

Influence of Vapor–Gas Medium Heating due to the Condensation Heat on the Stage of Multicomponent Droplet Nucleation

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Abstract—The article describes the effect of phase transition heat on the temperature of a closed multicomponent vapor–gas metastable phase and on growing supercritical droplets and their size distribution at the stage of homogeneous formation and growth (nucleation stage) of the supercritical droplets. It is assumed that, between essentially supercritical droplets and the vapor–gas medium, a stationary diffusion transfer of condensing vapor molecules and heat is established, and, then, both the composition and temperature remain unchanged and the same for all supercritical droplets. A set of equations is derived to determine the composition, temperature, and growth rate of the essentially supercritical droplets via the initial temperature and supersaturation of vapors. Expressions are obtained for the deviation of vapor–gas medium temperature from its initial value and for the droplet size distribution function as depending on time.

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INTRODUCTION

Rather many works have been devoted to studying the nonisothermal homogeneous nucleation in supersaturated vapors. Usually, when the thermal effects of the nonisothermal nucleation are in question, the role of heating of one-component droplets with near-critical sizes and the resulting thermal deceleration of the nucleation [1, 2], the heating, variations in the droplet composition, thermal deceleration of the growth of one- and multicomponent supercritical droplets under the conditions of stationary and nonstationary exchange of matter and heat with a vapor–gas medium [3–9], and the effect of the heat of the phase transition in a closed one-component metastable vapor–gas phase on growing supercritical droplets and their size distribution at the stage of homogeneous formation and growth (nucleation stage) of supercritical droplets [10–12] are discussed.

In this article, we would like to include the description of the thermal effects of nonisothermal condensation in a closed vapor–gas metastable phase into the theory of the nucleation stage of supercritical droplets in multicomponent vapors, which we have recently formulated in [13, 14]. Therewith, we shall not discuss the evolution of the distribution of multicomponent near-critical droplets under the conditions of nonisothermal condensation at the incubation stage of the development of a stationary nucleation rate, because we consider this problem as requiring a separate study. The establishment of stationary composition and temperature of essentially supercritical droplets together

with the establishment of stationary diffusion of vapors into growing droplets will serve as factors that greatly simplify the study of the nucleation stage of supercritical droplets.

1. INITIAL RELATIONS

Let an initial system contain k number of components of condensable vapors and a noncondensable passive gas. Initial concentrations of vapors $n_{i,0}$, passive gas concentration n_g , and initial absolute temperature T_0 of the vapor–gas mixture are considered to be preset parameters.

As arising supercritical droplets monotonically grow, vapor concentrations $n_i(t)$ decrease as functions of time t , and the heat generated by condensation increases temperature $T(t)$ of the vapor–gas medium. In this case, the rate of generation of new supercritical droplets gradually decreases due to a reduction in the supersaturation of condensing vapors and an increase in the temperature of the metastable phase. For the current values of vapor supersaturation $\zeta_i(t)$, we have

$$\zeta_i(t) = \frac{n_i(t) - \tilde{n}_i(T)}{\tilde{n}_i(T)}, \quad i = 1, 2, \dots, k, \quad (1)$$

where $\tilde{n}_i(T)$ is the temperature-dependent concentration of saturated vapor of an i th component near a planar surface of a pure liquid of this component.

Accordingly, for the initial values of the supersaturations, we have

$$\zeta_{i,0} = \frac{n_{i,0} - \bar{n}_i(T_0)}{\bar{n}_i(T_0)}, \quad i = 1, 2, \dots, k. \quad (2)$$

Nucleation rate J of multicomponent droplets may be written in the following form [13–16]:

$$J = Ce^{-\Delta F_c}, \quad (3)$$

where ΔF_c is the work formation of a critical droplet (the value of droplet formation work at the saddle point corresponding to an unstable equilibrium of the droplet with the multicomponent vapor–gas medium) and C is a pre-exponential factor that depends on the way of transition through the saddle point of the work, the temperature of near-critical droplets, and supersaturation of the vapors. This factor varies slightly with time at the nucleation stage. Expression for work ΔF_c has the following form [14]:

$$\Delta F_c(t) = \Delta F_c(\{\zeta\}, T) = \frac{16\pi\sigma^3(\{\zeta\}, T)\nu^2(\{\zeta\}, T)}{3(k_B T)^3}, \quad (4)$$

where k_B is the Boltzmann constant, while surface tension coefficient σ of the droplet and parameter ν depend on critical droplet composition, which is, in turn, determined by supersaturations $\{\zeta\} = (\zeta_1, \zeta_2, \dots, \zeta_k)$ of the vapors.

As has been shown in [14], to find molar fractions $\{x_c\} = (x_{1c}, x_{2c}, \dots, x_{kc})$ of the components in a critical droplet and parameter ν as depending on the supersaturations, the following set of nonlinear equations may be obtained:

$$x_{ic} = \frac{\zeta_i + 1}{\gamma_i(\{x_c\}, T)} \exp\left(-\frac{\nu_i(\{x_c\}, T)}{\nu}\right), \quad (5)$$

$$i = 1, 2, \dots, k.$$

$$\sum_{i=1}^k \frac{\zeta_i + 1}{\gamma_i(\{x_c\}, T)} \exp\left(-\frac{\nu_i(\{x_c\}, T)}{\nu}\right) = 1. \quad (6)$$

In these equations, $\nu_i(\{x_c\}, T)$ is the partial volume of an i th component in the droplet and $\gamma_i(\{x_c\}, T)$ is the corresponding activity coefficient.

We define relative variations in the supersaturations of the vapors at the nucleation stage as

$$\varphi_i(t) \equiv \frac{\zeta_{i,0} - \zeta_i(t)}{\bar{\zeta}_0}, \quad i = 1, 2, \dots, k, \quad (7)$$

where $\bar{\zeta}_0$ is the total supersaturation of the multicomponent vapor [13, 14]:

$$\bar{\zeta}_0 \equiv \sum_{i=1}^k (\zeta_{i,0} + 1) - 1. \quad (8)$$

Bearing in mind the smallness of the relative variations in supersaturations $\varphi_i(t) \ll 1$ and temperature $\Delta T/T_0 = (T - T_0)/T_0$ of the vapor–gas medium at the stage of nucleation, we may take

$$\Delta F_c(t) \approx \Delta F_{c,0} + \sum_i \Gamma_i \varphi_i(t) + \Gamma_T \frac{\Delta T(t)}{T_0}, \quad (9)$$

$$J(t) = J_0 \exp\left(-\sum_i \Gamma_i \varphi_i(t) - \Gamma_T \frac{\Delta T(t)}{T_0}\right). \quad (10)$$

Here $J_0 = J|_{\{\zeta_0\}, T_0}$ is the nucleation rate at the initial values of supersaturations and, ignoring the heating of the vapor–gas medium but taking into account the heating of the near-critical droplets, $\Delta F_{c,0} \equiv \Delta F_c|_{\{\zeta_0\}, T_0}$,

$$\Gamma_i = -\bar{\zeta}_0 \left(\frac{\partial \Delta F_c}{\partial \zeta_i} \right)_{\{\zeta_0\}, T_0}, \quad (11)$$

$$\Gamma_T = \left(\frac{\partial \Delta F_c(\{\zeta_0\}, T_0)}{\partial \ln T_0} \right)_{\{\zeta_0\}, T_0}. \quad (12)$$

As the supercritical droplet grows, its composition and temperature vary, and a stationary regime of the growth and heat exchange with the vapor–gas medium is gradually established. In this regime, both the droplet composition, which is characterized by a set of mole fractions $\{x = x_s\}$, and its temperature T_d remain further unchanged and the same for all supercritical droplets. If the time required to establish the stationary regime of droplet growth is short compared to the total duration of the nucleation stage (this will be the case, provided that the maximum droplet size is sufficiently large by the end of the nucleation stage), it may be approximately assumed that this regime is realized throughout the growth time of supercritical droplets. We shall use this approximation in our consideration in Section 2.

2. STATIONARY COMPOSITION $\{x_s\}$, TEMPERATURE T_d AND GROWTH RATE OF A SUPERCRITICAL DROPLET

Under the conditions of stationary diffusion of vapor particles, we have the following expression for the rate of variations in number N_i of particles of an i th component in a droplet with radius R [14]:

$$\begin{aligned} \dot{N}_i &= 4\pi R^2 D_i \frac{n_i(t) - \gamma_i(\{x_s\}, T_d) x_{is} \bar{n}_i(T_d)}{R} \approx \\ &\approx 4\pi R^2 D_i \frac{n_{i,0} - \gamma_i(\{x_s\}, T_d) x_{is} \bar{n}_i(T_d)}{R}, \end{aligned} \quad (13)$$

where it has been taken into account that $n_{i,0} - n_i(t) \ll n_{i,0} - \gamma_i(\{x_s\}, T_d) x_{is} \tilde{n}_i(T_d)$. We determine the total number of particles in the droplet with composition $\{x_s\}$ by relation

$$N_R = \sum_{i=1}^k N_i. \quad (14)$$

Accordingly,

$$N_i = x_{is} N_R, \quad \dot{N}_i = x_{is} \dot{N}_R, \quad (15)$$

$$\frac{\dot{N}_1}{x_{1s}} = \frac{\dot{N}_2}{x_{2s}} = \dots = \frac{\dot{N}_k}{x_{ks}}. \quad (16)$$

From Eqs. (16) and (13), we obtain

$$\begin{aligned} D_1 \left(\frac{n_{1,0}}{x_{1s}} - \gamma_1(\{x_s\}, T_d) \tilde{n}_1(T_d) \right) &= \dots = \\ &= D_k \left(\frac{n_{k,0}}{x_{ks}} - \gamma_k(\{x_s\}, T_d) \tilde{n}_k(T_d) \right). \end{aligned} \quad (17)$$

Now, we take into account that a good approximation for $\tilde{n}_i(T_d)$ at $\Delta T_d = T_d - T_0 \ll T_0$ is relation

$$\frac{\tilde{n}_i(T_d)}{\tilde{n}_i(T_0)} = e^{\frac{q_{i,0} \Delta T_d}{k_B T_0^2}}, \quad (18)$$

where $q_{i,0}$ is the heat of one molecule evaporation from a droplet of pure liquid of i th component at temperature T_0 . Substituting Eq. (18) into Eq. (17), we find

$$\begin{aligned} D_1 n_{1,0} \left(\frac{1}{x_{1s}} - \gamma_1(\{x_s\}, T_d) e^{\frac{q_{1,0} \Delta T_d}{k_B T_0^2}} \right) &= \dots = \\ &= D_k n_{k,0} \left(\frac{1}{x_{ks}} - \gamma_k(\{x_s\}, T_d) e^{\frac{q_{k,0} \Delta T_d}{k_B T_0^2}} \right) \end{aligned} \quad (19)$$

at

$$\sum_{i=1}^k x_{is} = 1. \quad (20)$$

Set (19), (20) includes k number of equations and is supplemented with the condition of stationary heat balance, which, for a growing individual droplet, has the following form:

$$\begin{aligned} \sum_{i=1}^k D_i \tilde{n}_i(T_0) \left(\zeta_{i,0} + 1 - \gamma_i(\{x_s\}, T_d) x_{is} e^{\frac{q_{i,0} \Delta T_d}{k_B T_0^2}} \right) &\times \\ &\times q_i(\{x_s\}, T_d) = \kappa \Delta T_d, \end{aligned} \quad (21)$$

where κ is the thermal conductivity coefficient of the vapor–gas medium and q_i is the partial heat of condensation of i th component from a growing supercritical droplet. Here, inequality $T(t) - T_0 \ll T_d - T_0$ has been taken into account. This inequality means that

the increase in the temperature of the vapor–gas medium is substantially lower than the increase in the temperature of the growing supercritical droplet.

As a result, Eqs. (19)–(21) compose the required complete set of equations for stationary composition $\{x_s\}$ and temperature T_d of the droplet. In the general case, this set requires the knowledge of the activity coefficients for the solution in the supercritical droplet, and, even under the approximation of an ideal solution, when more than two vapors condense, it can be solved only numerically.

Let us now find an expression for the stationary growth rate of an essentially supercritical droplet. For such a droplet, its radius R and total number N_R of condensate molecules in it are obviously related as

$$\frac{4\pi R^3}{3} = v_s(\{x_s\}, T_d) N_R, \quad (22)$$

where

$$v_s(\{x_s\}, T_d) = \sum_{i=1}^k x_{is} v_i(\{x_s\}, T_d), \quad (23)$$

$v_i(\{x_s\}, T_d)$ is the partial volume for molecules of an i th component in the droplet. Differentiating both sides of Eq. (22) with respect to time and taking into account Eqs. (14), (15), and (13), we obtain

$$R\dot{R} = D_i v_s(\{x_s\}, T_d) \frac{n_{i,0} - \gamma_i(\{x_s\}, T_d) x_{is} \tilde{n}_i(T_d)}{x_{is}}. \quad (24)$$

Using relation $n_{i,0} = \tilde{n}_i(T_0)(\zeta_{i,0} + 1)$, which follows from Eq. (2), and Eq. (18), we rewrite Eq. (24) as

$$\begin{aligned} R\dot{R} &= D_i v_s(\{x_s\}, T_d) \tilde{n}_i(T_0) \\ &\times \left(\frac{\zeta_{i,0} + 1}{x_{is}} - \gamma_i(\{x_s\}, T_d) e^{\frac{q_{i,0} \Delta T_d}{k_B T_0^2}} \right) \equiv \frac{A(\{x_s\}, T_d)}{2}, \end{aligned} \quad (25)$$

so that

$$R^2(t) = A(\{x_s\}, T_d) t. \quad (26)$$

We see that, as in the isothermal case, the squared radius of the multicomponent droplet grows linearly with time. Substituting solutions $\{x_s\}$ and ΔT_d of Eqs. (19)–(21) into functions $v_s(\{x_s\}, T_d)$ and $\gamma_i(\{x_s\}, T_d)$ and using relations (25) and (26), we can find numerically the radius of a growing droplet at any time moment of the nucleation stage. Upon isothermal nucleation, $\Delta T_d = 0$, and Eq. (25) is transformed into relation (4.30) presented in [3]. Note that, taking into account identity $\sum_{i=1}^k x_{is} = 1$, expression for $R\dot{R}$ may be equivalently rewritten as

$$R\dot{R} = v_s(\{x_s\}, T_d) \times \sum_{i=1}^k D_i \tilde{n}_i(T_0) \left(\zeta_{i,0} + 1 - \gamma_i(\{x_s\}, T_d) x_{is} e^{\frac{q_{i,0}\Delta T_d}{k_B T_0^2}} \right). \quad (27)$$

3. VARIATIONS IN VAPOR–GAS MEDIUM TEMPERATURE

Now, let us find an explicit expression for the temperature of the vapor–gas medium. We assume that all of the heat released upon vapor condensation is transferred into the vapor–gas medium. The corresponding heat balance is expressed as

$$\sum_{i=1}^k q_i(\{x_s\}, T_d)(n_{i,0} - n_i(t)) \approx \left(c_g n_g + \sum_{i=1}^k c_i n_{i,0} \right) k_B \Delta T(t), \quad (28)$$

where

$$\Delta T(t) = T(t) - T_0, \quad (29)$$

$T(t)$ is the current value of the vapor–gas medium temperature, and

$$c_g n_g + \sum_{i=1}^k c_i n_{i,0} \equiv c \quad (30)$$

is the specific heat of vapor–gas medium unit volume in the units of Boltzmann constant k_B . Taking into account Eq. (30), Eq. (28) is rewritten as

$$\frac{\Delta T(t)}{T_0} = \sum_{i=1}^k \frac{q_i(\{x_s\}, T_d)}{c k_B T_0} (n_{i,0} - n_i(t)). \quad (31)$$

Let us express $\Delta T(t)/T_0$ via the values of $\varphi_i(t)$. Using definitions (7) and (2) and Eq. (18), we, at $q_{i,0}\Delta T/k_B T_0^2 \ll 1$ derive

$$\begin{aligned} \varphi_i(t) &= \frac{1}{\zeta_0} \left(\frac{n_{i,0} - n_i(t)}{\tilde{n}_i(T_0)} + \frac{n_i(t)}{\tilde{n}_i(T_0)} - \frac{n_i(t)}{\tilde{n}_i(T)} \right) \\ &\approx \frac{1}{\zeta_0 \tilde{n}_i(T_0)} \left(n_{i,0} - n_i(t) + n_i(t) \left(1 - e^{-\frac{q_{i,0}\Delta T}{k_B T_0^2}} \right) \right) \\ &\approx \frac{1}{\zeta_0 \tilde{n}_i(T_0)} \left(n_{i,0} - n_i(t) + n_{i,0} \frac{q_{i,0}\Delta T}{k_B T_0^2} \right). \end{aligned} \quad (32)$$

Expressing difference $n_{i,0} - n_i(t)$ from relation (32) via $\varphi_i(t)$, we find

$$n_{i,0} - n_i(t) = \zeta_0 \tilde{n}_i(T_0) \varphi_i(t) - n_{i,0} \frac{q_{i,0}\Delta T}{k_B T_0^2}. \quad (33)$$

Substituting this result into Eq. (31), we obtain

$$\frac{\Delta T(t)}{T_0} = \sum_{i=1}^k \frac{q_i(\{x_s\}, T_d)}{c k_B T_0} \left(\zeta_0 \tilde{n}_i(T_0) \varphi_i(t) - n_{i,0} \frac{q_{i,0}\Delta T}{k_B T_0^2} \right). \quad (34)$$

Solving Eq. (34) with respect to $\Delta T(t)/T_0$, we arrive at

$$\begin{aligned} \frac{\Delta T(t)}{T_0} &= \frac{\zeta_0 \sum_{i=1}^k \tilde{n}_i(T_0) q_i(\{x_s\}, T_d) \varphi_i(t)}{k_B T_0 c + \sum_{i=1}^k n_{i,0} \frac{q_{i,0} q_i(\{x_s\}, T_d)}{(k_B T_0)^2}} \\ &= \zeta_0 \frac{\sum_{i=1}^k \tilde{n}_i(T_0) \beta_i \frac{q_i(\{x_s\}, T_d)}{q_{i,0}} \varphi_i(t)}{c + \sum_{j=1}^k n_{j,0} \beta_j^2 \frac{q_j(\{x_s\}, T_d)}{q_{j,0}}}, \end{aligned} \quad (35)$$

where

$$\beta_i \equiv \frac{q_{i,0}}{k_B T_0}. \quad (36)$$

Under approximation $q_i(\{x_s\}, T_d) \approx q_i(\{x_s\}, T_0)$, expression (35) is reduced to

$$\frac{\Delta T(t)}{T_0} \approx \zeta_0 \frac{\sum_{i=1}^k \tilde{n}_i(T_0) \beta_i \frac{q_i(\{x_s\}, T_0)}{q_{i,0}} \varphi_i(t)}{c + \sum_{j=1}^k n_{j,0} \beta_j^2 \frac{q_j(\{x_s\}, T_0)}{q_{j,0}}}. \quad (37)$$

Using relation (37), expression (10) for time-dependent nucleation rate $J(t)$ can be rewritten as

$$J(t) = J_0 \exp \left(- \sum_i \tilde{\Gamma}_i \varphi_i(t) \right), \quad (38)$$

where

$$\tilde{\Gamma}_i = \Gamma_i + \Gamma_T \zeta_0 \frac{\tilde{n}_i(T_0) \beta_i \frac{q_i(\{x_s\}, T_0)}{q_{i,0}}}{c + \sum_{j=1}^k n_{j,0} \beta_j^2 \frac{q_j(\{x_s\}, T_0)}{q_{j,0}}}. \quad (39)$$

4. BALANCE OF MULTICOMPONENT SUBSTANCE AND SIZE DISTRIBUTION OF SUPERCRITICAL DROPLETS

The size distribution function of essentially supercritical droplets may be represented as

$$f(R^2, t) = \int_0^t d\tau J(\tau) \delta(R^2 - R^2(t, \tau)), \quad (40)$$

where, according to relation (26),

$$R^2(t, \tau) = A(\{x_s\}, T_d)(t - \tau). \quad (41)$$

Substituting Eq. (41) into Eq. (40), we obtain

$$\begin{aligned} f(R^2, t) &= \int_0^t d\tau J(\tau) \delta(R^2 - A(\{x_s\}, T_d)(t - \tau)) \\ &= \int_0^t d\tau \delta(R^2 - A(\{x_s\}, T_d)\tau) J(t - \tau) \\ &= \frac{J\left(t - \frac{R^2}{A(\{x_s\}, T_d)}\right)}{A(\{x_s\}, T_d)}. \end{aligned} \quad (42)$$

Using expression (38) for nucleation rate $J(t)$ in Eq. (42), we have

$$\begin{aligned} f(R^2, t) &= \frac{J_0}{A(\{x_s\}, T_d)} \\ &\times \exp\left(-\sum_i \tilde{\Gamma}_i \varphi_i\left(t - \frac{R^2}{A(\{x_s\}, T_d)}\right)\right). \end{aligned} \quad (43)$$

The substance balance equation for an i th condensing component may be written as follows:

$$n_{i,0} - n_i(t) = \frac{4\pi}{3} \frac{x_{is}}{V_s(\{x_s\}, T_d)} \int_0^{R_m^2(t)} R^3 f(R^2, t) dR^2, \quad (44)$$

where $R_m^2(t) = A(\{x_s\}, T_d)t$ is the maximum droplet size at a time moment t (this is the radius of the droplets arising at the moment $t = 0$).

Following [10], let us introduce notation

$$\Psi_i(t) \equiv \frac{n_{i,0} - n_i(t)}{\zeta_0 \tilde{n}_i(T_0)}. \quad (45)$$

Employing notation (45) and expression (43) for $f(R^2, t)$ in (44), we rewrite the substance balance equation for the i th condensing component in the form of

$$\begin{aligned} \Psi_i(t) &= \frac{4\pi}{3} \frac{J_0}{A(\{x_s\}, T_d)} \frac{x_{is}}{\zeta_0 \tilde{n}_i(T_0) V_s(\{x_s\}, T_d)} \\ &\times \int_0^{R_m^2(t)} R^3 e^{-\sum_j \tilde{\Gamma}_j \varphi_j\left(t - \frac{R^2}{A(\{x_s\}, T_d)}\right)} dR^2. \end{aligned} \quad (46)$$

Now we need to express functions $\{\varphi(t)\}$ via functions $\{\Psi(t)\}$. Using relation (31) in expression (32), we derive

$$\begin{aligned} \varphi_i(t) &= \frac{n_{i,0} - n_i(t)}{\zeta_0 \tilde{n}_i(T_0)} \\ &+ \frac{n_{i,0}}{\zeta_0 \tilde{n}_i(T_0)} \frac{q_{i,0}}{k_B T_0} \sum_{j=1}^k \frac{q_j(\{x_s\}, T_d)}{c k_B T_0} (n_{j,0} - n_j(t)). \end{aligned} \quad (47)$$

Substituting notation (45) into Eq. (47) and using notations (36), we arrive at the sought relation

$$\varphi_i(t) = \sum_{j=1}^k \left(\delta_{ij} + \beta_i^2 \frac{n_{i,0} \tilde{n}_j(T_0) q_j(\{x_s\}, T_d)}{c \tilde{n}_i(T_0) q_{i,0}} \right) \Psi_j(t). \quad (48)$$

Taking into account Eq. (48), we rewrite $\sum_j \tilde{\Gamma}_j \varphi_j(t)$ as

$$\sum_i \tilde{\Gamma}_i \varphi_i(t) = \sum_j \Gamma'_j \Psi_j(t), \quad (49)$$

where

$$\Gamma'_j \equiv \sum_i \tilde{\Gamma}_i \left(\delta_{ij} + \beta_i^2 \frac{n_{i,0} \tilde{n}_j(T_0) q_j(\{x_s\}, T_d)}{c \tilde{n}_i(T_0) q_{i,0}} \right). \quad (50)$$

With regard to definition (39) for $\tilde{\Gamma}_i$, relation (50) can be written as

$$\begin{aligned} \Gamma'_j &= \sum_i \left(\Gamma_i + \Gamma_T \zeta_0 \frac{\tilde{n}_i(T_0) \beta_i \frac{q_i(\{x_s\}, T_0)}{q_{i,0}}}{c + \sum_{m=1}^k n_{m,0} \beta_m^2 \frac{q_m(\{x_s\}, T_0)}{q_{m,0}}} \right) \\ &\times \left(\delta_{ij} + \beta_i^2 \frac{n_{i,0} \tilde{n}_j(T_0) q_j(\{x_s\}, T_d)}{c \tilde{n}_i(T_0) q_{i,0}} \right). \end{aligned} \quad (51)$$

In the long run, Eq. (49) makes it possible to reduce relation (46) to closed set of equations for the $\Psi_i(t)$ functions:

$$\begin{aligned} \Psi_i(t) &= \frac{4\pi J_0}{3} \frac{x_{is} A^{3/2}(\{x_s\}, T_d)}{\zeta_0 \tilde{n}_i(T_0) V_s(\{x_s\}, T_d)} \\ &\times \int_0^t d\tau \tau^{3/2} \exp\left(-\sum_j \Gamma'_j \Psi_j(t - \tau)\right). \end{aligned} \quad (52)$$

It follows from here that

$$\begin{aligned} \sum_i \Gamma'_i \Psi_i(t) &= \frac{4\pi J_0 A^{3/2}(\{x_s\}, T_d)}{3 \zeta_0 V_s(\{x_s\}, T_d)} \\ &\times \sum_i \frac{x_{is} \Gamma'_i}{\tilde{n}_i(T_0)} \int_0^t d\tau \tau^{3/2} \exp\left(-\sum_j \Gamma'_j \Psi_j(t - \tau)\right). \end{aligned} \quad (53)$$

Confining ourselves to the first iteration in the solution of this equation, we find

$$\sum_i \Gamma'_i \Psi_i(t) \approx \frac{8\pi J_0 A^{3/2}(\{x_s\}, T_d)}{15 \zeta_0 V_s(\{x_s\}, T_d)} \sum_i \frac{x_{is} \Gamma'_i}{\tilde{n}_i(T_0)} t^{5/2}. \quad (54)$$

Substitution of relation (54) into expression (43) yields the required expression for the time-dependent drop-size distribution function in the form of

$$f(R^2, t) \approx \frac{J_0}{A(\{x_s\}, T_d)} \exp\left(-\frac{8\pi J_0 A^{3/2}(\{x_s\}, T_d)}{15\zeta_0 v_s(\{x_s\}, T_d)}\right) \times \sum_i \frac{x_{is} \Gamma'_i}{\tilde{n}_i(T_0)} \left(t - \frac{R^2}{A(\{x_s\}, T_d)}\right)^{5/2}. \quad (55)$$

Ignoring the thermal effects, parameters A and v_s are found under condition $T_d = T_0$, and, from Eq. (51), we have $\Gamma'_i = \Gamma_i$, so that distribution (55) is naturally reduced to the distribution obtained previously under the isothermal approximation [14] (unfortunately, relation (5.15) in [14] contains extra factor 2 in the denominator).

In the particular case of the condensation of a one-component vapor, relation (55) yields the expression for the distribution function that was obtained for this case in [11] under the condition of a stationary diffusion flux of a vapor (relation (37) in [11]). In the one-component case, expression (55) may be written as follows:

$$f(R^2, t) \approx \frac{J_0}{A(T_d)} \times \exp\left(-\frac{8\pi J_0 A^{3/2}(T_d)}{15\zeta_0 v_1(T_d)} \frac{\Gamma'}{\tilde{n}(T_0)} \left(t - \frac{R^2}{A(T_d)}\right)^{5/2}\right), \quad (56)$$

where $v_1(T_d)$ is the volume of a molecule in a droplet, and, for the value of $A(T_d)$, relation (25), yields expression $A(T_d) = 2Dv_1(T_d)(n_0 - \tilde{n}(T_d)) \equiv 2Da$. Further, we have relation $\zeta_0 \tilde{n}(T_0) v_1(T_d) = v_1(T_d)(n_0 - \tilde{n}(T_0)) \equiv a_0$. Parameters a and a_0 introduced in this way coincide with the corresponding parameters in [11]. As a result, expression (56) is rewritten as

$$f(R^2, t) \approx \frac{J_0}{2Da} \times \exp\left(-2^{5/2} \frac{4\pi a^{3/2}}{15a_0} \Gamma' J_0 D^{3/2} \left(t - \frac{R^2}{2Da}\right)^{5/2}\right). \quad (57)$$

In addition, for the parameter Γ' , relation (51) with regard to Eq. (2) yields

$$\Gamma' = \Gamma \left(1 + \beta^2 \frac{n_0}{c}\right) \left(1 + \frac{\Gamma_T}{\beta \Gamma} \frac{\zeta_0}{\zeta_0 + 11 + n_0 \beta^2 / c}\right). \quad (58)$$

Using expression (4) for the work of formation of a critical droplet and the definitions of parameters Γ and Γ_T , it is easy, in the one-component case under consideration, to ascertain that relation (58) between

Γ' and Γ is identical to the relation between the values of Γ'_0 and Γ_0 in [11] (expression (23) in [11]). Thus, relation (57) is indeed identical to the expression obtained earlier in [11] for the distribution function in the case of condensation of a one-component vapor (relation (37) in [11]).

CONCLUSIONS

We have derived thermodynamic equations and relations that completely describe the established composition, temperature, and diffusion growth rate of essentially supercritical droplets at the stage of non-isothermal phase transition, at which the homogeneous nucleation of supercritical droplets occurs in a closed metastable multicomponent vapor–gas phase. The parameters of these equations and relations are the initial supersaturations of the vapors and the initial temperature of the vapor–gas medium. Moreover, we have related the current variation in the temperature of the vapor–gas medium at the stage of nucleation to the initial values of the supersaturations and temperature of the medium. These results have enabled us to find the current distribution of supercritical droplets over their squared radii at the nucleation stage.

The relations obtained extend and supplement the general theoretical description of the stage of homogeneous nucleation in multicomponent supersaturated vapors [13, 14] for the case of nonisothermal nucleation.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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