

# Diffusion Growth of Supercritical Droplets in the Theory of Their Nucleation on the Macroscopic Condensation Nuclei during Gradual Creation of the Metastable State in Vapor

F. M. Kuni, A. P. Grinin, A. K. Shchekin, and T. Yu. Novozhilova

Department of Theoretical Physics, Institute of Physics (Petrodvorets Branch), St. Petersburg State University, ul. Ul'yanovskaya 1, Petrodvorets, 198904 Russia

Received June 18, 1997

**Abstract**—The stage corresponding to effective droplet nucleation on the macroscopic condensation nuclei during the gradual creation of the metastable state in vapor was studied in a case when the diffusion growth of supercritical droplets prevails. The conditions of the applicability of the kinetic theory were analyzed. It was revealed that the macroscopicity of the condensation nuclei results in more severe conditions. The algorithm of the calculation of the all important kinetic characteristics of the droplet nucleation process, i.e., the total number of nucleating droplets, the time of the beginning of the droplet nucleation and the duration of this process, and the width of the droplet size spectrum, was formulated. It was shown that under the given properties of the vapor–gas medium and the liquid condensing from vapor, as well as at the given dimensions of the condensation nuclei, the algorithm allows us to cover the entire range of the characteristic times of the creation of the metastable state in vapor and the initial concentration of condensation nuclei admitted by the conditions of the applicability of the kinetic theory. Based on the algorithm, numerical calculations were performed demonstrating the ability of the proposed theory to make some interesting and practical predictions in a rather wide range of the values of the initial parameters. The factors were revealed, which determine the prevalence of the diffusion or free molecular absorption of vapor by the supercritical droplets at the stage corresponding to their effective nucleation at the given initial parameters of the theory. The ability to apply the theory to the case of polydisperse condensation nuclei was demonstrated.

## INTRODUCTION

We continue to study the stage corresponding to the effective nucleation of supercritical droplets on the macroscopic condensation nuclei during the gradual creation of the metastable state in vapor which was begun in [1–3]. The interest in macroscopic nuclei is 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.

We remind the reader what has already been accomplished in the study which we undertook earlier. In [1], we constructed the kinetic theory of condensation for macroscopic nuclei during the gradual creation of the metastable state in vapor. In its initial stage, this theory is not restricted by any regime of the exchange of matter between the droplets and the vapor. In the case where at the stage corresponding to the effective nucleation of supercritical droplets the free molecular growth of these droplets prevails, the theory constructed in [1] was elaborated to the form [2] enabling us to perform simple calculations of all practically relevant kinetic characteristics of the nucleation process of supercritical droplets. Typical kinetic times at the

stage corresponding to the effective nucleation of the supercritical droplets and the hierarchy of these times were established in [3]. This hierarchy enabled us to describe the stage corresponding to the effective nucleation of the supercritical droplets and to understand the complex multistep mechanism of this stage in the cases where the free molecular or the diffusion absorption of vapor by supercritical droplets prevail.

The main aim of this work is to formulate the algorithm of the calculations for the case of the prevalence of diffusion growth of the supercritical droplets at the stage corresponding to their effective nucleation and to perform (using this algorithm) numerical calculations of all practically relevant kinetic characteristics of droplet nucleation on the macroscopic condensation nuclei under the conditions of the gradual creation of the metastable state in vapor. The great deal of attention, which will be focused on the calculation algorithm and numerical calculations on the conditions of the applicability of this theory, is explained by the severity of these conditions at the macroscopicity of condensation nuclei that was elucidated in this work.

As in [1, 3], we consider the condensation nuclei to be soluble in nucleating droplets, whereas the substance comprising the nuclei is assumed to be the surface-inactive substance. The generalization of the kinetic theory to the case of the partially soluble or

insoluble condensation nuclei and to the case of surface activity of a substance comprising the nuclei will be made in forthcoming publications.

As in [1–3], in the main part of this paper we assume that all condensation nuclei are identical. The possibility of the generalization of the theory to the case of polydisperse condensation nuclei will be demonstrated at the end of this work.

## 1. INITIAL RELATIONSHIPS OF THE KINETICS OF DROPLET NUCLEATION

Let us denote the number of molecules (or ions) in a condensation nucleus by  $v_n$ . If the condensation nuclei are macroscopic, then  $v_n^{1/3} \gg 1$ .

The supersaturation of vapor, denoted by  $\zeta$ , is defined by the equality

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

where  $n$  is the number of vapor molecules per unit volume of the vapor-gas medium, and  $n_\infty$  is the number of molecules per unit volume of saturated vapor. For the threshold supersaturation  $\zeta_{th}$  of vapor above which the formation of droplets on condensation nuclei is barrierless, we have [1, equation (1.3)]

$$\zeta_{th} = 2(2a)^{3/2}/27v_n^{1/2}, \quad (1.2)$$

where

$$a = (4\pi\sigma/kT)(3v/4\pi)^{2/3}, \quad (1.3)$$

$\sigma$  is the surface tension of a droplet,  $k$  is the Boltzmann constant,  $T$  is the temperature of the droplets and the surrounding vapor-gas medium at the stage corresponding to effective nucleation of the supercritical droplets, and  $v$  is the molecular volume of the condensing liquid. At  $v_n^{1/3} \gg 1$ , we have the inequality  $\zeta_{th} \ll 1$ .

In the kinetic theory of supercritical droplet nucleation, the important parameter is the time required for the establishment of the steady-state (to be more exact, quasi-steady-state) regime of overcoming the activation barrier of droplet nucleation. According to formula (5.2) from [1], this time denoted by  $t_s$  is expressed as

$$t_s \approx \left(\frac{3}{2}\right)^{7/2} \frac{\tau v_n^{4/3}}{\alpha a^2}. \quad (1.4)$$

Here,  $\alpha$  is the condensation coefficient of the saturated vapor molecules, and  $\tau$  is the mean free time of saturated vapor molecules. This time is expressed by the equality

$$\tau = 12/[(36\pi)^{1/3} v^{2/3} n_\infty v_T], \quad (1.5)$$

where  $v_T$  is the average thermal velocity of the vapor molecules ( $v^{2/3}$  is introduced to estimate the cross section of molecular collision).

The number of molecules of matter condensed in a droplet from the vapor is denoted by  $v$ . As was shown earlier [4], when the condensation nuclei are macroscopic and the solubility of nuclei-forming matter in droplets is high, the solution of this matter is already rather dilute in the droplets overcoming the activation barrier of nucleation. Apparently, the solution will be even more dilute in droplets that have overcome this barrier. Then, for supercritical droplets with a high degree of accuracy, we have

$$v = 4\pi R^3/3v, \quad (1.6)$$

where  $R$  is the droplet radius.

Whatever the exchange regime for condensing matter between a droplet and vapor is, we always pass from the variable  $v$  to such a variable  $\rho$ , which is the function of  $v$  and increases in time for all supercritical droplets with a velocity that is independent of  $\rho$  (and of  $v$ ) and is determined only by the vapor supersaturation. In the case under consideration, when the diffusion growth of supercritical droplets prevails at the stage corresponding to their effective nucleation, an appropriate variable  $\rho$  for describing the behavior of supercritical droplets is given by the equality [3]

$$\rho = v^{2/3}. \quad (1.7)$$

The normalization of variable  $\rho$  is defined by (1.7), when  $\rho^{3/2}$  governs the number of molecules condensed in a droplet from vapor, is important for the forthcoming analysis.

The gradual creation of the metastable state in vapor is described by the law of the growth of ideal supersaturation  $\Phi$  with time determined by the equality

$$\Phi = (n_{tot}/n_\infty) - 1, \quad (1.8)$$

where  $n_{tot}$  is the total number of molecules of matter condensing in the unit volume of the vapor-gas medium, also including the molecules contained in droplets ( $n_{tot}$  is larger than  $n$  by the number of vapor molecules condensed by the droplets contained in the unit volume of the vapor-gas medium). The ideal supersaturation is dependent only on the external conditions of the creation of the metastable state in vapor. As in [1–3], we assume the power approximation

$$\Phi = (t/t_\infty)^m, \quad (1.9)$$

as the law of the growth of the ideal supersaturation with time. This equality contains two independent positive parameters, namely, the scaling time  $t_\infty$  and the exponent  $m$ . The time  $t$  is counted from the moment when according to power approximation (1.9)  $\Phi = 0$ . The approximation (1.9) will be significant only at the stage corresponding to the effective nucleation of the supercritical droplets, which is our main concern. It was shown [2] that this approximation is rather appropriate; it was also demonstrated [2] how the parameters  $t_\infty$  and  $m$  can be determined using the law (which was

set by experiment) of the creation of the metastable state in vapor.

The reference parameter in the kinetic theory [1, 2] is time moment  $t_*$  by which half the total number of supercritical droplets that originate during condensation have already appeared. This moment is expressed as [2, equation (3.1)]

$$t_* \approx t_\infty \zeta_{th}^{1/m}. \quad (1.10)$$

The total number of supercritical droplets that originate during condensation is the most important kinetic characteristic of this process. This number is referred to as the unit volume of the vapor-gas medium and is denoted by  $N$ . This quantity is expressed as [1, equation (4.9)]

$$N = \eta(-\infty)[1 - \exp(-1/h)]. \quad (1.11)$$

Here,  $\eta(-\infty)$  denotes the initial concentration of the 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 the supercritical droplets. The dimensionless parameter  $h$  describing the dependence of the activation energy of nucleation on vapor supersaturation is defined by the relationship (5.9) [3]

$$h = \frac{81\pi^{1/2}}{24^{1/4}32} \left(\frac{2^{5/2}}{27}\right)^{3(m+1)/2m} \times \frac{\eta(-\infty)}{n_\infty} \left(\frac{t_\infty}{m\tau_D}\right)^{3/2} \frac{a^{(3m+9)/4m}}{v_n^{(7m+9)/12m}}, \quad (1.12)$$

where  $\tau_D$  is the time characterizing the prevalence of the diffusion absorption of vapor. This parameter is defined by the equality

$$\tau_D = (3/8\pi)(4\pi/3v)^{1/3}/Dn_\infty, \quad (1.13)$$

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

At  $h \gg 1$  and  $h \ll 1$  from (1.11), we have

$$N \approx \eta(-\infty)/h \quad (h \gg 1), \quad (1.14)$$

and

$$N \approx \eta(-\infty) \quad (h \ll 1). \quad (1.15)$$

According to (1.14), supercritical droplets in the  $h \gg 1$  case consume only a very small fraction of the initial amount of the condensation nuclei (each droplet consumes one such nucleus). On the other hand, according to (1.15), in the  $h \ll 1$  case, supercritical droplets consume almost the entire initial amount of the condensation nuclei. Extreme cases ( $h \gg 1$  and  $h \ll 1$ ) are of interest due to both their comparative simplicity and physical clearness, as well as due to the fact that, at linear dependence of the  $h$  parameter on  $\eta(-\infty)$  demonstrated by relationship (1.12), these situations occur within the entire wide range of the initial nuclei con-

centration  $\eta(-\infty)$  much more often than the intermediate situation when  $h \sim 1$ .

In the kinetic theory of nucleation of supercritical droplets the important parameter is also the time period  $\Delta t$  of the duration of the stage corresponding to the effective nucleation of the supercritical droplets. This time is estimated as [3, equation (5.14)]

$$\Delta t \approx \frac{6^{1/2}}{8} \left(\frac{2^{5/2}}{27}\right)^{1/m} \frac{t_\infty a^{3/2m}}{m v_n^{(4m+3)/6m}} \quad (1.16)$$

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

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

According to [2], let us pass from the scaling time  $t_\infty$  of an increase in the ideal supersaturation to the dimensionless parameter equal to the  $\Delta t/t_*$  quantity. Denoting this parameter by  $\kappa$ , we have

$$\kappa = \Delta t/t_*. \quad (2.1)$$

Although, contrary to the time  $t_\infty$ , the  $\kappa$  parameter is not the key parameter, which seems to be more appropriate (as in [2]) for the theory. As we will see below, the converse passage from the parameter  $\kappa$  to the time  $t_\infty$  does not at all affect the final results.

Deriving from (1.4) and (1.16) relationship

$$\frac{\Delta t}{t_*} \approx \frac{1}{2^{3/2}} \left(\frac{2^{5/2}}{27}\right)^{(m+1)/m} \frac{\alpha t_\infty a^{(4m+3)/2m}}{m\tau v_n^{(4m+1)/2m}} \quad (2.2)$$

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

solving this expression with respect to  $t_\infty$  and taking into account definition (2.1), we obtain the equation

$$t_\infty \approx 2^{3/2} \left(\frac{27}{2^{5/2}}\right)^{(m+1)/m} \frac{\kappa m \tau v_n^{(4m+1)/2m}}{\alpha a^{(4m+3)/2m}} \quad (2.3)$$

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

which expresses the scaling time  $t_\infty$  via the parameter  $\kappa$  and the external parameters  $m$ ,  $\tau$ ,  $\alpha$ ,  $v_n$ , and  $a$  of a theory. The linear dependence of the  $t_\infty$  time on the  $\kappa$  parameter enables us to pass easily from the parameter  $\kappa$  to the time  $t_\infty$ .

Substituting (2.3) into (1.12), we find

$$h \approx \frac{81\pi^{1/2}}{2^{7/2}3^{1/4}} \frac{\eta(-\infty)}{n_\infty} \left(\frac{\kappa\tau}{\alpha\tau_D}\right)^{3/2} \frac{v_n^{29/12}}{a^{9/4}} \quad (2.4)$$

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

From (1.14) and (2.4) we obtain

$$N \approx \frac{2^{7/2}3^{1/4}}{81\pi^{1/2}} n_\infty \left(\frac{\alpha\tau_D}{\kappa\tau}\right)^{3/2} \frac{a^{9/4}}{v_n^{29/12}} \quad (h \gg 1). \quad (2.5)$$

As is seen, at  $h \gg 1$ , the number of droplets  $N$  is independent of the concentration  $\eta(-\infty)$  [at  $h \ll 1$ , the number of droplets  $N$  is set by relationship (1.15)].

In the theory of nucleation of supercritical droplets, the width of the droplet size spectrum is also an important parameter. Obviously, this parameter (as independent of time) may be valid only at the  $\rho$ -axis, which moves with time at the same (at each present moment) rate for all the supercritical droplets. According to relationship (7.16) [3], the width of the supercritical droplet size spectrum (denoted by  $\Delta\rho$ ) at the  $\rho$ -axis, which is introduced by means of (1.7), is defined as

$$\Delta\rho \approx \frac{3^{1/2} \kappa \tau v_n^{5/6}}{2 \alpha \tau_{D a}^{1/2}} \quad (h \gg 1 \text{ or } h \ll 1). \quad (2.6)$$

In this formula, we took into account definition (2.1).

Note that the  $m$  parameter of the power approximation (1.9) remained only in relationships (2.2) and (2.3) and is not present in expressions (2.4)–(2.6), thus indicating the advantage of the  $\kappa$  variable introduced instead of the  $t_\infty$  time.

In accordance with definition (1.7), the  $N(\Delta\rho)^{3/2}$  quantity estimates the number of vapor molecules contained in the supercritical droplets by the end of the stage corresponding to effective nucleation. From (2.5) and (2.6) and with an allowance made for (1.2) at  $h \gg 1$ , we obtain for this quantity the following relationship

$$N(\Delta\rho)^{3/2} \approx (3^{1/2} 4/\pi^{1/2}) n_\infty \zeta_{th}/\Gamma \quad (h \gg 1), \quad (2.7)$$

where

$$\Gamma = (24/6^{1/2}) v_n^{2/3}. \quad (2.8)$$

The equality (2.8) coincides with the equality (4.12) from [1] for the parameter  $\Gamma$ . According to the physical meaning of the parameter  $\Gamma$  [1] and the conditions of the beginning and the termination of the stage corresponding to the effective nucleation of supercritical droplets, the  $n_\infty \zeta_{th}/\Gamma$  in (2.7) estimates the number of vapor molecules consumed at this stage by the supercritical droplets.

Hence, the relationship (2.7) has the significance of being the balance equation for the number of vapor molecules. The validity of the theory, which we developed, is verified by the fact that this equation is fulfilled within the framework of this theory. In particular, the fact that the right-hand part of equation (2.7) is independent of the  $\kappa$  parameter [which is demonstrated by expressions (1.2) and (2.8)] confirms the agreement between the dependences of the  $N$  and  $\Delta\rho$  quantities on this parameter. The latter dependence is set by relationships (2.5) and (2.6) and is proportional to  $\kappa^{-3/2}$  and  $\kappa$ , respectively.

### 3. CONDITIONS OF THE APPLICABILITY OF KINETIC THEORY

It was revealed earlier [3] that only three conditions of the applicability of the kinetic theory are independent.

First, this is condition  $t_s \ll \Delta t$ , securing the steady-state (actually, quasi-steady-state) regime of overcoming (by droplets) the activation barrier of nucleation during the entire stage corresponding to the effective nucleation of supercritical droplets. Making an allowance for definition (2.1), the condition  $t_s \ll \Delta t$  may be written as

$$\kappa \gg 1. \quad (3.1)$$

Second, the  $t_{rel} \ll \Delta t$  condition provides the quasi-steady-state of vapor during the entire stage corresponding to effective nucleation of supercritical droplets. Here,  $t_{rel}$  is the time required for the establishment of this state. With respect to definition (2.1), the condition  $t_{rel} \ll \Delta t$  in its disclosed form is reduced to the inequalities [3, inequality (7.8)]

$$\frac{3^{5/3} \pi}{2^{7/2}} \frac{1}{(n_\infty v)^{1/3}} \frac{1}{a^{1/2} v_n^{5/18}} \gg 1 \quad (h \gg 1) \quad (3.2)$$

and [3, inequality (7.7)]

$$\eta^{2/3}(-\infty) \gg \left(\frac{2}{3}\right)^{7/2} \frac{1}{\pi^2} \frac{\alpha a^2}{D \kappa \tau v_n^{4/3}} \quad (h \ll 1), \quad (3.3)$$

which was expressed as the restriction on the concentration  $\eta(-\infty)$  of the condensation nuclei. We approximated the numerical factors in order to follow them more easily.

Finally, the  $\Delta\rho/\rho_l \gg 1$  condition provides the prevalence of the diffusion growth of the supercritical droplets at the stage corresponding to effective nucleation. Here,  $\rho_l$  is the characteristic droplet size at the  $\rho$ -axis introduced by equation (1.7), above which the mass exchange between the droplet and vapor occurs by the diffusion mechanism. With account for definition (2.1), the  $\Delta\rho/\rho_l$  condition at  $h \gg 1$  and  $h \ll 1$  is reduced to inequality [3, inequality (7.18)]

$$\kappa \gg \frac{3^{5/6}}{2^{8/3} \pi^{1/3}} \frac{1}{\alpha(n_\infty + n_g)} \frac{a^{1/2}}{v_n^{5/6}}, \quad (3.4)$$

which was expressed as the restriction on the  $\kappa$  parameter. The number of the molecules of passive gas per unit volume of the vapor-gas medium was denoted by  $n_g$ .

Although the treatment of extreme conditions, where  $h \gg 1$  or  $h \ll 1$ , simplifies the theory, it suggests, in addition to the aforementioned conditions, the fulfillment of two additional conditions that determine the implementation of these same extreme situations. As is apparent from (2.4), these conditions are reduced, respectively, to inequalities

$$\eta(-\infty) \geq \frac{2^{7/2} 3^{1/4}}{81 \pi^{1/2}} n_{\infty} \left( \frac{\alpha \tau_D}{\kappa \tau} \right)^{3/2} \frac{a^{9/4}}{v_n} \quad (h \geq 1), \quad (3.5)$$

$$\eta(-\infty) \leq \frac{2^{7/2} 3^{1/4}}{81 \pi^{1/2}} n_{\infty} \left( \frac{\alpha \tau_D}{\kappa \tau} \right)^{3/2} \frac{a^{9/4}}{v_n^{29/12}} \quad (h \leq 1), \quad (3.6)$$

imposing additional [to inequality (3.3)] restrictions on the concentration  $\eta(-\infty)$  of the condensation nuclei. As a result, the concentration  $\eta(-\infty)$  appears only in inequalities (3.3), (3.5), (3.6), and in the relationship (1.15).

Let us analyze the conditions of the applicability of the kinetic theory formulated above. Let us begin with the case  $h \geq 1$ . Here, these conditions are reduced to inequalities (3.1), (3.2), (3.4), and (3.5). The inequality (3.2) is independent of both the  $\kappa$  parameter and the concentration  $\eta(-\infty)$ . Moreover, inequalities (3.1) and (3.4) are the lower limits of the  $\kappa$  parameter. It is the most severe out of these restrictions that determines the lower limit of the variation of the  $\kappa$  parameter admitted by the theory. Finally, inequality (3.5) determines the theoretically admissible range of the variation of the  $\eta(-\infty)$  concentration.

Let us turn now to the case  $h \leq 1$ . Here, the conditions of the applicability of the kinetic theory are reduced to inequalities (3.1), (3.3), (3.4), and (3.6). As before, inequalities (3.1) and (3.4) are still the lower limits of the  $\kappa$  parameter. The strictest of these inequalities determines the admissible lower bound of the variation of the  $\kappa$  parameter imposed by the theory. Inequality (3.3) and converse inequality (3.6) determine the admissible range of the variation of the  $\eta(-\infty)$  concentration imposed by the theory. Apparently, to make these inequalities compatible, the fulfillment of relationship

$$\frac{3^{5/3} \pi}{2^{7/2}} \frac{1}{(n_{\infty} v)^{1/3}} \frac{1}{a^{1/2} v_n^{5/18}} \geq 1 \quad (h \leq 1) \quad (3.7)$$

is needed, where the equality (1.13) is taken into account. Inequality (3.7) is equivalent to inequality (3.2), which was established at  $h \geq 1$ , based on other considerations. The independence of inequalities (3.2) and (3.7) of the  $\kappa$  parameter and the concentration  $\eta(-\infty)$  makes these parameters sensitive to the only parameter of a theory, namely, to the  $v_n$  quantity (the values of  $n_{\infty} v$ , and  $a$  virtually remain unchanged).

The larger the  $v_n$  value, i.e., the more macroscopic the condensation nuclei, the worse the inequalities (3.2) and (3.7) are fulfilled. As is seen from (2.1) and (2.2), the inequality (3.1), which was taken as the basic relationship for the  $\kappa$  parameter introduced by means of equation (2.1), is also fulfilled less well.

As a result, although inequality (3.4) becomes weaker with an increase in  $v_n$ , we can make the following general statement. The macroscopicity of the condensation nuclei introduces significant simplification

into the theory of heterogeneous nucleation of supercritical droplets during the gradual creation of the metastable state in vapor results despite the severity of the conditions of the applicability of the theory. The same statement was made in [2], when the free molecular growth of supercritical droplets prevails at the stage corresponding to effective nucleation.

Our great interest in these conditions in [2] and in the present paper is explained by the severity of the conditions of the applicability of the theory in the case of macroscopic condensation nuclei.

#### 4. CALCULATION ALGORITHM AND NUMERICAL CALCULATIONS OF THE KINETIC CHARACTERISTICS OF DROPLET NUCLEATION

Let us formulate the calculation algorithm for all the important characteristics of the nucleation of supercritical droplets on the condensation nuclei during the gradual creation of the metastable state in vapor. In addition to parameter  $\kappa$  determining the scaling time  $t_{\infty}$  and the initial concentration of condensation nuclei  $\eta(-\infty)$ , all other initial parameters of the theory:  $a$ ,  $\alpha$ ,  $n_{\infty}$ ,  $n_g$ ,  $v$ ,  $\tau$ ,  $D$ ,  $v_n$ , and  $m$  we assume to be the parameters set in the algorithm (moreover, the value of  $v_n$  must satisfy constraint  $v_n^{1/3} \geq 1$  imposed on the macroscopicity of the condensation nuclei). Parameter  $\kappa$  and concentration  $\eta(-\infty)$  may be varied, however, within the limits of the conditions of the theory applicability. Of course, this considerably widens the possibility of the calculation algorithm and improves its efficiency.

Before we begin the calculations, we first must be sure that at the selected initial parameters of the theory of equivalent inequalities (3.2) and (3.7) are satisfied and then to establish the admissible range of the variation of parameter  $\kappa$  using the most severe inequality [(3.1) or (3.4)].

We begin our calculations with the quantities  $\zeta_m$  and  $t_s$  using formulas (1.2) and (1.4), which do not contain parameter  $\kappa$  and concentration  $\eta(-\infty)$ .

Further, the quantity  $t_{\infty}$  is determined at  $h \geq 1$  and  $h \leq 1$  by formula (2.3). In this case, we may return easily from  $t_{\infty}$  back to  $\kappa$ . This converse passage enables us to imagine the general behavior of all important kinetic characteristics of the nucleation of supercritical droplets as dependent on  $h \leq 1$  (the initial parameter of a theory).

Using formula (2.5), we then calculate the  $N$  quantity at  $h \geq 1$ . At  $h \leq 1$ ,  $N$  is defined by relationship (1.15).

Then, using equation (2.1) and the calculated value of  $t_s$ , we determined  $\Delta t$ .

The value of  $\Delta p$  was determined by formula (2.6) at  $h \geq 1$  and  $h \leq 1$ .

Using formula (1.10) and the already calculated values of  $\zeta_m$  and  $t_{\infty}$ , we calculated  $t_*$  at the time moment

(accepted in the theory) at which, according to the power approximation (1.9),  $\Phi = 0$ . The  $t_{on}$  and  $t_{off}$  times of the beginning and the end of effective nucleation of droplets may be obtained by the approximate equalities

$$t_{on} \approx t_* - \Delta t/2, \quad t_{off} \approx t_* + \Delta t/2, \quad (4.1)$$

where it was considered that the  $t_*$  moment is located approximately at the middle of the time interval corresponding to the effective nucleation of the supercritical droplets [5, 6]. The generalization of formula (1.10) to the case of arbitrary (in time) gradual creation of the metastable state in vapor was demonstrated in [2].

The calculation algorithm is ended by the establishment of the range of concentrations  $\eta(-\infty)$  admitted by the inequality (3.5) (in the  $h \gg 1$  case) and matched by inequalities (3.3) and (3.6) (in the  $h \ll 1$  case). According to (1.15), at  $h \ll 1$ , this range also determines the theoretically admissible variation in the number of droplets  $N$ .

It is apparent from (2.5) and (1.15) that, as the concentration  $\eta(-\infty)$  decreases, i.e., as we pass from inequality (3.5) to inequality (3.6), the number of supercritical droplets diminishes, irrespective of the fact that the ever larger fraction of condensation nuclei becomes involved in the nucleation of supercritical droplets.

Note that the determination of parameter  $h$  is beyond the scope of the calculation algorithm. Parameter  $h$  is needed only to indicate (by means of inequalities  $h \gg 1$  and  $h \ll 1$ ) the extreme situations where supercritical droplets consume only a fairly small fraction or almost the entire initially stored amount of the condensation nuclei, respectively.

Based on the algorithm thus formulated, let us carry out the numerical calculations. Let us set the following values of the initial parameters of a theory:

$$\begin{aligned} a \approx 10, \quad \alpha \approx 1, \quad n_\infty \approx 10^{23} \text{ m}^{-3}, \quad n_g \approx 10^{25} \text{ m}^{-3}, \\ v \approx 10^{-28} \text{ m}^3, \quad \tau \approx 10^{-6} \text{ s}, \quad D \approx 10^{-4} \text{ m}^2 \text{ s}^{-1}, \quad (4.2) \\ \tau_D \approx 4.1 \times 10^{-11} \text{ s}, \quad v_n \approx 10^3, \quad m \approx 1. \end{aligned}$$

The selected value of  $v_n$  satisfies constraint  $v_n^{1/3} \gg 1$  imposed on the macroscopicity of the condensation nuclei. For completeness, we included the  $\tau_D$  time into the initial parameters, although this quantity [due to definition (1.13)] is a function of  $n_\infty$ ,  $v$ , and  $D$ . The value of time  $\tau_D$  in (4.2) was determined by means of equality (1.13).

The data shown in (4.2) are realistic magnitudes for a typical condensing liquid (water and its vapor at common temperatures), as well as for the passive gas at pressures close to atmospheric pressure. The value of  $\alpha \approx 1$  is admitted by the results of a number of recent experiments [7] and studies into molecular dynamics [8, 9].

As is seen from (4.2), the equivalent inequalities (3.2) and (3.7) are fulfilled, although almost as the limiting case. It is also apparent from (4.2) that (3.4) is the

severest inequality with respect to inequality (3.1). According to this constraint, the admissible range of the variation of parameter  $\kappa$  is determined by the inequality

$$\kappa \gg 10. \quad (4.3)$$

This range is fairly wide.

Using formulas (1.2) and (1.4) and making an allowance for (4.2), we obtain

$$\zeta_{th} \approx 2.1 \times 10^{-1}, \quad (4.4)$$

$$t_s \approx 4.1 \times 10^{-4} \text{ s}. \quad (4.5)$$

Then, using formula (2.3) and taking into account (4.2), we obtain

$$t_\infty \approx 6.5 \times 10^{-1} \kappa \text{ s} \quad (\kappa \gg 10). \quad (4.6)$$

Hereafter, the range of possible variations of parameter  $\kappa$  is determined by the inequality (4.3). The measurement units are indicated in the relationships for the dimensional quantities.

Then, by formula (2.5) and making allowance for (4.2), we obtain at  $h \gg 1$

$$N \approx 1.8 \times 10^{10} \kappa^{-3/2} \text{ m}^{-3}. \quad (4.7)$$

At  $h \ll 1$ , the  $N$  value is defined by relationship (1.15).

Using definition (2.1) and calculated [by (4.5)] value of  $t_s$ , we obtain

$$\Delta t \approx 4.1 \times 10^{-4} \kappa \text{ s}. \quad (4.8)$$

Then, according to formula (2.6) and accounting for (4.2), we find that

$$\Delta p \approx 2.1 \times 10^6 \kappa. \quad (4.9)$$

Using formula (1.10) and known [from (4.4) and (4.6)] values of  $\zeta_{th}$  and  $t_\infty$ , we have

$$t_* \approx 1.4 \times 10^{-1} \kappa \text{ s} \quad (4.10)$$

at the time moment (accepted in a theory) at which, according to the power approximation (1.9),  $\Phi = 0$ . Then the moments  $t_{on}$  and  $t_{off}$  may be readily determined by formulas (4.1) and the already calculated values of  $\Delta t$  and  $t_*$ .

Equalities (4.4), (4.5), and (4.8) are valid regardless of the value of parameter  $h$ . Equalities (4.6), (4.9), and (4.10) are valid at both  $h \gg 1$  and  $h \ll 1$ .

According to (3.5) and (4.2), the range of the variation of the  $\eta(-\infty)$  quantity admitted by the theory at  $h \gg 1$  is set by the inequality

$$\eta(-\infty) \gg 1.8 \times 10^{10} \kappa^{-3/2} \text{ m}^{-3}. \quad (4.11)$$

At the same time, according to (3.3), (3.6), and (4.2), the range of the variation of parameter  $\eta(-\infty)$

admitted by the theory at  $h \ll 1$  is restricted by the following conditions

$$\begin{aligned} 3.8 \times 10^9 \kappa^{-3/2} \text{ m}^{-3} &\ll \eta(-\infty) \\ &\ll 1.8 \times 10^{10} \kappa^{-3/2} \text{ m}^{-3}. \end{aligned} \quad (4.12)$$

This range, which also determines [in view of (1.15)] the range of the possible variations of the number of droplets  $N$ , is rather narrow, because according to the initial data accepted in (4.2) inequality (3.7) [responsible for the compatibility of inequalities (3.3) and (3.6)] is fulfilled (as was mentioned above) as the limiting case.<sup>1</sup> Note that the quantity in the right-hand parts of inequalities (3.5) and (3.6) was already calculated: it is equal to the quantity in the right-hand part of relationship (4.7). Of course, this fact makes our calculations easier.

## 5. ANALYSIS OF THE CALCULATION RESULTS OF THE KINETIC CHARACTERISTICS OF DROPLET NUCLEATION

According to (4.6), the scaling time  $t_\infty$  of an increase in the ideal saturation, which (but not the auxiliary parameter  $\kappa$ ) is the initial parameter of the theory, varies within a wide range of  $t_\infty \gg 6.5$  s, that is, quite realistic in practice.

The values of the characteristics of droplet nucleation, which are defined by relationships (4.4), (4.5), and (4.8)–(4.10) also seem to be realistic for the experiment. Possible experimental determination of time  $t_s$  was discussed at the end of our previous publication [1]. According to relationships (4.6) and (4.8), the scaling time  $t_\infty$  of the creation of the metastable state in vapor is much longer than the time  $\Delta t$  of the duration of droplet nucleation. This conclusion is also true in general of the proposed theory; we can ascertain this conclusion with the equality (1.16).

The values of the most important of all kinetic characteristics, namely, the total number  $N$  of supercritical droplets nucleated in the unit volume of the vapor-gas medium, is determined by relationship (4.7) at the concentration of condensation nuclei  $\eta(-\infty)$  satisfying inequality (4.11) and by relationship (1.15), provided that  $\eta(-\infty)$  is satisfied by the double inequality (4.12). The range of possible values of the number of droplets  $N$  covered by relationship (4.7) is fairly wide and realistic. It extends down from value  $N \sim 10^8 \text{ m}^{-3}$  where constraint (4.3) is virtually fulfilled. Moreover, the range of concentrations  $\eta(-\infty)$  admitted by inequality (4.11) is even wider and still more realistic. However, the range of the number of droplets  $N$  covered by relationship (1.15) and restricted by inequalities (4.12) at the selected [in (4.12)] values of the initial parameters of the theory is rather narrow; naturally, we disregarded

the footnote for relationship (1.15) and inequality (4.12), which was made in the previous section of this paper.

The dependence of the kinetic behavior on parameter  $\kappa$  selected in the calculation algorithm instead of the scaling time  $t_\infty$  as independent parameter [this dependence was described by relationships (4.6)–(4.12)] is as obvious as the dependence on time  $t_\infty$ . In order to return from the parameter  $\kappa$  to time  $t_\infty$ , it is sufficient only to solve linear relationship (4.6) with respect to  $\kappa$  and then to substitute the result obtained into the relationships (4.7)–(4.12).

It follows from (4.6) and (4.7) that the longer time  $t_\infty$  is, i.e., the slower the establishment of the metastable state in vapor, the smaller the number of droplets  $N$  is.

The surface area  $A = 4\pi R^2$  of the droplet is a more appropriate parameter than the "size"  $\rho$  of a droplet introduced by equality (1.7). According to (1.6) and (1.7), for this surface area we have

$$A = (36\pi v^2)^{1/3} \rho. \quad (5.1)$$

From equality (5.1) at the proportionality of the values  $A$  and  $\rho$  that was demonstrated by this relationship, we obtain for the width  $\Delta A$  of the supercritical droplet size spectrum on the  $A$ -axis

$$\Delta A = (36\pi v^2)^{1/3} \Delta \rho. \quad (5.2)$$

The width  $\Delta A$  as well as width  $\Delta \rho$  are independent of time, because the  $A$  and  $\rho$  values grow at each present moment at the same rate for all supercritical droplets. It should be emphasized that at the diffusion absorption of vapor by supercritical droplets, which is considered here, it would not be possible to state that the supercritical droplet size spectrum at the axis of their radii is independent of time, since the growth rate of the radii of supercritical droplets is not identical at each present moment for all supercritical droplets.

At the accepted (4.2) value of volume  $v$ , we obtain from (4.9) and (5.2) the following relationship

$$\Delta A \approx 2.2 \times 10^{-12} \kappa \text{ m}^2 \quad (\kappa \gg 10). \quad (5.3)$$

The calculations performed demonstrate that the proposed theory is capable of predicting some promising practical results within a rather wide range of the magnitudes of the initial parameters of the theory, irrespective of the severe conditions (which were disclosed in the course of this work) of its applicability at the macroscopicity of the condensation nuclei.

The nontrivial behavior of the kinetic characteristics of the supercritical droplet nucleation on macroscopic condensation nuclei during the gradual creation of the metastable state in vapor, which is described by the theory and illustrated by the relevant calculations, is due to the fact that this process is characterized by nonlinear, nonstationary, and nonlocal time dynamics. It would be impossible to predict this behavior, even qualitatively, without the study of this dynamics performed in [1, 5, 6].

<sup>1</sup> However, it seems justified by the physical evidence that equation (1.15) remains valid even at the concentrations  $\eta(-\infty)$  lower than their minimal values admitted by inequalities (4.12) and (3.3).

The smallness of the threshold value  $\zeta_{th}$  of vapor supersaturation demonstrated by relationship (4.4) at the selected (4.2) values of the initial parameters of a theory and the closeness of the vapor supersaturations, causing heterogeneous vapor condensation, to its threshold value  $\zeta_{th}$  disclosed in [1] under the conditions of macroscopicity of the condensation nuclei and the gradual creation of the metastable state in vapor indicate that the macroscopic nuclei are active stimulants of the vapor condensation process at low vapor supersaturations. High sensitivity of the kinetic characteristics of the condensation process to the scaling time  $t_{\infty}$  of the creation of the metastable state in vapor demonstrated by relationships (4.6)–(4.10) is indicative of the possible control for the development of the condensation process at the gradual creation of the metastable state in vapor. Of course, the fact that the value of parameter  $m$  in the power (with respect to time) law of the creation of the metastable state in vapor was fixed in our calculations [according to (4.2), it was set as equal to unity] did not allow us to reveal the dependence of the kinetic characteristics of the condensation process on this parameter. However, the existence of such a dependence is illustrated by equality (2.3).

## 6. CONCLUSION

Let us find out what are the key factors that determine the prevalence of either the diffusion (considered above) or free molecular (treated in [2]) absorption of vapor by supercritical droplets at the stage corresponding to effective nucleation of the supercritical droplets.

Once expressed directly in terms of the initial parameters of the theory, the condition of the prevalence of the diffusion absorption of vapor by supercritical droplets at the stage corresponding to effective nucleation is described, according to inequality (7.18) and relationship (5.13) of [3], as

$$\begin{aligned} & \frac{2^{7/6} \pi^{1/3}}{3^{5/6}} \left( \frac{2^{5/2}}{27} \right)^{(m+1)/m} (n_{\infty} + n_g) \\ & \times v \frac{\alpha^2 t_{\infty} a^{3(m+1)/2m}}{m\tau v_n^{(7m+3)/6m}} \gg 1 \quad (6.1) \\ & (h \gg 1 \text{ or } h \ll 1), \end{aligned}$$

which is equivalent to inequality (3.4). On the contrary, according to inequality (7.13) and relationship (5.13) from [3], the condition of the prevalence of free molecular absorption of vapor by supercritical droplets at the stage corresponding to effective nucleation is described as

$$\begin{aligned} & \frac{3^{1/2}}{2^{5/2}} \left( \frac{2^{5/2}}{27} \right)^{(m+1)/m} (n_{\infty} + n_g) v \frac{\alpha^2 t_{\infty} a^{3(m+1)/2m}}{m\tau v_n^{(7m+3)/6m}} \ll 1 \quad (6.2) \\ & (h \gg 1 \text{ or } h \ll 1), \end{aligned}$$

where the extreme conditions at which supercritical droplets consume only a quite small fraction or almost all of the amount of the condensation nuclei are still indicated by inequalities  $h \gg 1$  or  $h \ll 1$ .

Inequalities (6.1) and (6.2) are responsible for the prevalence of either diffusion or free molecular regimes of the absorption of vapor by supercritical droplets at the stage corresponding to effective nucleation. The fact that these inequalities appeared to be virtually opposite to each other, i.e., securing natural distinction of the extreme regimes of vapor absorption, confirms the consistency of treatment undertaken in [2] and in this work.

The validity of inequality (6.1) imposes the lower bound on the values of  $(n_{\infty} + n_g)v$ ,  $\alpha$ , and  $t_{\infty}$  and the upper bound, on  $v_n$ . On the contrary, the validity of equality (6.2) sets the upper bound for the values of  $(n_{\infty} + n_g)v$ ,  $\alpha$ , and  $t_{\infty}$ , and imposes the lower bound on  $v_n$ . The bounds for  $\alpha$  (naturally, compatible with condition  $\alpha \leq 1$ ) are strongly exhibited in inequalities (6.1) and (6.2) due to the quadratic dependence of their left-hand sides on  $\alpha$ .

It is these values of the condensation coefficients ( $\alpha \approx 1$  and  $\alpha \approx 0.1$ ) selected in this work and in [2] that provide the prevalence of the diffusion or free molecular regimes of the absorption of vapor by supercritical droplets at the stage corresponding to effective nucleation, respectively, given that the values of other initial parameters are virtually identical.

It was assumed in this work that all condensation nuclei are identical. Let us demonstrate how the developed theory may be generalized to the case of polydisperse nuclei.

Because of the high sensitivity of the supercritical droplet nucleation intensity to the height of activation barrier nucleation, the nucleation of supercritical droplets has the time (at the gradual creation of the metastable state in vapor) to occur completely [1] within the prethreshold range of the vapor supersaturations  $\zeta$ , which at the macroscopic sizes of the condensation nuclei fills the entire range of supersaturation ( $0 < \zeta < \zeta_{th}$ ) rather than a narrow part with the width of the order of distance extending from this part to the upper boundary of the prethreshold range.

As was found in [1], in the actual case of polydispersity of the initial condensation nuclei only their small fraction (of the order of  $v_n^{-2/3}$ ) adjacent to the upper boundary of the initial nuclei size spectrum will be responsible for the effective nucleation of supercritical nuclei, because the prethreshold range of vapor supersaturation (provided that condensation nuclei are macroscopic) is narrow. In this case, it will not be difficult to generalize the proposed theory to the case of polydisperse condensation nuclei. We need only assume that the total nuclei concentration in the indicated upper part of their initial size spectrum (with the relative width of the order of  $v_n^{-2/3}$ ) is nothing other than the



$\eta(-\infty)$  quantity. With the present experimental accuracy, such a generalization will be quite sufficient.

#### ACKNOWLEDGMENTS

This work was supported by the Competition Center for Fundamental Natural Sciences at St. Petersburg State University, project no. 95-0-51-15.

#### REFERENCES

1. Kuni, F.M., Grinin, A.P., Shchekin, A.K., and Novozhilova, T.Yu., *Kolloidn. Zh.*, 1997, vol. 59, no. 2, p. 187.
2. Kuni, F.M., Grinin, A.P., Shchekin, A.K., and Novozhilova, T.Yu., *Kolloidn. Zh.* (in press).
3. Kuni, F.M., Grinin, A.P., Shchekin, A.K., and Novozhilova, T.Yu., *Kolloidn. Zh.* (in press).
4. Kuni, F.M., Shchekin, A.K., and Rusanov, A.I., *Kolloidn. Zh.*, 1993, vol. 55, no. 2, p. 34.
5. Grinin, A.P., Kuni, F.M., and Kurasov, V.B., *Kolloidn. Zh.*, 1990, vol. 52, no. 3, p. 430.
6. Grinin, A.P., Kuni, F.M., and Kurasov, V.B., *Kolloidn. Zh.*, 1990, vol. 52, no. 3, p. 437.
7. Barnes, G.T., *Adv. Colloid Interface Sci.*, 1986, vol. 25, nos. 1-4, p. 89.
8. Yusuoka, *et al.*, *J. Chem. Phys.*, 1994, vol. 101, p. 7904.
9. Matsumoto, M. *et al.*, *J. Chem. Phys.*, 1994, vol. 101, p. 7912.