

Theory of Droplet Nucleation on the Macroscopic Condensation Nuclei under the Conditions of Gradual Creation of the Metastable State in Vapor

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

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

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Abstract—The theory of heterogeneous condensation of vapor was elaborated for a case of practical interest: macroscopic condensation nuclei and the gradual creation of the metastable state in vapor. The reference value was found for ideal supersaturation, which ensures external control over the development of the condensation process. All the principal kinetic characteristics of heterogeneous nucleation of supercritical droplets in vapor were found in terms of the external parameters of the theory, which are determined by the properties of the vapor and the liquid condensing from it, by the dimensions of the condensation nuclei and their initial concentration, and by the rate of the external increase in ideal supersaturation. The conditions of applicability were formulated for the suggested theory. Fast convergence of the iterative method of contractive approximations in the determination of the total number of supercritical droplets originating per unit volume of the vapor–gas medium was demonstrated. The theory was shown to be directly generalizable for the case of polydisperse macroscopic condensation nuclei.

INTRODUCTION

The aim of this paper is to construct a theory of supercritical droplet nucleation in a case of practical interest, where droplets are formed on macroscopic condensation nuclei in vapor, and the metastable state of vapor is created gradually (during condensation) rather than instantly (that is, before the beginning of condensation).

The interest in macroscopic condensation nuclei is due to the fact that these exact particles can ensure vapor condensation at low supersaturations. As to the interest in the gradual, 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 are frequently encountered in nature.

The possibility of controlling and even regulating the condensation process has wide prospects for the theory suggested below. Its applications of practical importance include not only the use of condensation nuclei as phase transition stimulators, but also the possible environmental or technological necessity of removing such nuclei from some medium. In both cases, this theory enables us to formulate well

grounded recommendations for achieving the desired effect in practice.

As the initial principles of this research, we used the thermodynamic foundations [1] of supercritical droplet nucleation on the macroscopic nuclei and the kinetic principles [2] of overcoming the activation barrier of droplet nucleation on the macroscopic nuclei. On the other hand, the research is also based on the results of the homogeneous condensation theory under the conditions of gradual creation of the metastable state in vapor [3], as well as on the results obtained within the kinetic theory of heterogeneous condensation under the same conditions [4, 5].

Although the kinetic theory of heterogeneous condensation under the conditions of gradual creation of the metastable state in vapor [4, 5] is completely valid for macroscopic condensation nuclei as well, their macroscopicity may restrict its applicability. However, this macroscopicity also enables us to simplify the theory to a significant extent, and even to find analytical expressions for all the principal kinetic characteristics of the heterogeneous nucleation of supercritical droplets as dependent on the external parameters of the theory.

Just as in [1, 2], let us assume that condensation nuclei are soluble in the droplets that originate on them and consist of a surface-inactive material. Starting from

section 4 of this paper, we assume (as in [4, 5]) that the supercritical droplets, once they have originated, grow during 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 the cases of insoluble condensation nuclei and the growth of supercritical droplets outside the limits of the free-molecule regime. As in [2, 4, 5], all condensation nuclei are assumed to be identical. The possible direct generalization of the theory for the case of polydisperse macroscopic condensation nuclei is demonstrated in section 6 of this paper.

1. INITIAL THERMODYNAMIC AND KINETIC CONCEPTS 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

$$v_n^{1/3} \gg 1. \quad (1.1)$$

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

$$\zeta = (n/n_\infty) - 1, \quad (1.2)$$

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

Under the assumption that the condensation nucleus is readily soluble in the droplet that originated on it, the droplet must contain the material of this center in the dissolved form. As was shown in [1], the droplets that are getting over the activation barrier of nucleation and, moreover, the droplets that have already surmounted it and now grow irreversibly are so large if condition (1.1) is true that the solution of the center-forming material in them is dilute.

The threshold supersaturation of vapor ζ_{th} , above which the formation of supercritical droplets on condensation nuclei in vapor is barrierless, is [1, equation (11)]

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

where

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

σ 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 supercritical droplets, and v is the molecular volume of the condensing liquid. As follows from (1.1) and (1.3),

$$\zeta_{th} \ll 1. \quad (1.5)$$

Hereafter, we are interested in the subthreshold range of vapor metastability ($0 < \zeta < \zeta_{th}$), which is non-trivial from the kinetic standpoint. In this range, the curve representing the dependence between the work of droplet formation on the condensation nucleus in vapor and the droplet size includes a potential well and a potential barrier to the right of it [1]. The points of minimal and maximal work (which lie in the ranges of the potential well and barrier, respectively) correspond to the equilibrium and critical droplets. The chemical equilibrium of these droplets with vapor is stable and unstable, respectively. The difference between the height of the barrier and the depth of the well represents the activation energy of heterogeneous nucleation of supercritical droplets. Let us express the activation energy in thermal energy units kT and denote it as F . The closer the supersaturation of vapor ζ to its threshold value ζ_{th} , the deeper the potential well but the lower the activation energy [1].

For a droplet, the probability of being carried over the activation barrier of nucleation due to fluctuations is proportional to the exponent $\exp(-F)$. The steady-state (actually, quasi-steady-state) intensity of the heterogeneous nucleation of supercritical droplets j_s —that is, the number of supercritical droplets originating in a unit volume of the vapor-gas medium per unit time—is also proportional to this exponent [2]. The supercritical droplets, once they have emerged after overcoming the activation barrier, then grow irreversibly.

In addition, the intensity j_s is proportional [2] to the concentration of condensation nuclei η , that is, to their number per unit volume of the vapor-gas medium. Here, we consider only those condensation nuclei that are not yet inside the supercritical droplets formed earlier and, accordingly, still participate in the formation of new supercritical droplets. As a result, the intensity j_s depends [2] on the supersaturation of vapor and the concentration of condensation nuclei in proportion with $\eta \exp(-F)$.

Under natural and technical conditions, the external creation of the metastable state in the decomposing phase is usually gradual rather than instant. A new phase is then formed not after, but during the creation of the metastable state in this phase. As was noted in the introduction, the externally regulated gradual creation of the metastable state in the decomposing phase enables us to control and even master the development of the phase transition process. This is why this technique is often used in laboratory experiments as well.

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

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

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 conditions. It is by setting an increase in the ideal supersaturation over the course of time that we may implement external control over the development of supercritical droplet nucleation in time, as was shown in [3–5] and will be confirmed by all our further discussions. Ideal supersaturation Φ , defined by equation (1.6), cannot be smaller than the actual supersaturation ζ , defined by equation (1.2), where n is the actual number of vapor molecules per unit volume of the vapor–gas medium (with allowance made for vapor absorption by droplets).

According to [1, 2, 4, 5], the process of supercritical droplet nucleation may be outlined as follows.

As the ideal supersaturation Φ increases in time from the $\Phi = 0$ value (which corresponds to the beginning of the creation of the metastable state in vapor), the work of droplet formation at a condensation nucleus is characterized by a potential barrier that appears in addition to a potential well (the latter existed even at $\Phi < 0$). Over the course of time, the potential well deepens, and the activation energy F decreases but still remains very high. In this case, almost every condensation nucleus has sufficient time to entrap such a number of vapor molecules that the resultant droplet would descend to the bottom of the potential well. The concentration of condensation nuclei η , which was introduced above, is actually the concentration of such droplets—their number per unit volume of the vapor–gas medium (that is, the concentration of “solvated” condensation nuclei). The droplets that appear at the bottom of the potential well attempt to surmount the activation barrier of nucleation due to fluctuations. As the activation energy F decreases, the intensity of supercritical droplet nucleation j_s increases over the course of time in proportion to the $\exp(-F)$ exponent, but still remains very low. Hardly any supercritical droplets appear under such conditions, and, therefore, vapor absorption by droplets is virtually zero. Accordingly, the supersaturation of vapor ζ is virtually equal to its ideal supersaturation Φ . Both supersaturations increase at the same rate. Thus, we have described the preliminary stage in the process of supercritical droplet nucleation.

During a further increase in the ideal supersaturation Φ over the course of time, we arrive at a situation where the activation energy F is no longer too high, and the droplets that accumulate at the bottom of the potential well of their formation work are already capable of overcoming the activation barrier of nucleation due to fluctuations and thus turning into supercritical droplets, which then grow irreversibly. This is the beginning of the stage that is of interest to us—the effective nucleation of supercritical droplets.

Let us analyze this stage. The supercritical droplets, which originate after overcoming the activation barrier of nucleation, absorb vapor and, accordingly, reduce the supersaturation of vapor ζ in comparison with the ideal supersaturation Φ . The earlier a supercritical

droplet appears, the larger its size, and, accordingly, the greater the amount of vapor absorbed by it. In addition, supercritical droplets, once they have appeared, reduce the concentration of condensation nuclei η (to be more exact, the concentration of droplets that were accumulated at the bottom of the potential well, which corresponds to minimal work of droplet formation at a condensation nucleus). Each of the supercritical droplets, once formed, “removes” one of these nuclei.

The reduction of the vapor supersaturation ζ as compared to the ideal supersaturation Φ and the decrease in the concentration of condensation nuclei η retard the increase in the intensity of the nucleation of new supercritical droplets j_s [this intensity is proportional to $\eta \exp(-F)$ over the course of time]. Nevertheless, the intensity still increases in the initial part of the time period that corresponds to the stage of effective nucleation of supercritical droplets. Later, however, the intensity j_s starts to decrease and then becomes so small that effective nucleation of new supercritical droplets terminates, although the ideal supersaturation Φ still increases with time. This is the end of the stage that corresponds to the effective nucleation of supercritical droplets. If the ideal supersaturation Φ increases slowly enough over the course of time, the whole stage takes place in the range of vapor supersaturations ζ below the threshold value ζ_{th} .

As is clear from the above statement, studies concerning the stage of the effective nucleation of supercritical droplets require the solution of a complicated problem, which is essentially nonlinear, nonstationary, and nonlocal in time: we must determine how absorption of a supersaturated vapor by supercritical droplets and consumption of condensation nuclei by them are related to the rate of the external increase in the ideal supersaturation Φ in time—that is, to the rate of the external creation of vapor metastability. The problem is nonlinear, because the intensity of supercritical droplet nucleation j_s depends on the supersaturation of the vapor ζ via the $\exp(-F)$ exponent. It is nonstationary and nonlocal in time, because the supersaturation of the vapor ζ and the concentration of condensation nuclei η , which determine the intensity of the nucleation of new supercritical droplets j_s at any given moment, in turn, depend on the number and dimensions of all supercritical droplets formed earlier.

The principles of the problem solution, regardless of the dimensions of condensation nuclei, were given in the theory developed in [4, 5]. The essence of this theory is the iterative method of contractive approximations, which allows us to find all the important kinetic parameters that characterize the effective nucleation of supercritical droplets. The method is based on the physical idea already noted in [3]: because the intensity of saturated vapor absorption by supercritical droplets rapidly increases with their increasing size, vapor absorption is mostly due to the supercritical droplets that originated as early as in the period of virtually zero

vapor absorption, when the supersaturation of vapor was mostly determined by its external increase.

Effective nucleation of supercritical droplets on condensation nuclei may be terminated, in accordance with the above statements, by vapor absorption due to supercritical droplets. Because of this absorption, vapor supersaturation ζ may pass a maximal value and then decrease, while the external increase in the ideal supersaturation Φ is monotonic. The nucleation of supercritical droplets may also be suppressed when all of the condensation nuclei have been occupied by the supercritical droplets that have originated on them, whereas the supersaturation of vapor ζ still increases for some time because of the growing ideal supersaturation Φ . In section 4 of this paper, we will determine which of the two possible mechanisms prevails.

Finally, as the ideal supersaturation Φ increases further over the course of time after the end of the effective nucleation of supercritical droplets, the next stages of the phase transition process begin. These stages, at which no new supercritical droplets appear, are studied without any regard for the specific features that are due to the macroscopic nature of the condensation nuclei. This study is completely identical to the one conducted in [6], and we will not consider it below. However, the processes occurring after the end of the stage that corresponds to effective nucleation of supercritical droplets may be very important, as, for example, in the related problem [7, 8] of finding the optimal regime for removing the vapor of some admixture material from a vapor mixture.

2. THE REFERENCE VALUE OF IDEAL SUPERSATURATION

Let us represent the supersaturation of vapor ζ as

$$\zeta = \zeta_{th}(1 - \varepsilon), \quad (2.1)$$

where ε is the relative difference between this value and the threshold value ζ_{th} . In the subthreshold range $0 < \zeta < \zeta_{th}$, which is of interest to us, $0 < \varepsilon < 1$.

The expression for the activation energy F is [1, equation (28)]

$$F = (16/6^{1/2})v_n\varepsilon^{3/2}. \quad (2.2)$$

Note that the activation energy was denoted by ΔF in [1].

As was noted in the previous section, the intensity of supercritical droplet nucleation j_s is proportional to $\eta \exp(-F)$. Almost regardless of the concentration of condensation nuclei η , the only part of actual theoretical interest in the subthreshold range of vapor metastability is the range where

$$3 < F < 30. \quad (2.3)$$

Indeed, the $\exp(-F)$ exponent is no longer very small to the left of this range (that is, at $F < 3$). Nucleation is virtually barrierless here; as a result, the kinetic

theory of nucleation is trivial and, accordingly, is of no interest for us. To the right of this range, at $F > 30$, the $\exp(-F)$ value is so small that nucleation is virtually absent.

According to (2.2) and (2.3), we obtain

$$\varepsilon^{1/2} \approx v_n^{-1/3}, \quad (2.4)$$

where we make allowance for the fact that the range of $F^{1/3}$ values is much narrower than that of the F values, and, accordingly, we may assume $(6^{1/2}F/16)^{1/3} \approx 1$ with sufficient accuracy. The range of vapor metastability where equation (2.3) is true and, accordingly, $\varepsilon^{1/2}$ satisfies the approximate equality (2.4) is hereafter referred to as the prethreshold range, as in [1]. According to (1.1) and (2.4), the following equality is true in the prethreshold range:

$$\varepsilon^{1/2} \ll 1. \quad (2.5)$$

As is apparent from (2.4) and (2.5), the prethreshold range in the case of macroscopic condensation nuclei covers only a very narrow gap in the whole subthreshold range $0 < \varepsilon < 1$: the width of this gap is of the same order of magnitude as the distance from it to the upper boundary of the subthreshold range. As was shown in [1], it is in the prethreshold range and under the limiting condition (1.1) that formula (2.2) is true.

If the metastable state of vapor is created instantly (rather than gradually), under laboratory or especially technical conditions, it is a difficult practical problem to make the system fall within the prethreshold range of vapor supersaturations, which is very narrow for macroscopic condensation nuclei.

According to formula (2.1), which follows from the criterion (1.1) of the macroscopicity of condensation nuclei and the inferred inequalities (1.5) and (2.5), vapor supersaturation ζ is small in the entire prethreshold range of fairly intense but still essentially barrier-type heterogeneous nucleation; this smallness explains the interest in macroscopic condensation nuclei, which was noted in the introduction.

The most important kinetic characteristic of the condensation process is the total number of supercritical droplets originating during this process. The key moment t_* at the stage of effective nucleation of supercritical droplets is the moment [4, 5] by which half the total number of supercritical droplets that originate during condensation have already 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 externally set, the t_* moment is unambiguously related to the ideal supersaturation Φ at

this moment—the Φ_* value. 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 [4, 5] describing effective nucleation of supercritical droplets under the conditions of gradual creation of the metastable state in vapor. In this theory, a closed equation was obtained for Φ_* . However, the analytical solution of this equation without a computer was impossible because of the complex dependence between the activation energy F and vapor supersaturation ζ in the general case (arbitrary dimensions of condensation nuclei).

Let us show how the reference value Φ_* of ideal supersaturation Φ may be directly found with very high accuracy in the currently considered case of macroscopic condensation nuclei.

The intensity of supercritical droplet nucleation j_s , which is proportional to the $\exp(-F)$ exponent, is very sensitive to vapor supersaturation ζ ; therefore, the relationships

$$\zeta \approx \Phi \approx \zeta_* \approx \Phi_* \quad (2.6)$$

are true throughout the stage corresponding to effective nucleation of supercritical droplets (as was established in [4, 5]), although this stage itself is induced by the changes in the supersaturations Φ and ζ over the course of time. The accuracy of the approximate equalities (2.6) is very high for the currently considered case of macroscopic condensation nuclei, where the intensity j_s is especially sensitive to vapor supersaturation ζ . The equalities (2.6) are confirmed by the discussion in the next section.

If, as is assumed below, the ideal supersaturation Φ increases with time slowly enough, effective nucleation of supercritical droplets is fully completed as early as in the prethreshold range of vapor supersaturations. Considering that, according to (2.1) and (2.5), the approximate equality

$$\zeta \approx \zeta_{th} \quad (2.7)$$

is true within this range with a high degree of accuracy for our case of macroscopic condensation nuclei, we take the equalities (2.6) into account and obtain

$$\Phi_* \approx \zeta_{th}. \quad (2.8)$$

The equality (2.8), established for the case of macroscopic condensation nuclei and containing the known value ζ_{th} in its right-hand part, enables us to simplify the kinetic theory of [4, 5] to a significant extent. This equality is of decisive importance in the rest of the discussion. For macroscopic condensation nuclei, the accuracy of this formula is very high and completely sufficient for finding the values that comparatively slightly depend on Φ_* (power dependence); actually, finding them by using equation (2.8) is the only step required for further solution.

Of course, the accuracy of the equality (2.8) does not enable us to find the exponent $\exp(F|_{\zeta=\Phi_*})$, which is strongly dependent on Φ_* and even reduced to unity if the equality (2.8) is applied directly (because $F|_{\zeta=\zeta_{th}} = 0$). However, formula (2.8) enables us to write the rigorous equation derived in [4, 5] for the reference value Φ_* in such a form that the $\exp(F|_{\zeta=\Phi_*})$ exponent, which is strongly dependent on Φ_* , would be expressed in terms of a power function, which comparatively slightly depends on Φ_* and is easily found with a high degree of accuracy according to equation (2.8). For a simple dependence of F on ζ , which is determined by formulas (2.1) and (2.2) in the case of macroscopic condensation nuclei, the solution of this equation with respect to Φ_* is a simple problem, which is, however, of no interest to us [although it might be used to improve the accuracy of the approximate equality (2.4) at $\zeta = \Phi_*$]. We must only prove that this equation ensures adherence to the inequality

$$\exp(F|_{\zeta=\Phi_*}) \geq 1. \quad (2.9)$$

In section 5, we will show that inequality (2.9) is indeed true for a sufficiently slow increase in the ideal supersaturation Φ over the course of time, and, accordingly, effective nucleation of supercritical droplets indeed takes place in the prethreshold range of vapor supersaturations in this case. In the same section, we will also find the requirement that ensures the assumed sufficiently slow increase in the ideal supersaturation Φ over the course of time.

3. FUNDAMENTAL PARAMETERS OF THE THEORY

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 to some other variable ρ —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 (or v) for all supercritical droplets, but depends only on vapor supersaturation ζ . Passing to this variable, which is appropriate for our theory, we obtain

$$\dot{\rho} = \dot{\rho}(\zeta). \quad (3.1)$$

Below, we refer to the ρ variable as the droplet size.

An important kinetic characteristic describing the nucleation of supercritical droplets is the dimensionless parameter Γ , defined by the equality

$$\Gamma = -\Phi_* (\partial F / \partial \zeta)|_{\zeta=\Phi_*}. \quad (3.2)$$

This characterizes the extent of the dependence between the activation energy F and vapor supersaturation ζ in the vicinity of the $\zeta = \Phi_*$ value. As a rule, the Γ value is always large: $\Gamma \gg 1$. In the case of macroscopic condensation nuclei, it is even very large.

To change the activation energy F (in the vicinity of the $\zeta = \Phi_*$ point) by the ΔF value of the order of unity [that is, to produce a significant change in the intensity of supercritical droplet nucleation j_s , which is proportional to $\exp(-F)$], the $\Delta\zeta$ change in the vapor supersaturation ζ , as is apparent from definition (3.2), must adhere to the estimate

$$\Delta\zeta \sim \Phi_*/\Gamma \quad (\Delta F \sim 1) \quad (3.3)$$

(as is accepted, we omit the minus sign in our estimates).

In addition to Γ , another important quantity in the kinetics of supercritical droplet nucleation is the dimensionless parameter c defined by the equality

$$c = (\dot{\Phi})_*\Gamma/(\dot{\rho})_*\Phi_* \quad (3.4)$$

where $(\dot{\Phi})_*$ and $(\dot{\rho})_*$ are the derivatives of the ideal supersaturation Φ and the supercritical droplet size ρ with respect to the time t at the moment t_* .

As is apparent from definition (3.4), ideal supersaturation Φ in the vicinity of the $\Phi = \Phi_*$ point changes by the $\Delta\zeta$ value estimated by (3.3) during the time Δt estimated as

$$\Delta t \sim 1/(\dot{\rho})_*c \quad (3.5)$$

Let us show that this time period Δt represents (by an order of magnitude) the duration of the stage corresponding to effective nucleation of supercritical droplets.

To begin with, let us consider the typical situation already mentioned in section 1, where effective nucleation of supercritical droplets at condensation nuclei terminates because of vapor absorption by supercritical droplets rather than because of the decreasing concentration η . Then, the moment when maximal supersaturation ζ is reached virtually coincides with t_* . For the intensity j_s to be low (compared to its value at the t_* moment) at the beginning and the end of the stage corresponding to effective nucleation of supercritical droplets, the supersaturation of vapor ζ at the beginning and the end of this stage must be smaller than ζ_* by the $\Delta\zeta$ value estimated by formula (3.3). In the ascending part (up to the maximum) of the curve representing the time dependence of ζ , the vapor supersaturation ζ virtually coincides with the ideal supersaturation Φ . Therefore, the increase $\Delta\Phi$ in the ideal supersaturation Φ in this part of the curve is virtually equal to the change $\Delta\zeta$ in the vapor supersaturation ζ estimated by formula (3.3). As to the descending part of the same curve (after the supersaturation of vapor ζ has reached its maximum), the decrease in ζ is at least no slower than its increase in the ascending part of the curve, because the intensity of vapor absorption by growing

supercritical droplets increases according to a nonlinear law. Then, to terminate the effective nucleation of supercritical droplets completely, it is sufficient to change the ideal supersaturation Φ so that this change would be of the same order of magnitude as the $\Delta\zeta$ change in the vapor supersaturation ζ estimated by formula (3.3). So, effective nucleation of supercritical droplets takes place while the ideal supersaturation Φ changes by the $\Delta\zeta$ value [estimated by (3.3)] in the vicinity of the $\Phi = \Phi_*$ point. Accordingly, the Δt time estimated by (3.5) indeed represents the duration of the stage corresponding to effective nucleation of supercritical droplets.

Now let us consider the opposite typical situation (also mentioned in section 1), where effective nucleation of supercritical droplets at condensation nuclei terminates because the entire amount of these nuclei is exhausted. Then, the increase in vapor supersaturation ζ virtually coincides with the increase in the ideal supersaturation Φ throughout the entire stage corresponding to effective nucleation of supercritical droplets. If the ideal supersaturation Φ increases so that its increment is of the order of the $\Delta\zeta$ change in the vapor supersaturation ζ estimated by formula (3.3), the intensity of supercritical droplet nucleation j_s would increase dramatically if it were not limited by the exhaustion of the supply of condensation nuclei (because the intensity j_s is proportional to the decreasing concentration of condensation nuclei η). Indeed, the intensity j_s increases because of the increase in the ideal supersaturation Φ over the course of time; this process results in faster consumption of condensation nuclei, and the resultant decrease in their concentration η suppresses the increase in the intensity j_s in time. Thus, it is apparent that effective nucleation of supercritical droplets, just as before, takes place in the time range during which the ideal supersaturation Φ changes by the $\Delta\zeta$ value [estimated by formula (3.3)] in the vicinity of the $\Phi = \Phi_*$ point. Again, this result shows that the Δt time estimated by formula (3.5) indeed represents the duration of the stage that corresponds to effective nucleation of supercritical droplets.

Our estimate (3.5) for the duration of the stage corresponding to effective nucleation of supercritical droplets, obtained in a qualitative but physically convincing way, agrees with the results of quantitative studies [4, 5]. The above considerations explain why the duration of this stage is of the same order of magnitude for the two extreme characteristic situations discussed above, in spite of the marked difference in their physical meaning as far as termination of effective nucleation of supercritical droplets at condensation nuclei is concerned. These considerations are not limited by the actual regime of the droplet-vapor mass exchange. They confirm adherence to the approximate equalities (2.6) with a high degree of accuracy during the entire stage corresponding to effective nucleation of supercritical droplets. Also note that the above consid-

erations do not imply the macroscopicity of condensation nuclei. Only the $\Gamma \gg 1$ inequality must be true.

It is easy to estimate the maximal size $\Delta\rho$ (at the ρ -axis) of supercritical droplets that is reached by the end of the stage corresponding to effective nucleation of supercritical droplets. Considering the evident relationship $\Delta\rho \sim (\dot{\rho})_* \Delta t$ for this size, we use (3.5) and obtain the following estimate:

$$\Delta\rho \sim 1/c. \quad (3.6)$$

Evidently, the $\Delta\rho$ size also characterizes the width of the supercritical droplet size spectrum at the ρ -axis. According to (3.1), 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.

4. KINETIC CHARACTERISTICS OF DROPLET NUCLEATION

As was shown in [2], the activation barrier of nucleation is almost always surmounted by droplets in the free-molecule regime of the droplet-vapor mass exchange, in spite of the limitation (1.1). Following [4, 5], 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 determine the condition required for this assumption to be acceptable.

An appropriate variable for describing the growth of a droplet is the parameter

$$\rho = v^{1/3}. \quad (4.1)$$

We will use this variable (referred to as the size of the droplet) below. For the rate $\dot{\rho}$ of its increase in the free-molecule regime, we obtain

$$\dot{\rho} = \alpha\zeta/\tau, \quad (4.2)$$

that is, $\dot{\rho}$ does not depend on ρ (or v) but is determined only by the vapor supersaturation ζ , according to (3.1). In this expression, α is the condensation coefficient of vapor molecules, and τ is the characteristic time of free path for a molecule in saturated vapor. This time is determined as

$$\tau = 12/[(36\pi)^{1/3} v^{2/3} n_\infty v_T], \quad (4.3)$$

where v_T is the average thermal velocity of vapor molecules ($v^{2/3}$ is introduced to estimate the cross section of molecular collision). Just as 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 passage of vapor to the metastable state is the power approximation of the increase in the ideal supersaturation Φ over the course of time t :

$$\Phi = (t/t_\infty)^m. \quad (4.4)$$

Following [4], let us take advantage of this approximation. It contains two independent positive parameters; the scaling time t_∞ and the exponent m . According to (4.4), the time t is taken with reference to the moment corresponding to $\Phi = 0$, and the t_* moment is related to Φ_* as

$$t_* = t_\infty \Phi_*^{1/m}. \quad (4.5)$$

As a matter of fact, the power approximation (4.4) is important only during the stage that is of interest to us—effective nucleation of supercritical droplets. At this stage, the change in the ideal supersaturation Φ in the vicinity of the $\Phi = \Phi_*$ point is estimated, as was shown in the previous section, by the Φ_*/Γ value, which is extremely small as compared to Φ_* because of the inequality $\Gamma \gg 1$. Hence, the power approximation (4.4) is perfectly acceptable at this stage. The possible discrepancy between the power approximation (4.4) and the experimentally observed increase in the ideal supersaturation Φ in time during the preliminary stage of the supercritical droplet nucleation process is not of much significance. This discrepancy may affect only the difference between the theoretically and experimentally appropriate zero-time reference moments, at which the ideal supersaturation Φ is equal to zero according to the power approximation (4.4) and actually corresponds to zero, respectively. We may find this shift of the reference time, together with the parameters t_∞ and m of the power approximation (4.4) at the stage corresponding to effective nucleation of supercritical droplets, if we use the experimentally set arbitrary rate of the increase in the ideal supersaturation Φ in time; the solution to this problem was shown in [9].

Considering that, according to (2.6), the $\zeta_* = \Phi_*$ equality is true with high accuracy at the t_* moment, we may obtain another expression from (4.2) with an accuracy just as high:

$$(\dot{\rho})_* = \alpha\Phi_*/\tau, \quad (4.6)$$

where we used the sign of exact rather than approximate equality. Making allowance for (4.4) and (4.6) in the definition (3.4) of the c parameter, we obtain this parameter in the form [4, equation (31)]

$$c = \frac{m\tau\Gamma}{\alpha t_\infty \Phi_*^{(m+1)/m}} \quad (4.7)$$

To describe the process of supercritical droplet nucleation at condensation nuclei under the conditions of the gradually created metastable state of vapor, another important parameter is needed in addition to

the already introduced Γ and c : the dimensionless quantity h , which is defined by the following equality [5, equation (20)] in the case of the free-molecule regime of mass exchange between supercritical droplets and vapor:

$$h = 6 \frac{\eta(-\infty) \Gamma}{n_\infty \Phi_* c^3}. \quad (4.8)$$

Here, $\eta(-\infty)$ denotes the initial concentration η 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. Evidently, the $\eta(-\infty)$ value may be regarded as an external parameter of the theory.

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 equality [5, equation (28)]

$$N = \eta(-\infty) [1 - \exp(-1/h)]. \quad (4.9)$$

At $h \gg 1$ and $h \ll 1$, equation (4.9) yields the formulas

$$N = \eta(-\infty)/h \quad (h \gg 1), \quad (4.10)$$

and

$$N = \eta(-\infty) \quad (h \ll 1). \quad (4.11)$$

According to (4.10), 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 (4.11), supercritical droplets in the $h \ll 1$ case consume the entire initial amount of condensation nuclei. Thus, it is the h parameter that determines whether effective nucleation of supercritical droplets terminates because of vapor absorption or because of the exhausted supply of condensation nuclei. If the initial concentration of condensation nuclei $\eta(-\infty)$ is so high that the parameter h introduced by formula (4.8) satisfies the inequality $h \gg 1$, then the first of the aforementioned mechanisms prevails. If, on the contrary, the initial concentration of condensation nuclei $\eta(-\infty)$ is so low that the parameter h introduced by formula (4.8) satisfies the inequality $h \ll 1$, then the second mechanism is the predominant one.

Now let us consider the possibility of simplifying the problem by making allowance for the macroscopicity of condensation nuclei. From (2.1), (2.2), (2.4), and (2.8) in definition (3.2), we obtain

$$\Gamma \approx (24/6^{1/2}) v_n^{2/3}. \quad (4.12)$$

Then, using (1.3) and (2.8) in formula (4.6), we find

$$(\dot{\rho})_* \approx \frac{2^{5/2} \alpha a^{3/2}}{27 \tau v_n^{1/2}}. \quad (4.13)$$

Finally, using (1.3), (2.8), and (4.12) in the power (with respect to Φ_*) expressions (4.7) and (4.8), we arrive at

$$c \approx \frac{24}{6^{1/2}} \left(\frac{27}{2^{5/2}} \right)^{(m+1)/m} \frac{m \tau v_n^{(7m+3)/6m}}{\alpha t_\infty a^{3(m+1)/2m}}, \quad (4.14)$$

$$h \approx \frac{27}{4^2 2^{5/2}} \left(\frac{2^{5/2}}{27} \right)^{3(m+1)/m} \times \frac{\eta(-\infty) (\alpha t_\infty)^3 a^{(6m+9)/2m}}{n_\infty (m \tau)^3 v_n^{(14m+9)/6m}}. \quad (4.15)$$

Note that the accuracy of formulas (4.12)–(4.15) is very high if the condensation nuclei are macroscopic.

Formulas (3.5), (3.6), and (4.9)–(4.11), together with (4.13)–(4.15), express Δt , $\Delta \rho$, and N (the main kinetic characteristics of the supercritical droplet nucleation process at macroscopic condensation nuclei under the conditions of gradual creation of the metastable state in vapor) in the analytical form in terms of the external parameters of the theory. Some of these parameters are determined by the properties of the vapor and the liquid condensing from it. They include the numerical density of molecules in saturated vapor n_∞ , the dimensionless surface tension of a droplet a , the condensation coefficient of vapor molecules α , and the characteristic time of the free path of a molecule in saturated vapor τ . As was noted above, these parameters depend on the temperature of the droplets and the vapor-gas medium at the stage corresponding to effective nucleation of supercritical droplets. Then, part of the external parameters contains information on the condensation nuclei: the number of molecules (or ions) in a condensation nucleus v_n and the initial concentration of these nuclei $\eta(-\infty)$. Finally, some external parameters are determined by the rate of the power increase in the ideal supersaturation over the course of time: the scaling time t_∞ and the exponent m .

The nontrivial behavior of the kinetic characteristics Δt , $\Delta \rho$, and N , which is described by formulas (3.5), (3.6), and (4.9)–(4.11) expanded by the relationships (4.13)–(4.15), is due to the fact (already noted in section 1) that the supercritical droplet nucleation process is characterized by nonlinear, nonstationary, and nonlocal in time dynamics. It would be impossible to predict this behavior, even qualitatively, without the study of these dynamics performed in [4, 5].

The high sensitivity of the kinetic characteristics Δt , $\Delta \rho$, and N , to the rate of the external creation of the metastable state in vapor (to the t_∞ and m parameters), which is revealed by formulas (3.5), (3.6), (4.9), and (4.10) expanded by the relationships (4.13)–(4.15), explains our statement in the introduction to this paper: the development of the condensation process may be controlled and even regulated if the metastable state of vapor is gradually created. In the case of its instant creation, control over the development of the condensation

process and, moreover, its regulation would be impossible.

Using (1.3), (2.8), and (4.5), we may also add the following fairly accurate expression for the characteristic time t_* to the above theoretical results:

$$t_* \approx \frac{2^{5/2m}}{27^{1/m}} t_\infty \frac{a^{3/2m}}{v_n^{1/2m}} \quad (4.16)$$

It was calculated in relation to the theoretically accepted reference time corresponding to $\Phi = 0$, according to the power approximation (4.4).

5. THE CONDITIONS OF THE THEORY APPLICABILITY

As was assumed in the theory developed above, droplets are carried over the activation barrier of nucleation during the entire stage corresponding to effective nucleation of supercritical droplets in the steady-state (to be more exact, quasi-steady-state) regime. Evidently, the following inequality must be true in this case:

$$\Delta t / t_s \gg 1. \quad (5.1)$$

Here, t_s is the time required for establishment of the steady-state (actually, quasi-steady-state) regime of supercritical droplet nucleation with the intensity j_s . Using formulas (17), (25), and (27) from [2] and considering the above definition (4.3) of the characteristic time τ and the inequality $\zeta \ll 1$, we obtain an expression for t_s in the prethreshold range of vapor supersaturations, where the approximate equality (2.4) is true:

$$t_s \approx \frac{27}{8} \left(\frac{3}{2} \right)^{1/2} \frac{\tau v_n^{4/3}}{\alpha a^2}. \quad (5.2)$$

The t_s value may be experimentally determined. This is referred to as the incubation time or the delay time. After this period, supercritical nuclei of the stable phase begin to appear in the metastable phase with the intensity j_s . However, even if condition (5.1) is true, the whole process of effective nucleation of supercritical droplets is nevertheless nonstationary and nonlocal in time.

Then, the theory assumes that the supercritical droplets, once they have appeared, grow throughout the entire stage of their effective nucleation in the free-molecule regime. For this assumption to be true, the radius of a supercritical droplet R , which is, according to (4.1), related to the ρ variable by the evident equality

$$R = (3v/4\pi)^{1/3} \rho, \quad (5.3)$$

must satisfy the inequality

$$R \ll l/\alpha, \quad (5.4)$$

where l is the free path of a vapor molecule in the vapor-gas medium surrounding the droplets. According to the kinetic theory of gases, l is estimated as

$$l \sim (n + n_g)^{-1} v^{-2/3}, \quad (5.5)$$

where n_g is the number of molecules of a passive gas per unit volume of the vapor-gas medium, and $v^{2/3}$ is (by an order of magnitude) the cross section of a collision between a vapor molecule and molecules of the vapor-gas medium. Considering (5.3) and (5.5), let us write inequality (5.4) as

$$\rho \ll \rho_l, \quad (5.6)$$

where

$$\rho_l = (4\pi/3v)^{1/3} l/\alpha. \quad (5.7)$$

From (5.5) and (5.7), we obtain the estimate

$$\rho_l \sim \alpha^{-1} (n_\infty + n_g)^{-1} v^{-1}, \quad (5.8)$$

where we assume $n \approx n_\infty$ (because of $\zeta \ll 1$). For inequality (5.6) to be true even for the largest supercritical droplets, whose size ρ at the stage corresponding to effective nucleation of supercritical droplets is estimated by the $\Delta\rho$ value, the following evident inequality must be true:

$$\Delta\rho/\rho_l \ll 1. \quad (5.9)$$

Finally, as was implicitly assumed in the theory, the volume of the vapor-gas medium per one supercritical droplet is so small that the diffusion equilibrium is established in this volume before its vapor is absorbed by the supercritical droplet. The time required for the establishment of vapor diffusion equilibrium in the volume of the vapor-gas medium that corresponds to one supercritical droplet is estimated by the L^2/D value, where L is the linear size of this volume, and D is the diffusion coefficient of vapor molecules. For the establishment of diffusion equilibrium in vapor to take place ahead of vapor absorption by supercritical droplets, and, accordingly, for the state of vapor to be equilibrium (actually, quasi-equilibrium), the following inequality must be satisfied:

$$L^2/D \ll \Delta t. \quad (5.10)$$

Taking the evident estimate $L \sim 1/N^{1/3}$ into account, we may represent (5.10) in the form

$$DN^{2/3} \Delta t \gg 1. \quad (5.11)$$

The constraint thus found agrees with formula (19) and inequality (22) in [10]. As a result, the n_g , v , and D values are added to the external parameters of the theory [earlier, the volume v was used only in expression (1.4), which defines the dimensionless surface tension of a droplet a , rather than directly].

Inequalities (5.1), (5.9), and (5.11), together with inequality (2.9), represent the conditions of applicability for the kinetic theory of supercritical droplet nucle-

ation developed above. The quantities in the left-hand parts of inequalities (5.1), (5.9), and (5.11) are easily estimated by the formulas derived in sections 3 and 4 for Δt , $\Delta\rho$, and N , used together with the relationships (5.2) and (5.8). For example, the left-hand part of inequality (5.1) is estimated as

$$\frac{\Delta t}{t_s} \sim \frac{2}{81} \left(\frac{2^{5/2}}{27} \right)^{1/m} \frac{\alpha t_\infty a^{(4m+3)/2m}}{m \tau v_n^{(4m+1)/2m}} \quad (5.12)$$

As follows from (5.12) and the equation for Φ_* in section 2, adherence to condition (5.1) means that condition (2.9) is also satisfied (possibly near the limit in the case of $h \ll 1$). In turn, adherence to condition (2.9) substantiates the statement (section 2) that effective nucleation of supercritical droplets takes place in the prethreshold range of vapor supersaturations. Thus, the approximate equality (2.8) is confirmed.

The greater the scaling time t_∞ in the power approximation (4.4)—that is, the lower the rate of the creation of the metastable state in vapor—the greater the $\Delta t/t_s$ value in accordance with (5.12) and the better the adherence to condition (5.1), as well as to condition (2.9). Thus, we have revealed the essence of the requirement to sufficiently slow creation of the metastable state in vapor, which was mentioned in section 2.

Note that the higher the v_n parameter [that is, the stronger the requirement to macroscopicity of condensation nuclei set by the limitation (1.1)], the worse the compliance with condition (5.1), according to (5.12). Therefore, the macroscopicity of condensation nuclei, although significantly simplifying the theory of heterogeneous nucleation of supercritical droplets, may at the same time restrict the range of its applicability, as was noted in the introduction. At least, it restricts an important condition of its applicability—inequality (5.1).

In addition to the above expressions setting the conditions of applicability for the kinetic theory, among which the three inequalities (5.1), (5.9), and (5.11) are independent, we may also mention the criterion (1.1) of the macroscopicity of condensation nuclei and condition (1.5) ensured by it: the smallness of the threshold value of vapor supersaturation.

6. DISCUSSION

Expression (4.9) corresponds to the second approximation in the iterative method of contractive approximations [5]. In this approximation, the number N of supercritical droplets originating during condensation in a unit volume of the vapor-gas medium is smaller than the actual number of such droplets. On the contrary, the number of droplets in the third approximation is greater than the actual quantity. Denoting the ordinal number of the approximation by a subscript at N , we obtain [5, equations (29) and (30)]

$$N_3 = \eta(-\infty)[1 - \exp(-\psi/h)], \quad (6.1)$$

where

$$\psi = \int_{-\infty}^{\infty} d\xi \exp \left[\xi - \frac{1}{6} \int_{-\infty}^{\xi} d\xi' (\xi - \xi')^3 \exp \left(\xi' - \frac{h+1}{h} e^{\xi'} \right) \right]. \quad (6.2)$$

Accordingly, substituting N in (4.9) by N_2 , we see that the number of droplets, this extremely important kinetic parameter of the condensation process, is found in the second approximation with a relative error that surely does not exceed $(N_3 - N_2)/N_2$. Numerical calculations with the use of (4.9), (6.1), and (6.2) show that this error is smaller than 0.16 [5]. The number of droplets is then found in the second approximation with an accuracy that is wholly sufficient for the present-day experimental level.

In this study, just as in [2, 4, 5], we assumed the condensation nuclei to be identical, that is, monodispersed. The polydispersity of condensation nuclei presents no problem when they are microscopic objects—separate molecules, ions, etc., which are always identical for the given sort of particles. However, the polydispersity problem does exist for macroscopic condensation nuclei.

If the condensation nuclei are polydispersed, we must consider distribution of their initial concentrations with respect to the number v_n of molecules or ions in them. Let us make a perfectly realistic assumption that the function describing this distribution is virtually zero at $v_n > \bar{v}_n$ and significantly differs from zero at $v_n \leq \bar{v}_n$, where \bar{v}_n is the number of molecules or ions in the largest condensation nuclei existing in fact. The actual dependence of the initial concentration distribution of condensation nuclei on v_n at $v_n \leq \bar{v}_n$ is not essential for further analysis. The only important requirement is that this distribution must depend on v_n smoothly enough compared to the jump at the transition from $v_n > \bar{v}_n$ to $v_n \leq \bar{v}_n$.

As the v_n value decreases, the prethreshold supersaturation range [whose width at the ζ -axis is of the order of $\zeta_{th} v_n^{-2/3}$, according to (2.1) and (2.4)] shifts upward along the ζ -axis at approximately the same rate as the threshold value ζ_{th} . As the metastable state is gradually created in vapor, we will fall within the prethreshold supersaturation range with respect not only to nuclei with $v_n = \bar{v}_n$ but to all nuclei with the dimensions in the $\bar{v}_n - \delta v_n \leq v_n \leq \bar{v}_n$ range, where δv_n satisfies the estimate

$$(\partial \zeta_{th} / \partial v_n) |_{v_n = \bar{v}_n} \delta v_n \sim \zeta_{th} |_{v_n = \bar{v}_n} \bar{v}_n^{-2/3}. \quad (6.3)$$

All these nuclei will be the possible nuclei of effective nucleation of supercritical droplets. Using (6.3) and considering (1.3), we obtain

$$\delta v_n / \bar{v}_n \sim 2\bar{v}_n^{-2/3}. \quad (6.4)$$

For such an important kinetic characteristic of the condensation process as the total number of supercritical droplets appearing in it, the dependence on v_n is especially strong at $h \gg 1$, as is apparent from (4.9) and (4.15). This dependence on v_n is the strongest among all kinetic characteristics and, therefore, "critical" in the case of polydisperse condensation nuclei. According to (4.10) and (4.15), at $h \gg 1$ we obtain

$$\frac{\partial N}{\partial v_n} \approx \frac{14m + 9}{6m} \frac{N}{v_n}. \quad (6.5)$$

For the above theory to be applicable in the case of polydisperse condensation nuclei, an evident inequality must be satisfied:

$$\left(\frac{1}{N} \frac{\partial N}{\partial v_n} \right) \Big|_{v_n = \bar{v}_n} \delta v_n \ll 1. \quad (6.6)$$

Using (6.4) and (6.5), we may reduce condition (6.6) to the inequality

$$\bar{v}_n^{2/3} \gg (14m + 9)/3m. \quad (6.7)$$

Apparently, the criterion of the macroscopicity of condensation nuclei (1.1) ensures compliance with inequality (6.7) if the m parameter is not too small.

Naturally, if condensation nuclei are polydispersed, all formulas of the above theory must contain v_n instead of \bar{v}_n and the total initial concentration of condensation nuclei with the dimensions in the $\eta(-\infty) \bar{v}_n - \delta v_n \leq v_n \leq \bar{v}_n$ range (which is responsible for effective nucleation of supercritical droplets) instead of δv_n . The width δv_n of the range in question should be estimated by formula (6.4).

In laboratory or technical devices and generally in nature, an external increase in ideal supersaturation over the course of time is caused by adiabatic expansion of the vapor-gas medium. A one-to-one relationship between an increase in the ideal supersaturation and the temperature drop in the vapor-gas medium during its adiabatic expansion was revealed in [3]. This relationship enables us to establish how the ideal supersaturation (which, as was shown above, regulates the development of supercritical droplet nucleation as the "driving force" of this process) increases with the decreasing temperature of the vapor-gas medium (actually observed in practice). The same relationship enables us to find the temperature of the vapor-gas medium, which is equal (under the conditions of thermal equilibrium) to that of the droplets; as a result, we may also determine the temperature-dependent external parameters of the theory (n_∞ , a , α , and τ) at the stage corresponding to effective nucleation of super-

critical droplets, where ideal supersaturation reaches the values determined with high accuracy by the relationships (2.6) and (2.8).

For our study, it was unimportant whether the vapor-gas medium contained a one-component or a multicomponent passive gas. If the passive gas in the vapor-gas medium is multicomponent, chemical (for example, photochemical) reactions releasing vapor molecules may take place in this medium. Then, an external increase in the ideal supersaturation over the course of time may be due to "pumping" of vapor into the vapor-gas medium because of chemical reactions that take place within it. If this 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 temperature of this medium will remain virtually constant in time. Accordingly, it will be the same at the stage corresponding to effective nucleation of supercritical droplets as at the very beginning of the creation of the metastable state in vapor.

In section 5, we noted that the time t_s required for establishment of the steady-state intensity j_s of supercritical droplet nucleation may be experimentally determined. We meant an experiment in which supersaturation of vapor is instantly created so as to fall within the prethreshold range (the only range where a steady-state process may take place with a significant intensity j_s). Although, as was noted in section 2, it is difficult to fall within the prethreshold range of vapor supersaturations (very narrow for macroscopic condensation nuclei) in practice if the supersaturation of vapor is instantly created, let us determine the situations in which experimental observation of the time t_s becomes possible.

Evidently, the necessary condition is that the t_s moment, after which supercritical droplets begin to emerge in the entire volume V of the vapor-gas medium at the regular frequency $j_s V$, must satisfy the inequality

$$t_s \gg 1/j_s V \quad (6.8)$$

(the time t_s and the intensity j_s are independent of the volume V). The time t_s may be manifested as the incubation (or delay) time only if limitation (6.8) is satisfied. Considering expressions (25) and (24) in [2] for the time t_s and the intensity j_s (and making allowance for the equality $\Delta v_e = \Delta v_c$, which was established in [1] for macroscopic condensation nuclei and relates the Δv_e and Δv_c values in the expression for the intensity j_s), we may reduce constraint (6.8) to the inequality

$$(V\eta/2) \exp(-F) \gg 1. \quad (6.9)$$

(The η and F values were denoted as n_n and ΔF in [1, 2].) If the volume V of the vapor-gas medium is sufficiently large, inequality (6.9) may be satisfied. Accordingly, the time t_s may be experimentally observed.

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