho^2\left[1 - \exp\left(-\Gamma_0\left(\frac{\zeta_0 - \zeta(\rho)}{\zeta_0} + \gamma_0\frac{(1+\zeta_0)\ln(1+\zeta_0)}{2\zeta_0}\frac{T(\rho) - T_0}{T_0}\right)\right)\right]. \qquad (49)$$

Note that the $(\zeta_0 - \zeta(\rho))/\zeta_0$ and $T(\rho) - T_0$ values are interrelated. Taking into account definitions (5) and Clapeyron–Clausius formula (6), we arrive at

$$\frac{\zeta_0 - \zeta(\rho)}{\zeta_0} = \frac{\zeta_0 + 1}{\zeta_0} - \frac{n(\rho)}{\zeta_0 n_\infty(T_0)}\exp\left(-\beta_0\frac{T(\rho) - T_0}{T_0}\right). \qquad (50)$$

With no regard to the Stefan flux, the nonstationary equations for the diffusion of the new phase substance to a particle and the heat transfer from the particle to the medium have the following forms [18–22]:

$$\frac{\partial n(r,t)}{\partial t}=\frac{D}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial n(r,t)}{\partial r}\right]-\frac{R^2(t)}{r^2}\frac{dR(t)}{dt}\frac{\partial n(r,t)}{\partial r}, \quad (51)$$

$$\frac{\partial T(r,t)}{\partial t}=\frac{\chi}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial T(r,t)}{\partial r}\right]-\frac{R^2(t)}{r^2}\frac{dR(t)}{dt}\frac{\partial T(r,t)}{\partial r}. \quad (52)$$

As in Section 1, diffusion coefficient D of metastable substance molecules in the medium and thermal diffusivity χ of the medium in Eqs. (51) and (52) are assumed to be constant. Equations (51) and (52) are written in self-similar variables (45) as follows:

$$\frac{d^2n(\rho)}{d\rho^2}+\left[\frac{2}{\rho}+b\left(\rho-\frac{1}{\rho^2}\right)\right]\frac{dn(\rho)}{d\rho}=0, \quad (53)$$

$$\frac{d^2T(\rho)}{d\rho^2}+\left[\frac{2}{\rho}+\frac{D}{\chi}b\left(\rho-\frac{1}{\rho^2}\right)\right]\frac{dT(\rho)}{d\rho}=0, \quad (54)$$

where time- and coordinate-independent parameter b is determined with the help of the equation for the rate of supplying the substance to a supercritical particle

$$\frac{d}{dt}\left(\frac{4\pi}{3}n_l\left(T_\mathrm{d}\right)R^3\right)=\left(4\pi r^2D\frac{\partial n(r,t)}{\partial r}\right)\Bigg|_{r=R}$$

in the following way:

$$b\equiv\frac{R}{D}\frac{dR}{dt}=\frac{1}{n_l\left(T_\mathrm{d}\right)}\frac{dn(\rho)}{d\rho}\bigg|_{\rho=1}. \quad (55)$$

The boundary conditions for Eqs. (53) and (54) have the forms of

$$n(\rho)\xrightarrow[\rho\to\infty]{}n_0,\quad n(\rho=1)=n_\infty\left(T_\mathrm{d}\right)=\mathrm{const}, \quad (56)$$

$$T(\rho)\xrightarrow[\rho\to\infty]{}T_0,\quad T(\rho=1)=T_\mathrm{d}. \quad (57)$$

The following self-similar solutions satisfy Eqs. (53) and (54) with boundary conditions (56) and (57):

$$n(\rho)=n_\infty\left(T_\mathrm{d}\right)+\left(n_0-n_\infty\left(T_\mathrm{d}\right)\right)\times\frac{\int_1^\rho\frac{dx}{x^2}\exp\left[-\frac{b}{2}\left(x^2+\frac{2}{x}-3\right)\right]}{\int_1^\infty\frac{dx}{x^2}\exp\left[-\frac{b}{2}\left(x^2+\frac{2}{x}-3\right)\right]}, \quad (58)$$

$$T(\rho)=T_\mathrm{d}+\left(T_0-T_\mathrm{d}\right)\times\frac{\int_1^\rho\frac{dx}{x^2}\exp\left[-\frac{Db}{2\chi}\left(x^2+\frac{2}{x}-3\right)\right]}{\int_1^\infty\frac{dx}{x^2}\exp\left[-\frac{Db}{2\chi}\left(x^2+\frac{2}{x}-3\right)\right]}, \quad (59)$$

where parameter b satisfies the following integral equation, which results from relation (55) and definition (32) of parameter a:

$$b\int_1^\infty\frac{dx}{x^2}\exp\left[-\frac{b}{2}\left(x^2+\frac{2}{x}-3\right)\right]=a. \quad (60)$$

Temperature T_d of a supercritical particle is found using the nonstationary heat balance equation, which has the following form in the self-similar variables:

$$\kappa\frac{dT(\rho)}{d\rho}\bigg|_{\rho=1}=-q_0D\frac{dn(\rho)}{d\rho}\bigg|_{\rho=1}. \quad (61)$$

Substituting expressions (58) and (59) into Eq. (61) and taking into account Eq. (60), we arrive at the following set of two equations:

$$\begin{cases}\dfrac{\kappa\left(T_\mathrm{d}-T_0\right)}{q_0Dn_\infty\left(T_0\right)}=\left(\zeta_0+1-\exp\left(\beta_0\dfrac{T_\mathrm{d}-T_0}{T_0}\right)\right)\times\dfrac{\int_1^\infty\frac{dx}{x^2}\exp\left[-\frac{Db}{2\chi}\left(x^2+\frac{2}{x}-3\right)\right]}{\int_1^\infty\frac{dx}{x^2}\exp\left[-\frac{b}{2}\left(x^2+\frac{2}{x}-3\right)\right]},\\ bn_l\left(T_\mathrm{d}\right)\int_1^\infty\frac{dx}{x^2}\exp\left[-\frac{b}{2}\left(x^2+\frac{2}{x}-3\right)\right]=n_\infty(T_0)\left(\zeta_0+1-\exp\left(\beta_0\dfrac{T_\mathrm{d}-T_0}{T_0}\right)\right).\end{cases} \quad (62)$$

In conclusion, to calculate desired coefficient μ at an arbitrary value of parameter a, relations (58) and (59), as well as the results of the solution of the set of equations (62) for b and T_d should be substituted into formula (49) under integral with allowance for Eq. (50).

2.2. Asymptotics at Weak Nonstationarity of Diffusion and Heat Transfer

The difference between parameters b and a characterizes the nonstationarity of diffusion and heat transfer in the process of the growth of supercritical particles of a new phase. In particular, at a weak nonstationarity, when $a^{1/2}\ll 1$, Eq. (60) yields

$$b\approx a\left(1+\sqrt{\pi a/2}\right). \quad (63)$$

At $a^{1/2}\ll 1$, set (62) is reduced to the following equation:

$$Dn_\infty(T_0)\left(\zeta_0 + 1 - \exp\left(\beta_0 \frac{T_\mathrm{d} - T_0}{T_0}\right)\right) q_0 = \kappa(T_\mathrm{d} - T_0), \tag{64}$$

which coincides with Eq. (30) for the temperature of growing droplets under the mean-field approximation of supersaturation. Under the same conditions, when $b \ll 1$, the following approximate expressions may be used instead of relations (58) and (59) for $n(\rho)$ and $T(\rho)$:

$$n(\rho) = \frac{n_0 \int\limits_1^\rho \frac{dx}{x^2} \exp\left(-\frac{bx^2}{2}\right) + n_\infty(T_\mathrm{d}) \int\limits_\rho^\infty \frac{dx}{x^2} \exp\left(-\frac{bx^2}{2}\right)}{\int\limits_1^\infty \frac{dx}{x^2} \exp\left(-\frac{bx^2}{2}\right)}, \tag{65}$$

$$T(\rho) = T_\mathrm{d} - (T_\mathrm{d} - T_0) \frac{\int\limits_1^\rho \frac{dx}{x^2} \exp\left(-\frac{bD}{2\chi} x^2\right)}{\int\limits_1^\infty \frac{dx}{x^2} \exp\left(-\frac{bD}{2\chi} x^2\right)}. \tag{66}$$

Relations (63)–(66) enable us to obtain the analytical asymptotic estimate for excluded volume coefficient μ at $b \ll 1$. Let us rewrite expression (49) in the form of

$$\mu = 3\int\limits_1^\infty d\rho \rho^2 [1 - \exp(-\Gamma_0 \omega(\rho))], \tag{67}$$

where the $\omega(\rho)$ function may be represented with allowance for relations (50), (65), and (66) as

$$\begin{aligned} \omega(\rho) &= \frac{\zeta_0 + 1}{\zeta_0}\Bigg(1 - B(\rho, b) \\ &\times \exp\left(-\frac{q_0(T_\mathrm{d} - T_0)}{k_\mathrm{B} T_0^2}[1 - C(\rho, b)]\right)\Bigg) \\ &- \frac{1}{\zeta_0}[1 - B(\rho, b)] \exp\left(\frac{q_0(T_\mathrm{d} - T_0)}{k_\mathrm{B} T_0^2} C(\rho, b)\right) \\ &+ \gamma_0 \frac{(1 + \zeta_0)\ln(1 + \zeta_0)}{2\zeta_0} \frac{T_\mathrm{d} - T_0}{T_0}[1 - C(\rho, b)], \end{aligned} \tag{68}$$

$$B(\rho, b) \equiv \frac{\int\limits_1^\rho \frac{dx}{x^2} \exp\left[-\frac{b}{2}\left(x^2 + \frac{2}{x} - 3\right)\right]}{\int\limits_1^\infty \frac{dx}{x^2} \exp\left[-\frac{b}{2}\left(x^2 + \frac{2}{x} - 3\right)\right]}, \tag{68a}$$

$$C(\rho, b) \equiv \frac{\int\limits_1^\rho \frac{dx}{x^2} \exp\left[-\frac{Db}{2\chi}\left(x^2 + \frac{2}{x} - 3\right)\right]}{\int\limits_1^\infty \frac{dx}{x^2} \exp\left[-\frac{Db}{2\chi}\left(x^2 + \frac{2}{x} - 3\right)\right]}. \tag{68\text{б}b}$$

Integrating Eq. (67) by parts, we find

$$\begin{aligned} \mu &= \exp(-\Gamma_0 \omega(1)) - 1 \\ &- \Gamma_0 \int\limits_1^\infty d\rho \rho^3 \exp(-\Gamma_0 \omega(\rho)) \frac{d\omega(\rho)}{d\rho}, \end{aligned} \tag{69}$$

where

$$\omega(1) = 1 + \gamma_0 \frac{(1 + \zeta_0)\ln(1 + \zeta_0)}{2\zeta_0} \frac{T_\mathrm{d} - T_0}{T_0}. \tag{70}$$

The main contribution to the integrand that represents μ in formula (69) at $b \ll 1$ is determined by a range of $\rho \geq b^{-1/2} \gg 1$, $\rho \geq \left(\frac{Db}{\chi}\right)^{-1/2} \gg 1$. Accordingly, the integration in Eq. (69) may be performed using the following approximate expression:

$$\begin{aligned} \frac{d\omega(\rho)}{d\rho} &= -\frac{\zeta_0 + 1 - \exp\left(\frac{q_0(T_\mathrm{d} - T_0)}{k_\mathrm{B} T_0^2}\right)}{\zeta_0} \\ &\times \frac{\exp\left(-\frac{b}{2}\rho^2\right)}{\rho^2} - \frac{\zeta_0 + 1}{\zeta_0}\left(1 + \gamma_0 \frac{\ln(1 + \zeta_0) k_\mathrm{B} T_0}{2q_0}\right) \\ &\times \frac{q_0(T_\mathrm{d} - T_0)}{k_\mathrm{B} T_0^2} \frac{\exp\left(-\frac{Db}{2\chi}\rho^2\right)}{\rho^2}. \end{aligned} \tag{71}$$

If b is so small that the conditions $\Gamma_0 b^{1/2} \ll 1$, $\Gamma_0 \left(\frac{Db}{\chi}\right)^{1/2} \ll 1$, are also fulfilled, $\exp(-\Gamma_0 \omega(\rho)) \approx 1$ may also be placed under the integral. As a result, with regard to definition $a_0 = (n_0 - n_\infty(T_0))/n_l(T_\mathrm{d})$ we obtain

$$\begin{aligned} \mu &\approx \exp(-\Gamma_0 \omega(1)) - 1 + \frac{\Gamma_0}{b} \\ &\times \left(\frac{a}{a_0} + \frac{\zeta_0 + 1}{\zeta_0 b} \frac{\chi q_0 (T_\mathrm{d} - T_0)}{D k_\mathrm{B} T_0^2}\left(1 + \gamma_0 \frac{\ln(1 + \zeta_0) k_\mathrm{B} T_0}{2q_0}\right)\right). \end{aligned} \tag{72}$$

Taking into account formulas (63) and (64), relation $\kappa = (c_g n_g + c n_0)\chi$ between the thermal conductivity coefficient and thermal diffusivity, and definitions of a and a_0, we have

$$\frac{\zeta_0+1}{\zeta_0}\frac{\chi q\left(T_\mathrm{d}-T_0\right)}{Dk_\mathrm{B}T_0^2} = \frac{\zeta_0+1}{\zeta_0}\frac{q^2}{k_\mathrm{B}T_0^2}\frac{\chi}{\kappa}\left(n_0-n_\infty\left(T_\mathrm{d}\right)\right) = \frac{a}{a_0}k'. \tag{73}$$

Substituting expression (73) into relation (72) and taking into account definition (23), we arrive at

$$\mu \approx \frac{\Gamma_0}{a_0}\left(1+k_0'\right)\left(1+\gamma_0\frac{k_0'}{k_0'+1}\frac{\ln\left(1+\zeta_0\right)}{2\beta_0}\right) = \frac{\Gamma_0'}{a_0}. \tag{74}$$

2.3. Characteristics that Take Place by the End of the Stage of Nucleation

Since coefficient μ is independent of supercritical particle size, the relation of volumes $V_\mathrm{ex}(t) = \mu V_R(t)$ obtained for one particle may be extended to the entire ensemble of supercritical particles. In other words, if the total volume of particles at time moment t is equal to V_l, the nucleation of new particles in the medium is suppressed in volume $V_\mathrm{ex}^\mathrm{tot} = \mu V_l$. Let the total system volume be equal to V. Then, the expression for volume V_1, in which initial nucleation rate I_0 (renormalized according to formula (3) by the thermal effects at the incubation stage) remains preserved until time moment t, may be written in the form of $V_1(t) \equiv V - \mu V_l(t)$. This volume satisfies the following integral equation [6–8]:

$$V_1(t) = V - \mu I_0\int_0^t dt_1 V_R(t-\tau)V_1(\tau), \tag{75}$$

where, according to relations (48) and (55), $V_R(t-\tau)$ has the form of

$$V_R(t-\tau) = \frac{4\pi}{3}R^3(t-\tau) = \frac{4\pi}{3}\left(2Db(t-\tau)\right)^{3/2}. \tag{76}$$

Remember that, upon nonisothermal nucleation, parameter b is, according to expression (62), related to droplet temperature T_d via parameter a, and monotonically increases with a rise in the latter. Strong thermal effects reduce parameter a, thereby decreasing the effect of nonstationarity.

As was shown in [8], the solution of Eq. (75) at the stage of nucleation has the following form:

$$\frac{V_1(t)}{V} = 1 - \frac{8\pi}{15}I_0\mu(2Db)^{3/2}t^{5/2}. \tag{77}$$

Since the stage of nucleation is completed when V_1 vanishes, characteristic time t_1^ex of the duration of this stage is, according to the excluded-volume theory, equal to

$$t_1^\mathrm{ex} = \frac{1}{2}\left(\frac{15}{4\pi\mu}\right)^{2/5}\left(\frac{1}{bD}\right)^{3/5}I_0^{-2/5}. \tag{78}$$

The total number of supercritical particles nucleated in unit volume over time t_1^ex is determined as

$$N\left(t_1^\mathrm{ex}\right) = I_0\int_0^{t_1^\mathrm{ex}}\frac{V_1(t')}{V}dt' = \frac{5}{7}\left(\frac{15}{8\pi\mu}\right)^{2/5}\left(\frac{I_0}{2bD}\right)^{3/5}. \tag{79}$$

The maximum value of the squared radius of a supercritical particle reached by the end of the stage of nucleation is

$$\left(R_\mathrm{max}^2\right)^\mathrm{ex} = 2Dbt_1^\mathrm{ex} = \left(\frac{15bD}{4\pi\mu I_0}\right)^{2/5}. \tag{80}$$

3. GENERAL CONCLUSIONS

First, let us compare the results of approaches to the stage of nucleation using the mean-field and excluded-volume approximations. As in Sections 1 and 2, we shall be interested in the key characteristics, including the duration of the stage t_1, the total number of nucleated supercritical particles N_1, the squared radius of the largest particle R_max^2, and the deviation of the particle temperature from the initial temperature of the medium $\Delta T_\mathrm{d} \equiv T_\mathrm{d} - T_0$. The values found under the mean-field and excluded-volume approximations will be denoted by superscripts mf and ex, respectively. Using relations (38) and (78), (41) and (79), (39) and (80), (30), and (62) we find

$$\frac{t_1^\mathrm{mf}}{t_1^\mathrm{ex}} = \left(\frac{ba_0^2}{a^3}\right)^{1/5}\left(\frac{\mu b}{\Gamma_0'}\right)^{2/5}, \tag{81}$$

$$\frac{N_1^\mathrm{mf}}{N_1^\mathrm{ex}} = \frac{7}{5}0.78\left(\frac{ba_0^2}{a^3}\right)^{1/5}\left(\frac{\mu b}{\Gamma_0'}\right)^{2/5}, \tag{82}$$

$$\frac{\left(R_\mathrm{max}^2\right)^\mathrm{mf}}{\left(R_\mathrm{max}^2\right)^\mathrm{ex}} = \left(\frac{aa_0}{b^2}\right)^{2/5}\left(\frac{\mu b}{\Gamma_0'}\right)^{2/5}, \tag{83}$$

$$\frac{\Delta T_\mathrm{d}^\mathrm{mf}}{\Delta T_\mathrm{d}^\mathrm{ex}} = \frac{a}{b\displaystyle\int_1^\infty\frac{dx}{x^2}\exp\left[-\frac{Db}{2\chi}\left(x^2+\frac{2}{x}-3\right)\right]}. \tag{84}$$

At a weak nonstationarity of diffusion and heat transfer in the course of the growth of supercritical new-phase particles, when $\Gamma_0 b^{1/2} \ll 1$, $\Gamma_0\left(\frac{Db}{\chi}\right)^{1/2} \ll 1$, and formulas (81)–(83), (63), (74), and (84) yield

$$\frac{t_1^\mathrm{mf}}{t_1^\mathrm{ex}} = \left(\frac{b}{a}\right)^{3/5}\left(\frac{\mu a_0}{\Gamma_0'}\right)^{2/5} \approx 1, \tag{85}$$

$$\frac{N_1^{\mathrm{mf}}}{N_1^{\mathrm{ex}}} = \frac{7}{5}0.78\left(\frac{b}{a}\right)^{3/5}\left(\frac{\mu a_0}{\Gamma_0'}\right)^{2/5} \approx 1.1, \tag{86}$$

$$\frac{\left(R_{\max}^2\right)^{\mathrm{mf}}}{\left(R_{\max}^2\right)^{\mathrm{ex}}} = \left(\frac{a}{b}\right)^{2/5}\left(\frac{\mu a_0}{\Gamma_0'}\right)^{2/5} \approx 1, \tag{87}$$

$$\frac{\Delta T_{\mathrm{d}}^{\mathrm{mf}}}{\Delta T_{\mathrm{d}}^{\mathrm{ex}}} \approx 1. \tag{88}$$

It can be seen that the results of the above-considered approaches almost coincide with each other for the stage of nucleation at slightly nonstationary diffusion and heat transfer upon the growth of supercritical particles, weak nonstationarity being provided by the fulfillment of the strong inequality $a^{1/2} \ll 1$. As a rule, this inequality takes place for nucleation in supersaturated vapors in the atmosphere of an incondensable gas, e.g., water vapor under normal conditions of the Earth's atmosphere. Moreover, the consideration in terms of the excluded-volume approximation illustrates the diffusion mixing at the stage of nucleation. At a rather weak nonstationarity, diffuse clouds surrounding particles begin to efficiently overlap already at the stage of nucleation, thereby providing the feasibility of describing the process in terms of the mean-field approximation.

A question may arise as to the applicability of the continual diffusion regime to describing the stage of supersaturated vapor nucleation in terms of both the mean-field and excluded-volume approximations. Actually, the critical size of a new-phase nucleus in a supersaturated vapor is, as a rule, very small, and both the incubation stage of nucleation, at which nearcritical droplets are formed in the vapor, and the initial growth of supercritical droplets may occur in the free-molecular regime or an intermediate regime with respect to the Knudsen numbers [23].

Continuous-medium approximation is justified for a vapor–gas mixture, provided that, by the end of the stage of nucleation, the characteristic size of particles is much larger than the mean free path of vapor molecules. Let us estimate the possibility of this condition being fulfilled in a specific case of water-vapor condensation in air. Let $T_0 = 298$ K and air pressure be atmospheric. In this case, the concentration of air molecules is $n_g = 2.46 \times 10^{25}\,\mathrm{m}^{-3}$ while the mean free path of vapor molecules is found to be $l = 8.7 \times 10^{-8}$ m. Then, based on formula (80) and with allowance for relation (63) for parameter b, expression (32) for parameter a, Eq. (64) for droplet temperature T_{d}, relation (74) for parameter μ, and definitions (23) and (19), let us consider the dependence of maximum droplet radius $\sqrt{\left(R_{\max}^2\right)^{\mathrm{ex}}} \equiv R_{\mathrm{m}}$ (simultaneously, it is also the characteristic droplet size) on the initial supersaturation of the condensable vapor ζ_0. Nucleation rate I_0 is calculated according to formulas (1)–(3) as

$$I_0 = \frac{v_T}{2}\left(\frac{\sigma(T_0)}{k_{\mathrm{B}}T_0}\right)^{\frac{1}{2}}\frac{n_\infty^2(T_0)(1+\zeta_0)^2}{(1+k_0)\,n_l(T_0)} \times \exp\left(-\frac{4}{27}\left(\frac{4\pi\sigma(T_0)}{k_{\mathrm{B}}T_0}\right)^3\left(\frac{3}{4\pi n_l(T_0)}\right)^2\frac{1}{\ln^2(1+\zeta_0)}\right) \tag{89}$$

using the following values of the parameters:

$$\alpha_c = 1,\;\; v_T = 525\ \mathrm{m/s},\;\; \sigma(T_0) = 0.072\,\mathrm{n/m},$$
$$n_\infty(T_0) = 7.57\times10^{23}\ \mathrm{m}^3,\;\; v_T^g = 413\ \mathrm{m/s},\;\; c_g = 3.5,$$
$$c = 4.07,\;\; \frac{q_0}{k_{\mathrm{B}}T_0} = 17.78,\;\; \gamma_0 = -4.74, \tag{90}$$
$$k_0 = k(n_0, T_0),\;\; D = 2.19\times10^{-5}\ \text{м}^2/\text{c},$$
$$\kappa = 2.62\times10^{-2}\ \mathrm{W/(m\,K)}.$$

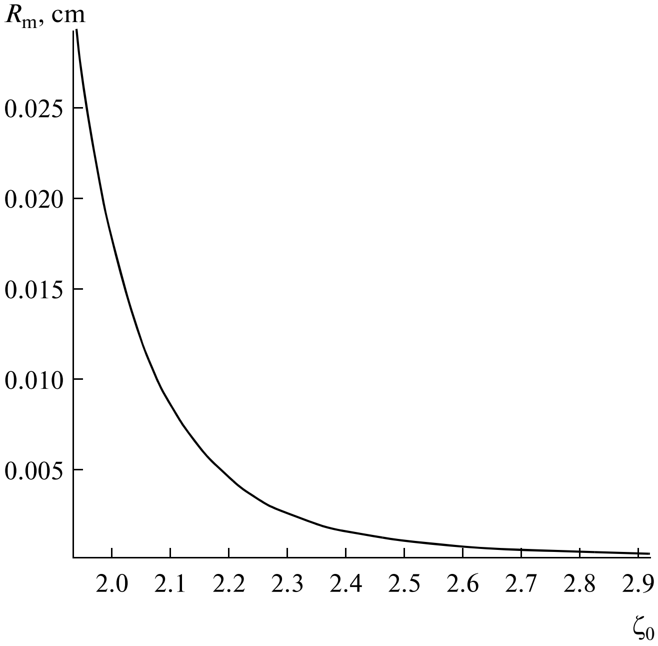

Fig. 1. Dependence of maximum droplet radius R_{m} on initial water-vapor supersaturation by the end of the stage of nucleation at $T_0 = 298$ K and $n_g = 2.46\times10^{25}$ m^{-3} (mean free path is $l = 8.7\times10^{-6}$ cm).

The calculated $R_{\mathrm{m}} = R_{\mathrm{m}}(\zeta_0)$ dependence is shown in Fig. 1. As the initial vapor supersaturation increases, the characteristic size of droplets formed by the end of the stage of nucleation monotonically decreases; i.e., at high supersaturations, many small droplets are formed. The $R_{\mathrm{m}} \gg l$ condition, which is necessary for the applicability of the continuous-medium approximation and continual diffusion regime of the growth

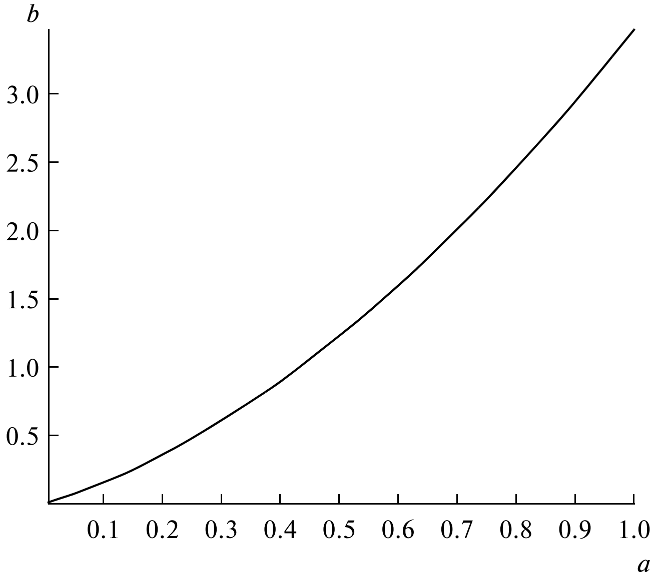

Fig. 2. Universal dependence of parameter *b* on nonstationarity parameter *a* for nonisothermal nucleation.

of supercritical droplets, is well fulfilled for the system under consideration in an initial supersaturation range of $\zeta_0 < 2.5$, therewith, the inequality $R_\mathrm{m}/l > 10^2$ takes place.

In conclusion, let us illustrate the behavior of parameter b and deviation ΔT_d of droplet temperature at a moderate nonstationarity of diffusion and heat transfer upon the growth of supercritical new-phase particles, this nonstationarity being realized at $a \sim 1$ (as has already been mentioned, this can hardly take place for nucleation in a vapor). Figure 2 demonstrates the universal dependence of parameter b on parameter a, this dependence resulting from the numerical solution of Eq. (60). It can be seen that the linear dependence between these parameters, which corresponds to asymptotics (63), takes place below nearly $a = 0.05$; at larger a values, the growth rate of parameter b increases. The result of the substitution of the obtained $b(a)$ dependence into expression (84) for $\Delta T_\mathrm{d}^\mathrm{mf}/\Delta T_\mathrm{d}^\mathrm{ex}$ depends, to a substantial extent, on the D/χ ratio between the diffusion coefficient of the metastable substance and the thermal diffusivity of the medium. If the $D/\chi = 1$, equality were to take place, then, as follows from formula (60), the $\Delta T_\mathrm{d}^\mathrm{mf}/\Delta T_\mathrm{d}^\mathrm{ex} = 1$ equality would be fulfilled at any a values. The behavior of the $\Delta T_\mathrm{d}^\mathrm{mf}/\Delta T_\mathrm{d}^\mathrm{ex}$ ratio as a function of parameter a is illustrated in Fig. 3 at $D/\chi = 1.131$ (water vapor in air) and $D/\chi = 0.01$ (solution separation).

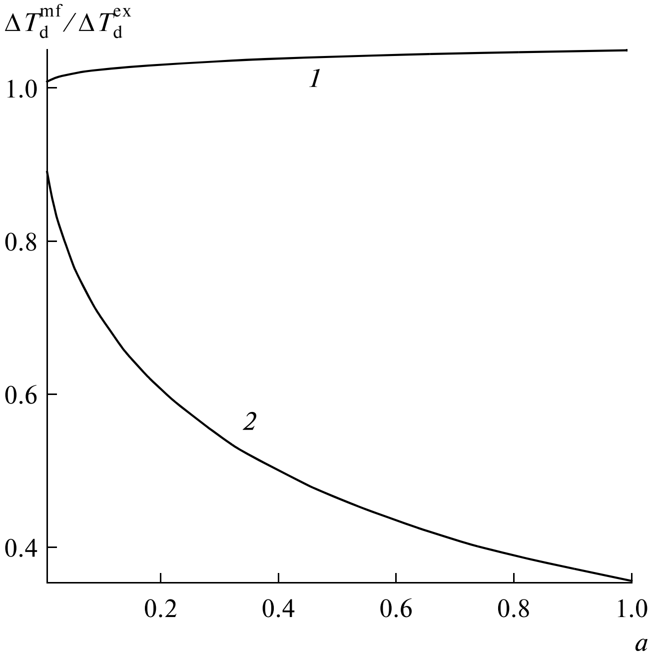

Fig. 3. Dependences of $\Delta T_\mathrm{d}^\mathrm{mf}/\Delta T_\mathrm{d}^\mathrm{ex}$ on nonstationarity parameter *a* for nonisothermal nucleation at $D/\chi = 1.131$ (*1*) and $D/\chi = 0.001$ (*2*).

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