Calculation and Analysis of Kinetic Characteristics of Droplet Nucleation on the Macroscopic Condensation Nuclei under the Conditions of Gradual Creation of the Metastable State in Vapor

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Abstract—The algorithm of the calculations of all principal kinetic characteristics of nucleation of supercritical droplets under the gradual creation of the metastable state in vapor (total number of emerging droplets, beginning time and duration of droplet emergence, and dimensions of droplets) was formulated. It was shown that under the given properties of the vapor–gas medium, the liquid condensing from it, as well as at given dimensions of condensation nuclei, the algorithm allows us to cover the entire range of the characteristic time of the creation of the metastable state in vapor and that of the initial concentration of the condensation nuclei admitted by the conditions of the theory applicability. It was elucidated that the macroscopicity of condensation nuclei results in more rigorous conditions of applicability. Based on the algorithm, numerical calculations demonstrated the ability of the theory proposed to make practical prospects in a rather wide range of external parameters of the theory. The theory was generalized for the case of the gradual creation, arbitrarily changing in time, of the metastable state in vapor.

INTRODUCTION

We continue the study [1] of the nucleation of supercritical droplets as it occurs when macroscopic nuclei act as the centers of droplet nucleation in vapor and when the metastable state in vapor is not created instantaneously, i.e., before condensation, but gradually in the condensation process. As was already mentioned [1], interest in macroscopic condensation nuclei is raised due to the fact that these particles can ensure vapor condensation at low supersaturations. As to the interest in the gradual and externally regulated creation of the metastable state in vapor, it is explained by the fact that such a regime enables us to control the development of the condensation process and even master it. Both macroscopic condensation nuclei and gradual creation of the metastable state in vapor are frequently encountered in nature.

We remind the reader that the thermodynamic foundations [2] of supercritical droplet nucleation on the macroscopic nuclei and the kinetic principles [3] of overcoming the activation barrier of droplet nucleation on such nuclei were used as the initial principles of the research performed in [1]. On the other hand, the research [1] was also based on the results of the kinetic theory of heterogeneous condensation under conditions of gradual creation of the metastable state in vapor developed in [4, 5]. The combination of the theories proposed in [2, 3] and [4, 5] enables us to take into account both nuclei macroscopicity and the gradual creation of the metastable state in vapor [1].

The aim of this paper is to elaborate on the developed theory [1] to such a level that all principal (from the practical viewpoint) kinetic characteristics of the nucleation of supercritical droplets may be adequately calculated with allowance made for the conditions of theory applicability. These calculations demonstrate that the theory suggested in [1] and employed in this paper enables us to formulate promising recommendations within a rather wide range of values of the external parameters of the theory encountered in practice despite the more rigorous conditions of its applicability at the macroscopicity of condensation nuclei, which was revealed below.

As in [1], we assume that the condensation nuclei are soluble in the droplets that originate on them and that the substance comprising nuclei consists of a surface-inactive material. Further, as in [1], we assume that the supercritical droplets, once they have originated, grow throughout the entire stage of their effective nucleation (the stage that is of interest to us) under the regime of free-molecule exchange between the droplet and the vapor. In our forthcoming communications, we will generalize the theory for cases of insoluble condensation nuclei and the growth of supercritical droplets outside the limits of the free-molecular regime. Finally, as in [1], all condensation nuclei are assumed to be identical. The possible direct generalization of the

theory substantiated in [1] for the case of polydisperse condensation nuclei will be discussed at the end of this paper.

1. INITIAL RELATIONSHIPS OF DROPLET NUCLEATION KINETICS

Let us summarize the relevant data [1–5] to the forthcoming exposition.

Let us denote the number of molecules (or ions) in condensation nucleus by v_n. If the condensation nuclei are macroscopic, then

$$v_n^{1/3} \gg 1. \tag{1.1}$$

The supersaturation of vapor, denoted by ζ, is defined by the equality

$$\zeta = (n/n_\infty) - 1, \tag{1.2}$$

where n is the number of vapor molecules per unit volume of the vapor–gas medium and n_∞ is the number of saturated vapor molecules per unit volume of this vapor.

Under the assumption that the condensation nucleus is readily soluble in the droplet, the nucleus must represent the solution of the nucleus substance in a liquid condensed from vapor. As shown in [2], the droplets that are surmounting the activation barrier of nucleation and, moreover, that have already surmounted it and now grow irreversibly are so large that the solution of the center-forming material in them is dilute, provided that condition (1.1) is true.

The threshold supersaturation of vapor ζ_{th}, above which the formation of supercritical droplets on condensation nuclei is barrierless, is [1, equation (1.3)]

$$\zeta_{th} = 2(2a)^{3/2}/27v_n^{1/2}, \tag{1.3}$$

where

$$a = (4\pi\sigma/kT)(3v/4\pi)^{2/3}. \tag{1.4}$$

Here, σ is the surface tension of a droplet, k is the Boltzmann constant, T is the temperature of the droplet and the surrounding vapor–gas medium at the stage corresponding to effective nucleation of supercritical droplets, and v is the molecular volume of the condensing liquid. As follows from (1.1) and (1.3),

$$\zeta_{th} \ll 1. \tag{1.5}$$

Let us describe the gradual creation of the metastable state in vapor by an increase in the ideal supersaturation Φ over the course of time. Ideal supersaturation Φ is defined by the equation

$$\Phi = (n_{tot}/n_\infty) - 1, \tag{1.6}$$

where n_{tot} is the total number of molecules of the condensing substance per unit volume of the vapor–gas medium, including the molecules within the droplets. Ideal supersaturation depends only on the external con-

ditions. We may implement external control over the development of supercritical droplet nucleation in time by setting an increase in the ideal supersaturation over the course of time, as was shown in [1, 4, 5]. Ideal supersaturation Φ, defined by equation (1.6), cannot be smaller than the actual supersaturation ζ, defined by equality (1.2), where n accounts for the vapor absorption by the droplets.

The most important kinetic characteristic of the condensation process is the total number of supercritical droplets originating during this process. The key factor in this case is the moment t_* [1, 4, 5] by which half the total number of supercritical droplets have appeared. If the metastable state of vapor is created gradually, the t_* moment is not known in advance. The higher the accuracy of its determination, the more adequate the theoretical prediction for the total number of supercritical droplets appearing during the condensation process. If the rate of the increase in the ideal supersaturation Φ over the course of time t is set externally, the t_* moment is unambiguously related to the ideal supersaturation Φ_* at this moment. Hereafter, the subscript (*) indicates the quantities at the moment t_*.

The Φ_* value of the ideal supersaturation Φ plays the role of a reference value in the theory [1, 4, 5] describing the effective nucleation of supercritical droplets under the conditions of gradual creation of the metastable state in vapor. Let us remind the reader how this value was found in [1] in the case of macroscopic condensation of the nuclei.

The intensity of supercritical droplet nucleation is very sensitive to the height of the activation barrier of nucleation; therefore, the nucleation of supercritical droplets is fully completed [1] as early as in the prethreshold range of vapor supersaturation ζ covering in the entire prethreshold range $0 < \zeta < \zeta_{th}$ of supersaturation ζ in the fairly narrow region with a width approximately equal to the distance from this region to the upper boundary of the prethreshold range. The reference value Φ_* falls just into the prethreshold range. Due to the proximity of this range to the threshold value ζ_{th} of supersaturation ζ for the case of macroscopic nuclei, we obtain with a high degree of accuracy

$$\Phi_* \approx \zeta_{th}. \tag{1.7}$$

[1, equality (2.8)]. The equality (1.7), containing the known value ζ_{th} on the right-hand side, enables us to simplify significantly the theory for the case of the gradual creation of the metastable state in vapor.

As follows from [1–5], let us denote the number of molecules that have condensed from vapor in a droplet by v. Regardless of the regime of mass exchange between the droplet and the vapor, we may always pass from the v variable (proportional to the droplet volume in the dilute solution of a substance comprising

nucleus) to some other variable ρ, which is such a function $\rho(v)$ of v that the rate of its increase $\dot{\rho}$ over the course of time t is independent of ρ (and v) for all supercritical droplets, but depends only on vapor supersaturation ζ. Passing to this variable, which is appropriate for our theory, we obtain

$$\dot{\rho} = \dot{\rho}(\zeta) \qquad (1.8)$$

[1, equality (3.1)]. Below, we refer to the ρ variable as the droplet size.

In accordance with [1], let us denote the duration of the stage corresponding to effective nucleation of supercritical droplets by Δt, and the maximal size (at the $\Delta \rho$ axis) of supercritical droplets that is reached by the end of this stage, by ρ. Evidently, the $\Delta \rho$ size also characterizes the width of the supercritical size spectrum at the ρ-axis. According to (1.8), all supercritical droplets "move" along the ρ-axis at the same rate; therefore, this spectrum (actually, each part of the spectrum that has been formed by the present moment) shifts along the ρ-axis as a whole without changing its shape. This is another important advantage of introducing ρ instead of v for describing the dynamics of supercritical droplet growth. For the Δt and $\Delta \rho$ values, we have the following estimates:

$$\Delta t \sim 1/(\dot{\rho})_* c \qquad (1.9)$$

and

$$\Delta \rho \sim 1/c \qquad (1.10)$$

[1, estimates (3.5) and (3.6)], where the dimensionless parameter c is defined by the equalities (3.2) and (3.4) [1] for the general case of arbitrary mass exchange between the droplets and the vapor and an increase in the ideal supersaturation with time. Parameter c accounts for the dependence between the height of the activation barrier of nucleation and vapor supersaturation in the vicinity of the $\zeta = \Phi_*$ value. Accounting for this dependence is important for the theory of droplet nucleation on the nuclei under the gradual creation of the metastable state in vapor.

As shown in [3], in spite of the constraint (1.1), the activation barrier of nucleation is almost always surmounted by the droplets under the free-molecule regime of the droplet-vapor mass exchange. Following from [1], let us assume that the same regime is preserved for supercritical droplets throughout the stage of their effective nucleation. In the next section, we will formulate the condition required for this assumption to be acceptable. An appropriate variable for describing the growth of a droplet over the course of time t at the rate which is independent of ρ (or v) for all supercritical droplets, but depends [in accordance with (1.8)] only on the vapor supersaturation ζ is the parameter

$$\rho = v^{1/3}, \qquad (1.11)$$

For the rate of an increase in a variable over the course of time, we obtain

$$\dot{\rho} = \alpha \zeta / \tau. \qquad (1.12)$$

where α is the condensation coefficient of vapor molecules, and τ is the characteristic time of the free path for a molecule in saturated vapor. This time is determined as

$$\tau = 12/[(36\pi)^{1/3} v^{2/3} n_\infty v_T], \qquad (1.13)$$

where v_T is the average thermal velocity of vapor molecules ($v^{2/3}$ is introduced to estimate the cross section of molecular collision). Like the n_∞ and a quantities introduced in (1.2) and (1.4), the α and τ values depend on the temperature of the droplets and the surrounding vapor-gas medium at the stage corresponding to effective nucleation of supercritical droplets. In section 6, we will show how to find this temperature.

A representative approximation for describing the external creation of the metastable state in vapor is the power approximation of the increase in the ideal supersaturation Φ over the course of time t:

$$\Phi = (t/t_\infty)^m. \qquad (1.14)$$

Following [1, 4, 5], let us take advantage of this approximation. It contains two independent positive parameters: the scaling time t_∞ and the exponent m. According to (1.14), the time t is taken with the reference to the moment corresponding to $\Phi = 0$. The generalization of the theory for the case of the gradual creation, arbitrarily changing in time, of the metastable state in vapor will be discussed in Section 5.

For parameter c at the free-molecular regime of the growth of supercritical droplets, the following approximate relationship was obtained in [1]

$$c \approx \frac{24}{6^{1/2}} \left(\frac{27}{2^{5/2}}\right)^{(m+1)/m} \frac{m\tau}{\alpha t_\infty} \frac{v_n^{(7m+3)/6m}}{a^{3(m+1)/2m}} \qquad (1.15)$$

[1, relation (4.14)].

In addition to parameter c, the dimensionless parameter h is important for the allowance of the dependence between the height of the activation barrier of nucleation and vapor supersaturation in the vicinity of the $\zeta = \Phi_*$ value. This parameter is defined as

$$h \approx \frac{27}{4^2 2^{5/2}} \left(\frac{2^{5/2}}{27}\right)^{3(m+1)/m} \frac{\eta(-\infty)}{n_\infty}$$
$$\times \left(\frac{\alpha t_\infty}{m\tau}\right)^3 \frac{a^{(6m+9)/2m}}{v_n^{(14m+9)/6m}} \qquad (1.16)$$

[1, relation (4.15)]. Here, $\eta(-\infty)$ denotes the initial concentration of condensation nuclei, that is, their number per unit volume of the vapor-gas medium at the beginning of the stage corresponding to effective nucleation of supercritical droplets.

The total number N of supercritical droplets that originate during condensation in a unit volume of the vapor-gas medium is expressed in terms of the h parameter by the equation [1, equation (4.9)]

$$N \approx \eta(-\infty)[1 - \exp(-1/h)]. \qquad (1.17)$$

We used in this equation, the sign of the approximate rather than the exact equality, because the relationship (1.16) is an approximation per se. At $h \gg 1$ and $h \ll 1$, equation (1.17) yields the formulas

$$N \approx \eta(-\infty)/h \quad (h \gg 1), \qquad (1.18)$$

and

$$N \approx \eta(-\infty) \quad (h \ll 1). \qquad (1.19)$$

According to (1.18), supercritical droplets in the $h \gg 1$ case consume only a very small fraction of the initial amount of condensation nuclei (each droplet consumes one such nucleus). On the other hand, according to (1.19), supercritical droplets in the $h \ll 1$ case consume almost the entire initial amount of condensation nuclei.

Using the results of the quantitative study of the size spectrum of supercritical droplets obtained in [4, 5], we can make estimates (1.9) and (1.10) more precise for the $h \gg 1$ and $h \ll 1$ cases by replacing them for the approximate equalities

$$\Delta t \approx 3/(\dot{\rho})_* c \quad (h \gg 1 \text{ or } h \ll 1), \qquad (1.20)$$

and

$$\Delta \rho \approx 3/c \quad (h \gg 1 \text{ or } h \ll 1). \qquad (1.21)$$

Our interest in the extreme $h \gg 1$ and $h \ll 1$ cases is explained both by their relative simplicity and physical clearness and by the fact that, for linear dependence between h and $\eta(-\infty)$ demonstrated by relationship (1.16), these situations may be encountered in practice for a wide range of the initial nucleus concentrations $\eta(-\infty)$ more often than the intermediate case where $h \sim 1$.

2. PARAMETRIZATION OF THE SCALING TIME OF THE INCREASE IN THE IDEAL SUPERSATURATION

Let us recall the conditions of applicability of the kinetic theory developed in [1] and employed in this work. It was revealed that out of all of the conditions only three are independent.

First, the condition [1, inequality (5.1)]

$$\Delta t/t_s \gg 1, \qquad (2.1)$$

where t_s is the time required for the establishment of the steady-state (actually, quasi-steady-state) regime of supercritical droplet nucleation. For the t_s time, we have the approximate equality [1, expression (5.2)]:

$$t_s \approx \left(\frac{3}{2}\right)^{7/2} \frac{\tau \, v_n^{4/3}}{\alpha \, a^2}. \qquad (2.2)$$

Condition (2.1) guarantees that the droplets are carried over the activation barrier of nucleation throughout the entire stage corresponding to the effective nucleation of supercritical droplets in the steady-state (to be more exact, quasi-steady-state) regime. As was elucidated in [1], condition (2.1) also guarantees that the reference

value Φ_* of ideal supersaturation actually lies in the prethreshold range of vapor supersaturation.

Secondly, this is the condition [1, inequality (5.9)]

$$\Delta \rho/\rho_l \ll 1. \qquad (2.3)$$

Here, ρ_l is the characteristic droplet size at the ρ-axis below which the mass exchange between the droplet and the vapor occurs in a free-molecular regime. For this size, the following estimate [1, equation (5.8)]

$$\rho_l \sim \alpha^{-1}(n_\infty + n_g)^{-1} v^{-1} \qquad (2.4)$$

is true, where n_g is the number of molecules of a passive gas per unit volume of the vapor–gas medium. Condition (2.3) states that the free-molecule growth of supercritical droplets occurs throughout the entire stage corresponding to the effective nucleation of supercritical droplets.

Finally, this is the condition [1, inequality (5.11)]

$$DN^{2/3}\Delta t \gg 1, \qquad (2.5)$$

where D is the diffusion coefficient of vapor molecules in the vapor–gas medium. Condition (2.5) guarantees that the state of vapor remains to be equilibrium (actually, quasi-equilibrium) within the entire stage corresponding to the effective nucleation of the droplets in spite of the vapor absorption by supercritical droplets.

Below, we confine ourselves to the consideration of the typical and (as was already noted) most widely encountered extreme practical situations, where $h \gg 1$ or $h \ll 1$. This consideration makes our speculations easier; however, in addition to the three conditions (2.1), (2.3), and (2.5), an account of the other two conditions determining the whole existence of such extreme situations ($h \gg 1$ or $h \ll 1$) is required.

The necessity to control all five aforementioned conditions complicates the calculations of the kinetic characteristics of nucleation directly from formulas (1.15)–(1.21). To simplify the calculations, it is appropriate to choose condition (2.1) as "principal" and then monitor the validity of the four remaining conditions.

With this aim, let us use as reference parameter the dimensionless parameter equal to $\Delta t/t_s$ in condition (2.1) instead of the scaling time t_∞ of the increase in the ideal supersaturation. Denoting this parameter by κ, we obtain:

$$\kappa = \Delta t/t_s. \qquad (2.6)$$

As before, we consider all remaining external parameters of the theory (except for the scaling time t_∞) as the initial parameters. As ascertained below, the reverse passage from the κ parameter to the t_∞ time in final results will not be unduly difficult.

From (1.20) and (2.2) with allowance for (1.3), (1.12), (1.15) and the approximate equality $\zeta_* \approx \zeta_{th}$, we obtain

$$\frac{\Delta t}{t_s} \approx \frac{2}{27}\left(\frac{2^{5/2}}{27}\right)^{1/m} \frac{\alpha t_\infty a^{(4m+3)/2m}}{m\tau \, v_n^{(4m+1)/2m}} \qquad (2.7)$$

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

Using relationship (2.7) in definition (2.6) and solving this equality with respect to t_∞, we obtain:

$$t_\infty \approx \frac{27}{2}\left(\frac{27}{2^{5/2}}\right)^{1/m}\frac{\kappa m\tau}{\alpha}\frac{v_n^{(4m+1)/2m}}{a^{(4m+3)/2m}} \tag{2.8}$$

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

This equation parametrizes the scaling time t_∞ by expressing it via the κ parameter and external parameters of the theory m, τ, α, v_n, and a. The linear dependence between the t_∞ time and the κ parameter makes it possible to pass readily from the κ parameter to the t_∞ time.

Substituting (2.8) into (1.15), (1.16), and (1.18), we obtain:

$$c \approx 3^{1/2}2\frac{1}{\kappa}\frac{a^{1/2}}{v_n^{5/6}} \quad (h \gg 1 \text{ or } h \ll 1), \tag{2.9}$$

$$h \approx \frac{27}{4}\kappa^3\frac{\eta(-\infty)}{n_\infty}\frac{v_n^{11/3}}{a^3} \quad (h \gg 1 \text{ or } h \ll 1), \tag{2.10}$$

and

$$N \approx \frac{4}{27}\frac{n_\infty}{\kappa^3}\frac{a^3}{v_n^{11/3}} \quad (h \gg 1). \tag{2.11}$$

Expression (1.19) for N at $h \ll 1$ does not require any transformations.

Further, substituting (2.2) into (2.6), we get:

$$\Delta t \approx \left(\frac{3}{2}\right)^{7/2}\frac{\kappa\tau}{\alpha}\frac{v_n^{4/3}}{a^2}. \tag{2.12}$$

Finally, substitution of (2.9) into (1.21) yields

$$\Delta\rho \approx \frac{3^{1/2}}{2}\kappa\frac{v_n^{5/6}}{a^{1/2}} \quad (h \gg 1 \text{ or } h \ll 1). \tag{2.13}$$

Note that the identical linear dependence of the Δt and $\Delta\rho$ values on the κ parameter represented by relationships (2.12) and (2.13) follows directly from (1.20), (1.21), and (2.6) and from the fact that $(\dot\rho)_*$ and t_s are independent of the κ parameter.

Relationships (2.8)–(2.13) reflect all the basic data on the kinetics of nucleation of supercritical droplets on macroscopic condensation nuclei via auxiliary parameter κ (introduced instead of the t_∞ time) and the external parameters of the theory additional to the t_∞ time.

Using (2.4), (2.11)–(2.13), and (1.19), we obtain

$$\frac{\Delta\rho}{\rho_l} \sim \frac{3^{1/2}}{2}\kappa\alpha(n_\infty + n_g)v\frac{v_n^{5/6}}{a^{1/2}} \tag{2.14}$$

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

$$DN^{2/3}\Delta t \approx \frac{3^{3/2}}{2^{13/6}}Dn_\infty^{2/3}\frac{\tau}{\kappa\alpha}\frac{1}{v_n^{10/9}} \quad (h \gg 1), \tag{2.15}$$

and

$$DN^{2/3}\Delta t \approx \left(\frac{3}{2}\right)^{7/2}D\eta^{2/3}(-\infty)\frac{\kappa\tau}{\alpha}\frac{v_n^{4/3}}{a^2} \quad (h \ll 1). \tag{2.16}$$

According to (2.6) and (2.14)–(2.16), conditions (2.1), (2.3), and (2.5) are written in terms of the κ variable as:

$$\kappa \gg 1, \tag{2.17}$$

$$k \ll \frac{2}{3^{1/2}}\frac{1}{\alpha(n_\infty + n_g)v}\frac{a^{1/2}}{v_n^{5/6}} \tag{2.18}$$

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

$$\kappa \ll \frac{3^{3/2}}{2^{13/6}}Dn_\infty^{2/3}\frac{\tau}{\alpha}\frac{1}{v_n^{10/9}} \quad (h \gg 1), \tag{2.19}$$

and

$$\eta^{2/3}(-\infty) \gg \left(\frac{2}{3}\right)^{7/2}\frac{\alpha}{D\tau}\frac{1}{\kappa}\frac{a^2}{v_n^{4/3}} \quad (h \ll 1). \tag{2.20}$$

In order to make monitoring of the values easier, we do not approximate numerical multipliers in our estimations of the order of magnitudes.

Additional conditions that determine the implementation of extreme situations, where $h \gg 1$ or $h \ll 1$, are written in accordance with (2.10) as:

$$\eta(-\infty) \gg \frac{4}{27}\frac{n_\infty}{\kappa^3}\frac{a^3}{v_n^{11/3}} \quad (h \gg 1), \tag{2.21}$$

and

$$\eta(-\infty) \ll \frac{4}{27}\frac{n_\infty}{\kappa^3}\frac{a^3}{v_n^{11/3}} \quad (h \ll 1). \tag{2.22}$$

Note that the m parameter of exponential approximation (1.14) remains only in relationships (2.7) and (2.8) and does not enter into relationships (2.9)–(2.22). This indicates that the κ variable introduced instead of the t_∞ time is preferable.

In conformity with definition (1.11), the $N(\Delta\rho)^3$ value estimates the number of vapor molecules contained in supercritical droplets by the end of the stage corresponding to their effective nucleation. From (2.11) and (2.13) and with allowance for (1.3), we have the following relationship for this quantity at $h \gg 1$:

$$N(\Delta\rho)^3 \approx (9/2)n_\infty\zeta_{th}/\Gamma \quad (h \gg 1), \tag{2.23}$$

where

$$\Gamma \approx (24/6^{1/2})v_n^{2/3}. \tag{2.24}$$

Equality (2.24) coincides with equality (4.12) from [1] for the Γ parameter. According to the physical meaning of the Γ parameter [1], we may state that when the vapor supersaturation ζ in the vicinity of the $\zeta = \Phi_*$ value is varied by about Φ_*/Γ, the intensity of the nucleation of supercritical droplets varies to a significant degree. It was shown in [1] that in the $h \gg 1$ case it is the absorption of vapor molecules by supercritical droplets that stops effective nucleation of these droplets; therefore, we see [with account for (1.2) and (1.7)] that the $n_\infty\zeta_{th}/\Gamma$ value in (2.23) estimates the number of vapor molecules absorbed by supercritical droplets at the stage corresponding to the effective nucleation of the droplets.

The established physical meaning of relationship (2.23) as the balance of the number of vapor molecules confirms the validity of the treatment performed in this section. Besides, relationship (2.23), together with equality (2.24), explains why the $N(\Delta\rho)^3$ value is independent of the κ parameter at $h \gg 1$.

Hence, the substantiated linear dependence of the Δt and $\Delta\rho$ values on the κ parameter at $h \gg 1$ and $h \ll 1$ supports the reciprocal cube dependence of the N value on the κ parameter at $h \gg 1$.

3. ALGORITHM OF CALCULATIONS OF THE KINETIC CHARACTERISTICS OF DROPLET NUCLEATION

Let us formulate the calculation algorithm for all principal kinetic characteristics of the nucleation of *supercritical droplets on macroscopic condensation nuclei during the gradual creation of the metastable state in vapor*. In this algorithm, we consider all external parameters of the theory (a, α, τ, n_∞, D, n_g, v, v_n, and m), except for the κ parameter (determining the scaling time t_∞) and initial concentration of condensation nuclei $\eta(-\infty)$, as the preset values. It is assumed that the κ parameter and concentration $\eta(-\infty)$ may be varied, however, within the conditions (2.17)–(2.22) of the theory applicability. Of course, this will broaden the possibility of the calculation algorithm and make it more efficient.

We begin our calculations with the determination of the ζ_{th} and t_s values by the formulas (1.3) and (2.2); the κ parameter and concentration $\eta(-\infty)$ do not enter into these formulas at all.

Further, using formula (2.8), we find the t_∞ value at $h \gg 1$ and $h \ll 1$.

Then, from equation (2.11), we calculate the N value at $h \gg 1$. At $h \ll 1$, the N value is given by formula (1.19).

The Δt value is calculated from formula (2.12) or directly from definition (2.6) and the already known t_s value.

Using formula (2.13), we determine the $\Delta\rho$ value at $h \gg 1$ and $h \ll 1$.

Finally, by the formula

$$t_* \approx t_\infty \zeta_{th}^{1/m} \tag{3.1}$$

following from (1.7) and (1.14) and from the already known ζ_{th} and t_∞ values, we calculate the t_* moment at the time taken (as accepted in the theory) with the reference to the moment corresponding by power approximation (1.14) to $\Phi = 0$. The t_{on} and t_{off} moments of the onset and the end of effective nucleation of supercritical droplets may be determined using the following approximate equalities:

$$t_{on} \approx t_* - \Delta t/2, \tag{3.2}$$

and

$$t_{off} \approx t_* + \Delta t/2. \tag{3.3}$$

In these equations, it was taken into account that the t_* moment is located [4, 5] almost at the middle part of the time interval corresponding to the effective nucleation of supercritical droplets. The generalization of formula (3.1) for the case of the gradual creation, arbitrarily changing in time, of the metastable state in vapor will be discussed in Section 5.

Let us analyze the variation of the κ parameter and concentration $\eta(-\infty)$, which is admitted by the conditions of the theory applicability.

To begin with, let us consider the case where $h \gg 1$. Condition (2.17) is the lower boundary of the κ parameter. On the contrary, conditions (2.18) and (2.19) are the upper boundaries of this parameter. The most rigorous of these conditions determines the upper admissible boundary of the κ parameter. In order to make conditions (2.18) and (2.19) consistent with condition (2.17), the inequalities

$$\frac{2}{3^{1/2}}\frac{1}{\alpha(n_\infty + n_g)v}\frac{a^{1/2}}{v_n^{5/6}} \gg 1 \quad (h \gg 1), \tag{3.4}$$

and

$$\frac{3^{3/2}}{2^{13/6}}Dn_\infty^{2/3}\frac{\tau}{\alpha}\frac{1}{v_n^{10/9}} \gg 1 \quad (h \gg 1) \tag{3.5}$$

should be fulfilled. Once inequalities (3.4) and (3.5) are fulfilled, we may begin with the calculations. The range of concentration $\eta(-\infty)$ variation admissible at $h \gg 1$ is determined by condition (2.21).

Let us turn now to the $h \ll 1$ case. As before, condition (2.17) and contrary condition (2.18) are the lower and the upper boundaries of the κ parameter. In order to make condition (2.18) consistent with condition (2.17), the inequality

$$\frac{2}{3^{1/2}}\frac{1}{\alpha(n_\infty + n_g)v}\frac{a^{1/2}}{v_n^{5/6}} \gg 1 \quad (h \ll 1), \tag{3.6}$$

which is similar to inequality (3.4), should be fulfilled. The range of concentration $\eta(-\infty)$ variation admissible

at $h \ll 1$ is determined by condition (2.20), which is the lower boundary of the $\eta(-\infty)$ value and by the contrary condition (2.22), which is the upper boundary of the $\eta(-\infty)$ concentration. The consistency of both these conditions is secured by the inequality

$$\kappa \ll \frac{3^{3/2}}{2^{13/6}} D n_\infty^{2/3} \frac{\tau}{\alpha} \frac{1}{v_n^{10/9}} \quad (h \ll 1). \tag{3.7}$$

Similarly to condition (2.19), this inequality is the upper boundary of the κ parameter, which is additional to constraint (2.18). In order to make condition (3.7) consistent with contrary condition (2.17), the inequality

$$\frac{3^{3/2}}{2^{13/6}} D n_\infty^{2/3} \frac{\tau}{\alpha} \frac{1}{v_n^{10/9}} \gg 1 \quad (h \ll 1), \tag{3.8}$$

which is similar to inequality (3.5), should be fulfilled. Once inequalities (3.6) and (3.8) are fulfilled, we may begin with the calculations. The most rigorous of conditions (2.18) and (3.7) determines the upper limit of the κ parameter variation. Note that, although conditions (2.19) and (3.7) are equivalent, they are based on different physical reasons.

Hence, both at $h \gg 1$ and $h \ll 1$, the range of admissible variation of the κ parameter is identical in the calculation algorithm. The wider this range, the weaker constraints (3.4) and (3.5) at $h \ll 1$, and, correspondingly, the weaker constraints (3.6) and (3.8) at $h \ll 1$. The range of the $\eta(-\infty)$ concentration variation is determined by inequality (2.21) at $h \gg 1$, whereas at $h \ll 1$, by inequalities (2.20) and (2.22) which are consistent because of constraint (3.7). The adherence to inequalities (2.21) or (2.20) may indicate which of these cases ($h \gg 1$ or $h \ll 1$) takes place in a particular process. Concentration $\eta(-\infty)$ is reflected only in formula (1.19) or inequalities (2.20)–(2.22).

The larger the v_n value, i.e., the more macroscopic the condensation nuclei, the more rigorous (at $h \gg 1$ and $h \ll 1$) conditions (2.18), (2.19), and (3.7) in determining the upper boundaries of the κ parameter, and [as is seen from (2.6) and (2.7)] the condition (2.17) is fulfilled less well. Note that this condition is the most necessary condition for the theory, and it was taken as the base for the calculation of the algorithm. The macroscopicity of condensation nuclei significantly simplifies the theory of heterogeneous nucleation of supercritical droplets at the gradual creation of the metastable state in vapor, thus resulting in more rigorous conditions of the theory applicability.

It follows from the discussion above that, for the theory to be applicable, the v_n value should not be too large. Moreover, the control of the criterion (1.1) of the macroscopicity of condensation nuclei and relevant smallness [due to condition (1.5)] of the threshold value of vapor supersaturation is a rather important factor for the calculation of the algorithm.

4. NUMERICAL CALCULATIONS OF THE KINETIC CHARACTERISTICS OF DROPLET NUCLEATION

Let us perform numerical calculations of all principal kinetic characteristics of the nucleation of supercritical droplets on macroscopic condensation nuclei at the gradual creation of the metastable state in vapor. We will adhere to the calculation algorithm formulated in the preceding section. During the calculations, we will analyze the results obtained and make some general conclusions.

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

$$a \approx 10, \quad \alpha \approx 10^{-1}, \quad n_\infty \approx 10^{23} \text{ m}^{-3}, \quad n_g \approx 10^{25} \text{ m}^{-3},$$

$$v \approx 10^{-29} \text{ m}^{-3}, \quad \tau \approx 10^{-6} \text{ s}, \tag{4.1}$$

$$D \approx 10^{-4} \text{ m}^2 \text{ s}^{-1}, \quad v_n \approx 10^3, \quad m \approx 1.$$

These data are rather realistic for a typical condensing liquid (for water and its vapor at ambient temperatures, as well as for passive gas at the pressures close to atmospheric values). So far, we will not specify the values of the κ parameter that determine the scaling time t_∞ and the values of initial concentration of condensation nuclei $\eta(-\infty)$, thus extending the calculation possibilities. The ranges of admissible variation of the κ parameter and the $\eta(-\infty)$ concentration we will determine somewhat later.

As is seen from (4.1), inequalities (3.4) and (3.5) are valid within rather large (and almost identical) excessive ranges. Conditions (2.18), (2.19), and (3.7) are almost equivalent and are virtually reduced to one and the same inequality $\kappa \ll 10^3$. In accordance with this inequality and condition (2.17), the range of variation of the κ parameter admitted by the algorithm is the interval

$$1 \ll \kappa \ll 10^3. \tag{4.2}$$

This range is sufficiently broad.

Using formulas (1.3) and (2.2) and allowing for (4.1), we obtain

$$\zeta_{th} \approx 2.1 \times 10^{-1}, \tag{4.3}$$

and

$$t_s \approx 4.1 \times 10^{-3} \text{ s}. \tag{4.4}$$

Further, by formula (2.8) with account for (4.1), we have

$$t_\infty \approx 6.5\kappa \text{ s} \quad (1 \ll \kappa \ll 10^3). \tag{4.5}$$

Hereafter, the range of possible variation of the κ parameter is governed by the double inequality (4.2).

The measurement units are indicated in the relationships for dimensional parameters.

Further, using (2.11) with the allowance made for (4.1), we obtain at $h \gg 1$:

$$N \approx 1.5 \times 10^{14} \kappa^{-3} \ \text{m}^{-3}. \tag{4.6}$$

At $h \gg 1$, the N value is given by formula (1.19).

By definition (2.6) and the t_s value determined according to (4.4), we obtain:

$$\Delta t \approx 4.1 \times 10^{-3} \kappa \ \text{s}. \tag{4.7}$$

Then, using formula (2.13) with allowance for (4.1), we find that

$$\Delta \rho \approx 8.7 \times 10 \kappa, \tag{4.8}$$

where $\Delta \rho$ is the dimensionless value.

Finally, by formula (3.1) and the ζ_{sh} and t_∞ values determined according to (4.3) and (4.4), we have

$$t_* \approx 1.4 \kappa \ \text{s} \tag{4.9}$$

taken at the time (as accepted in the theory) with the reference to the moment corresponding to $\Phi = 0$ according to power approximation (1.14). The determination of the t_{on} and t_{off} moments by formulas (3.2) and (3.3) and known [according to (4.7) and (4.9)] values of Δt and t_* is not difficult.

Equalities (4.3), (4.4), and (4.7) are valid irrespective of the value of the h parameter. Equalities (4.5), (4.8), and (4.9) are true at both $h \gg 1$ and $h \ll 1$. However, equality (4.6) is valid only at $h \gg 1$ [at $h \ll 1$, the N value is given by equality (1.19)].

According to (2.21) and (4.1), the admissible range of the $\eta(-\infty)$ concentration at $h \gg 1$ is determined by the inequality

$$\eta(-\infty) \gg 1.5 \times 10^{14} \kappa^{-3} \ \text{m}^{-3}. \tag{4.10}$$

According to (2.20), (2.22), and (4.1), the range of the $\eta(-\infty)$ concentration at $h \ll 1$ is determined by the double inequality

$$3.8 \times 10^9 \kappa^{-3/2} \ \text{m}^{-3} \ll \eta(-\infty)$$
$$\ll 1.5 \times 10^{14} \kappa^{-3} \ \text{m}^{-3}. \tag{4.11}$$

In view of relationship (1.19), the $\eta(-\infty)$ concentration and the number of supercritical droplets N lie in this range. It is apparent from (4.6) and (4.11) that, as the $\eta(-\infty)$ concentration lowers, i.e., as we pass from inequality (4.10) to double inequality (4.11), the number of supercritical droplets diminishes, although the ever increasing portion of condensation nuclei takes part in the nucleation of supercritical droplets. The conclusion about the decrease in the number of supercritical droplets N follows from (1.19), (2.11), and (2.22) and, in general, from the proposed theory.

Fulfillment of criterion (1.1) of the macroscopicity of condensation nuclei and condition (1.5) of the smallness of the threshold value of vapor supersaturation is indicated by the value of v_n (about 10^3) accepted in (4.1) and by equation (4.3).

According to (4.5), the scaling time t_∞ of the increase in ideal supersaturation, which (but not the auxiliary magnitude κ) is the external parameter of the theory, varies within a wide range $6.5 \ \text{s} \ll t_\infty \ll 6.5 \times 10^3 \ \text{s}$ that is very realistic in practice.

The values of the characteristics of droplet nucleation, which are represented by relationships (4.3), (4.4), and (4.7)–(4.9) seem to be also experimentally realistic. Possible experimental determination of the t_s time was discussed in [1]. According to relationships (4.5) and (4.7), the scaling time t_∞ of the creation of the metastable state in vapor is much longer than the Δt time of the duration of droplet nucleation. This conclusion is also valid for the theory proposed that might be proved by equalities (2.8) and (2.12).

The values of the most important of all kinetic characteristics (the total number N of the supercritical droplets originating in the volume unit of the vapor–gas medium) are given by relationship (4.6) at concentration $\eta(-\infty)$ of the condensation nuclei satisfying inequality (4.10) and by relation (1.19) at concentration $\eta(-\infty)$ of the condensation nuclei satisfying inequality (4.11). The range of possible values of N covered by relationship (4.6) is fairly wide and realistic. It is extended from $N \sim 10^6 \ \text{m}^{-3}$ (when constraint $\kappa \ll 10^3$ in (4.2) is still true) to $N \sim 10^{13} \ \text{m}^{-3}$ when constraint $\kappa \gg 1$ (4.2) is already fulfilled. Moreover, the range of concentration $\eta(-\infty)$ admitted by inequality (4.10) is also fairly wide and realistic.

At the same time, the range of possible values of the N number covered by formula (1.19) and that of concentration $\eta(-\infty)$ [coincided with the aforementioned range and admitted by double inequality (4.11)] are rather wide and realistic. Near the lower boundary of constraint (4.2), these ranges cover about five decimal orders beginning with values of about $10^8 \ \text{m}^{-3}$ and ending with those of about $10^{12} \ \text{m}^{-3}$. It is clear that at each value of the κ parameter satisfying constraint (4.2), the range of $\eta(-\infty)$ concentrations at $h \gg 1$ is not overlapped by the range of $\eta(-\infty)$ concentration at $h \ll 1$, because inequalities (4.10) and (4.11) are incompatible.

The kinetic behavior that is described by relationships (4.5)–(4.11) involving parameter κ (chosen instead of the scaling time t_∞ in the calculation algorithm) is as obvious as that involving dependence on time t_∞. Once we would like to pass from parameter κ to time t_∞, we should only solve linear relationship (4.5) with respect to κ and then substitute the result obtained into relationships (4.6)–(4.11).

The droplet radius R is a more appropriate experimental parameter than the droplet "size" ρ introduced by equality (1.11). In order to pass from ρ to R, we should only employ evident relation $R = (3v/4\pi)^{1/3}\rho$ in

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(4.8). Using the volume v accepted in (4.1), this relation is reduced to $R \approx 1.3 \times 10^{-10} \rho$ m.

The calculations performed demonstrated that regardless of more rigorous conditions of the theory applicability under the macroscopicity of condensation nuclei, the theory proposed in [1] and employed in this work makes it possible to make some predictions within a rather wide range of the values of the external parameters of the theory encountered in practice.

The nontrivial behavior of kinetic characteristics of the nucleation of supercritical droplets on macroscopic condensation nuclei at the gradual creation of the metastable state in vapor is caused by the nonlinear, non-stationary, and nonlocal (in time) character of the process of the nucleation of supercritical droplets. This behavior was described by the theory and illustrated by the calculations performed. It would be impossible to predict (even quantitatively) this behavior without studying the process dynamics that was carried out in [1, 4, 5].

The smallness of the vapor supersaturation in the prethreshold range is indicated from relationship (4.3) and the proximity of the prethreshold range of supersaturation to its threshold value ζ_{th}. The nucleation of supercritical droplets occurs just in this particular range; therefore, as was mentioned in the introduction, macroscopic nuclei are indeed the active stimulants of the vapor condensation at its low degrees of supersaturation. The high sensitivity of the kinetic characteristics of the condensation process to the scaling time t_∞ of the creation of the metastable state in vapor [demonstrated by relationships (4.5)–(4.9)] confirms the statement (expressed in introduction) on the possible control for the development of the condensation process and even its mastering at the gradual creation of the metastable state in vapor. The fixed value of parameter m in the time-dependent power law of the creation of metastable state in vapor [according to (4.1), assumed equal to unity] made it impossible to reveal (in the performed calculations) the dependence of the kinetic characteristics of the condensation process on this parameter. However, this dependence actually exists; it is indicated by equality (2.8).

5. GENERALIZATION OF THE THEORY FOR THE CASE OF ARBITRARY GRADUAL CREATION OF THE METASTABLE STATE IN VAPOR

The power approximation (1.14) of the increase in the ideal supersaturation Φ with time t was employed in [1, 4, 5] and in this work. This approximation was used from the moment when the ideal supersaturation Φ was equal to zero. This moment was taken as the reference moment $t = 0$. The moment t_* by which half the total number of supercritical droplets that originate during condensation had appeared was taken at the time axis with reference to this initial time t was determined by

formula (3.1). In this case, parameters t_∞ and m of approximation (1.14) were assumed to be preset values.

Approximation (1.14) is only important in both [1, 4, 5] and this work for the stage corresponding to effective nucleation of supercritical droplets, i.e., at $t_{on} < t < t_{off}$. At this stage, according to relationships (2.6) [1], the approximate equality

$$\Phi \approx \Phi_* \qquad (5.1)$$

is fulfilled with a high degree of accuracy. Hence, in view of (1.7), the relationship

$$\Phi \approx \zeta_{th} \qquad (5.2)$$

is also valid with a high degree of accuracy. The more macroscopic condensation nuclei, the more accurately relationships (5.1) and (5.2) are fulfilled. Hence, approximation (1.14) is quite appropriate at a rather low variation of the ideal supersaturation Φ provided at the stage corresponding to the effective nucleation of supercritical droplets by relationships (5.1) and (5.2).

Obviously, the stage corresponding to the effective nucleation of supercritical droplets is preceded by the preliminary stage when a metastable state in vapor is created externally but supercritical droplets have not yet appeared. At the arbitrary rate of external increase in ideal supersaturation in time, the approximation (1.14) can be invalid at the preliminary stage. However, due to relationships (5.1) and (5.2), an increase in the ideal supersaturation in time will be adequately described by approximation (1.14) at the stage corresponding to effective nucleation of the supercritical droplet when approximation (1.14) is used in the theory.

However, in this case, parameters t_∞ and m of approximation (1.14) will not be given in advance, but should be determined by the rate of an increase in ideal supersaturation Φ specified externally. Furthermore, the moment when ideal supersaturation Φ was actually equal to zero (denote this moment by t_0) will not coincide with moment $t = 0$ where, according to approximation (1.14), the ideal supersaturation Φ was equal to zero. Hence, moment t_0 should be determined together with parameters t_∞ and m at the time axis convenient for theoretical use where, according to approximation (1.14), $\Phi|_{t=0} = 0$. We may pass to time axis where time is taken with the reference to the onset of the creation of metastable state in vapor (which is more convenient from experimental standpoint) only after the determination of moment t_0. Once it is done, the position of approximation (1.14) at this axis will be determined.

Let us demonstrate how the values of t_∞, m, and t_0, as well as the t_* value are determined at the gradual creation, arbitrarily changing in time, of the metastable state in vapor. We will rely on speculations reported in [6], taking into account, however, that at the macroscopicity of condensation, nuclei relationship (1.7) (where the ζ_{th} value is known) is valid with a high degree of accuracy.

As before, we adhere to the time axis where, according to power approximation (1.14), $\Phi|_{t=0} = 0$; this axis

is convenient for the theory, however, it will be used only at the stage corresponding to the effective nucleation of supercritical droplets.

Hereafter, $\Phi(t)$ is recognized (unless otherwise stated) as the ideal supersaturation specified externally and arbitrary increasing with time. Hence

$$\Phi(t)|_{t = t_0} = 0. \tag{5.3}$$

Let us represent the ideal supersaturation $\Phi(t)$ as

$$\Phi(t) = \varphi(t - t_0), \tag{5.4}$$

where the $\varphi(t - t_0)$ function describes the "switching on" of the ideal supersaturation, i.e., its actual increase in time $t - t_0$ taken with the reference to the moment t_0 where ideal supersaturation $\Phi(t)$ was [in accordance with (5.3)] actually equal to zero. It is the $\varphi(t - t_0)$ function of inclusion of the ideal supersaturation that is employed to control externally the development of the nucleation process of supercritical droplets with time.

Further, we assume that the $\varphi(t - t_0)$ function is known, monotonic, and specified by the experiment, i.e., it satisfies the condition

$$\dot{\varphi}(t - t_0) > 0 \tag{5.5}$$

where the point denotes the derivative with respect to time. According to (1.7), (5.4), and condition $\Phi_* = \Phi|_{t = t_*}$, the equality

$$\varphi(t_* - t_0) = \zeta_{th} \tag{5.6}$$

is valid. Because of the high accuracy of relationship (1.7) at the macroscopicity of condensation nuclei we put in (5.6) the sign of exact (but not approximate) equality.

Let us choose the t_∞ and m parameters of approximation (1.14) so that at $t = t_*$, i.e., in the moment t_* most critical for the nucleation of supercritical droplets, this approximation would secure the actual values of the ideal supersaturation $\Phi(t)$ and its first $\dot{\Phi}(t)$ and second $\ddot{\Phi}(t)$ derivatives with respect to time. Taking into account (1.7), (5.4), (5.6), and condition $\Phi_* = \Phi|_{t = t_*}$, we arrive at:

$$(t_*/t_\infty)^m = \zeta_{th}, \tag{5.7}$$

$$m t_*^{m-1}/t_\infty^m = \dot{\varphi}(t_* - t_0), \tag{5.8}$$

and

$$m(m-1)t_*^{m-2}/t_\infty^m = \ddot{\varphi}(t_* - t_0). \tag{5.9}$$

Because of a rather high degree of relationship accuracy (1.7) at the macroscopicity of condensation nuclei, in (5.7) we used the sign of exact rather than approximate equality. Note that (5.7) is equivalent to (3.1).

When equalities (5.6)–(5.9) are fulfilled, approximation (1.14) will be fairly accurate at the stage corresponding to effective nucleation of supercritical nuclei. Correspondingly, the theory of the nucleation of supercritical droplets on the macroscopic condensation nuclei under the conditions of the gradual creation of the metastable state in vapor (which was proposed in [1] and employed in this work) will also be quite accurate. Inadequate (and purely formal) description of the actual increase in the ideal supersaturation with time will be displayed only in the fact that the initial (for the theory) moment $t = 0$ (when, according to approximation (1.14), $\Phi = 0$) cannot coincide with moment t_0 where, in conformity with (5.3), Φ is actually equal to zero. This description is made at the preliminary stage (which is insignificant for the creation of supercritical droplets) by approximation (1.14). Once the moment t_0 is determined, the passage from t to time $t - t_0$, which is more convenient for the experiment, will not be difficult.

Hence, the t_∞ and m parameters are not specified in advance, but are determined together with t_0 and t_* by the set of four equations (5.6)–(5.9) according to the known (from experiment) inclusion function $\varphi(t - t_0)$ of the ideal supersaturation. Let us solve these equations.

In view of inequality (5.5), equation (5.6) may be solved with respect to the $t_* - t_0$ difference, which is the function of ζ_{th} only:

$$t_* - t_0 = k(\zeta_{th}). \tag{5.10}$$

The introduced function k is reverse with respect to the φ function and is positive. It may be readily determined by the given function φ.

According to (5.10), the right-hand parts of equations (5.8) and (5.9) will also be functions of ζ_{th}. Let us divide these equations by equation (5.7) and introduce the $k_1(\zeta_{th})$ and $k_2(\zeta_{th})$ functions using definitions

$$\begin{aligned} k_1(\zeta_{th}) &= \zeta_{th}^{-1}\dot{\varphi}(k(\zeta_{th})), \\ k_2(\zeta_{th}) &= \zeta_{th}^{-1}\ddot{\varphi}(k(\zeta_{th})). \end{aligned} \tag{5.11}$$

Once the φ function is known, the $\dot{\varphi}$ and $\ddot{\varphi}$ derivatives together with the $k_1(\zeta_{th})$ and $k_2(\zeta_{th})$ functions will be also known. As a result,

$$m = k_1(\zeta_{th})t_*, \tag{5.12}$$

and

$$m(m-1) = k_2(\zeta_{th})t_*^2. \tag{5.13}$$

We need only to solve equations (5.7), (5.12), and (5.13) with respect to t_∞, m, and t_*. Dividing equation (5.13) by the square of equation (5.12), we obtain

$$m = \frac{k_1^2(\zeta_{th})}{k_1^2(\zeta_{th}) - k_2(\zeta_{th})}. \qquad (5.14)$$

Then, using (5.12), we also obtain

$$t_* = \frac{k_1(\zeta_{th})}{k_1^2(\zeta_{th}) - k_2(\zeta_{th})}. \qquad (5.15)$$

Finally, from (5.7) with allowance made for (5.14) and (5.15), we find that

$$t_\infty = \frac{k_1(\zeta_{th})}{k_1^2(\zeta_{th}) - k_2(\zeta_{th})} \zeta_{th}^{\frac{k_2(\zeta_{th}) - k_1^2(\zeta_{th})}{k_1^2(\zeta_{th})}}. \qquad (5.16)$$

As a result, formulas (5.10), and (5.14)–(5.16) enable us to determine the t_∞, m, t_0, and t_* values by the experimental data on the rate of external increase in the ideal supersaturation with time, i.e., the rate of the external creation of the metastable state in vapor.

As is apparent from (5.4), (5.11), and (5.14), the relationships $m < 1$ or $m > 1$ are predetermined by either delayed or accelerated growth of the ideal supersaturation with time in the vicinity of the moment $t = t_*$, i.e., by negative or positive values of the $k_2(\zeta_{th})$ function. In the case of an accelerated increase in the ideal supersaturation, for the positive value of m to become final, the following condition

$$k_1^2(\zeta_{th}) - k_2(\zeta_{th}) > 0 \qquad (5.17)$$

should be fulfilled. This condition will be accepted below.

According to (5.5) and (5.11), the inequality $k_1(\zeta_{th})$ is valid. Together with condition (5.17) and formulas (5.15) and (5.16), this inequality guarantees the fulfillment of intrinsic inequalities $t_* > 0$ and $t_\infty > 0$. However, in general, we can say nothing about the sign of this parameter, although relationship $t_* - t_0 > 0$ follows from (5.10) and inequality $k(\zeta_{th}) > 0$. It is obvious that when the ideal supersaturation increases with time rapidly at the preliminary stage, $t_0 > 0$. On the contrary, at a low increase in the ideal supersaturation at the preliminary stage, we should have $t_0 < 0$.

Let us follow the passage to the case when the power approximation (1.14) is valid throughout the entire period of the creation of the metastable state in vapor, i.e., when equality $\varphi(t - t_0) = (t/t_\infty)^m$ is true. Then, definitions stated in (5.10) and (5.11) yield the relationships

$$k(\zeta_{th}) = t_\infty \zeta_{th}^{1/m}, \quad k_1(\zeta_{th}) = \frac{m}{t_\infty} \zeta_{th}^{-1/m},$$

$$k_2(\zeta_{th}) = \frac{m(m-1)}{t_\infty^2} \zeta_{th}^{-2/m}. \qquad (5.18)$$

As might be expected, substitution of formulas (5.18) into formulas (5.10) and (5.14)–(5.16) results in equalities (3.1) and $t_0 = 0$; it also confirms that the t_∞ and m parameters actually coincide with the parameters of approximation (1.14) [equality $t_0 = 0$ is also directly indicated by (5.3)].

6. DISCUSSION OF THE RESULTS

Usually, an external increase in the ideal supersaturation over the course of time is caused by the adiabatic expansion of the vapor–gas medium. A one-to-one interrelation between an increase in the ideal supersaturation and a decrease in the temperature of the vapor–gas medium during its adiabatic expansion was revealed in [7]. This interrelation enables us to establish how the ideal supersaturation increases with the decreasing temperature of the vapor–gas medium. This interrelation also makes it possible to determine the temperature of the vapor–gas medium and the equal (under thermal equilibrium) temperature of the droplets at the stage corresponding to the effective nucleation of supercritical droplets, where the ideal supersaturation reaches the values defined with a high degree of accuracy by relationship (5.2).

An external increase in the ideal supersaturation over the course of time may be due to the "pumping" of vapor into the vapor–gas medium because of chemical (for example, photochemical) reactions that take place within it. If the pumping introduces a small amount of vapor (which is the only thing required for the condensation process to start at macroscopic condensation nuclei) and the fraction of passive gases in the vapor–gas medium is large, the temperatures of this medium and droplets will remain virtually constant in time. Accordingly, it will be the same at the stage corresponding to the effective nucleation of the supercritical droplets at the very beginning of the creation of the metastable state in vapor.

Hence, in both aforementioned cases, which are typical in practice, the temperatures of the vapor–gas medium and droplets may be easily found at the stage corresponding to the effective nucleation of supercritical droplets.

It was assumed in this work that all condensation nuclei are identical. As was shown in [1], in the actual case of initial polydisperse nuclei, only the rather narrow (by the relative width) (about $v_n^{-2/3}$) part of the initial size spectrum (adjacent to its upper boundary) is responsible for the effective nucleation of supercritical droplets due to the narrow prethreshold range of the vapor supersaturation, provided that the nuclei are mac-

roscopic. The generalization of this theory for this case is not difficult. It is only necessary to assume that the total nuclei concentration in the indicated upper part of their initial size spectrum is nothing but the $\eta(-\infty)$ value.

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