

Characteristic Kinetic Times and their Hierarchy at the Stage Corresponding to Supercritical Droplet Effective Nucleation on the Macroscopic Condensation Nuclei during Gradual Creation of the Metastable State in Vapor

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Abstract—The quasi-equilibrium state in vapor and the establishment of this state during free molecular and diffusion absorption of vapor by the growing supercritical droplets were studied. The time of the establishment of the quasi-equilibrium state in vapor, the duration of the stage corresponding to effective nucleation of the supercritical droplets, and the characteristic time of the variation of supercritical droplet radius at this stage were estimated under supercritical droplet nucleation conditions on the macroscopic condensation nuclei and the gradual creation of the metastable state in vapor. The hierarchy of the kinetic time scales was revealed. This hierarchy is needed to describe the stage corresponding to effective supercritical droplet nucleation and allows us to understand the complex multistage mechanism of this stage. The possibility of neglecting the curvature of the surface of supercritical droplets at the stage corresponding to their effective nucleation was substantiated. The smallness of the supercritical droplet radius at this stage when compared to the sphere radius of vapor absorption by the droplet was proved.

INTRODUCTION

Earlier [1, 2], we constructed the kinetic theory of supercritical droplet nucleation on the macroscopic condensation nuclei in vapor during the gradual creation of the metastable state in vapor and employed this theory in numerical calculations. The theory was restricted by the assumption that supercritical droplets grow during the entire stage corresponding to their effective nucleation in the free molecular regime.

As was shown in [3], in this regime, the droplets virtually always (regardless of the macroscopicity of the condensation nuclei) overcome the activation barrier of nucleation; however, after this event, the growth regime of the supercritical droplets can be changed gradually to the diffusion regime, which can even be predominant over the entire stage corresponding to effective nucleation of the supercritical droplets.

The estimation of the characteristic kinetic times at the stage corresponding to supercritical droplet effective nucleation and the disclosure of their hierarchy, which are needed to describe this stage and to understand the complex multistep mechanism of this stage under the possible prevalence of free molecular or diffusion absorption of vapor by supercritical droplets, are the main goals of this work.

Earlier [1, 2], this problem was only solved for the case of free molecular absorption of vapor by supercritical droplets. In this case, the condition of the establishment of the quasi-equilibrium state in vapor absorbed

by supercritical droplets was formulated with an accuracy of approximately an order of magnitude; this did not make it possible to generalize the developed theory [1, 2] pertaining to the case of the prevalence of the diffusion absorption of vapor by the supercritical droplets. The theoretically important characteristic time of the variation of supercritical droplet radius at the stage corresponding to droplet effective nucleation was not considered in [1, 2]. The assumption regarding the neglect of the surface curvature of supercritical droplets at the stage corresponding to their effective nucleation was not proved in [1, 2]. In addition, the smallness of the supercritical droplets when compared to the sphere radius of vapor absorption was also unsubstantiated [1, 2].

Relevant generalizations and substantiations will be done in this work. In its content, this work is similar to both publications [1, 2] and work [4], where the characteristic kinetic times were estimated and their hierarchy was revealed during the overcoming of the activation barrier of nucleation by the supercritical droplets generated at the macroscopic condensation nuclei. Although the entire stage corresponding to effective nucleation of the supercritical droplets is accompanied by this process, this is nothing other than the initial step.

The fact that the nucleation of the supercritical droplets in vapor occurs on the macroscopic condensation nuclei appears to be relevant only beginning with Section 5 of this work. For simplicity, we will assume

that the condensation nuclei are completely soluble in the generating droplets, whereas, the matter comprising the nuclei is surface-inactive. Thermodynamic data on the supercritical droplet nucleation will be taken from [5]. Beginning with Section 5, the gradual creation of the metastable state in vapor will also be significant. The practical importance of the macroscopicity of the condensation nuclei and the gradual creation of the metastable state in vapor was explained in [1, 2] and will be emphasized below.

The thermodynamic data needed for the generalization of this work concerning the case of the surface activity of the matter comprising condensation nuclei as well as regarding the case of partially soluble or completely insoluble condensation nuclei should be taken from [6–13].

1. QUASI-STEADY-STATE IN VAPOR DURING FREE MOLECULAR ABSORPTION BY SUPERCRITICAL DROPLETS

At a sufficiently uniform distribution of supercritical droplets in the vapor-gas medium, the vapor absorbed by each droplet, on the average, is present in a sphere which surrounds the droplet and has a radius L readily estimated by the relationship

$$L \sim 1/N^{1/3}, \quad (1.1)$$

where N is the total number of supercritical droplets per unit volume of the vapor-gas medium. Due to the large density of the matter comprising a droplet, the inequality $R \ll L$, where R is the droplet radius, is valid. This inequality will be discussed in more detail in section 9.

Let us denote the local density of the number of vapor molecules in the vapor-gas medium at a distance r from the droplet center at the current moment t by $n(r, t)$. Distance r fits the range $R \leq r \leq L$. The development of the local vapor concentration $n(r, t)$ in time in the range $R \leq r \leq L$ is determined by the diffusion equation

$$\partial n(r, t) / \partial t = (D/r) \partial^2 [rn(r, t)] / \partial r^2, \quad (1.2)$$

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

According to the kinetic theory of gas, the coefficient D is estimated as

$$D \sim \frac{1}{3} l v_T, \quad (1.3)$$

where l is the free path of the vapor molecules in the vapor-gas medium. This parameter is estimated as

$$l \sim (n + n_g)^{-1} v^{-2/3}, \quad (1.4)$$

where n and n_g are the average densities of the number of vapor molecules and passive gas in the vapor-gas medium, respectively; v is the molecular volume of the condensing liquid (the $v^{2/3}$ value determines the order of magnitude of the cross section of the collisions of the vapor molecules with the molecules of the vapor-gas

medium); and v_T is the thermal velocity of the vapor molecules.

To solve equation (1.2), two boundary conditions (at $r = L$ and $r = R$) are required. In this and the following sections, we will consider the case where the supercritical droplet absorbs the vapor in a free molecular regime. This case occurs, when

$$R \ll l/\alpha, \quad (1.5)$$

where α is the condensation coefficient of the vapor molecules.

In the case under consideration, the boundary conditions for equation (1.2) has the form

$$n(r, t)|_{r=L} = n, \quad (1.6)$$

$$D \partial n(r, t) / \partial r|_{r=R} = q[n(r, t)|_{r=R} - n_R], \quad (1.7)$$

where

$$q = \frac{1}{4} \alpha v_T \quad (1.8)$$

and n_R is the density of the number of vapor molecules, which is in a material equilibrium with the supercritical droplets of radius R . This parameter is set by the Gibbs-Kelvin equation. In addition to what has been said above, the n value acquires a more exact description of the density of the number of vapor molecules far from the surface of supercritical droplet. As the predetermined value, it is the density n that determines the intensity of nucleation of the new supercritical droplets, in addition to the droplets that are already present in supersaturated vapor. The inequality $qR \ll D$ follows from (1.3), (1.5), and (1.8).

The applicability of the diffusion equation (1.2) and relevant boundary condition (1.7) will be substantiated at the end of this section.

According to (1.2), (1.6), and (1.7), the solution in the quasi-steady-state ($\partial n(r, t) / \partial t = 0$) is

$$n_s(r) = n + \frac{qR^2(n - n_R)}{DL + qR(L - R)} - \frac{qLR^2(n - n_R)}{DL + qR(L - R)} \frac{1}{r}, \quad (1.9)$$

where $n_s(r)$ is the local density of the number of the vapor molecules at the quasi-steady-state. We will discuss assumption (1.9) regarding the quasi-immobility of the surface of supercritical droplets in Section 7.

In view of the already noted inequality $qR \ll D$ from (1.9), follows the equality

$$n_s(r) = n + \frac{qR^2(n - n_R)}{DL} - \frac{qR^2(n - n_R)}{Dr}. \quad (1.10)$$

At $qR \ll D$ and $R \ll L$ and according to (1.10), the $n_s(r)$ concentration virtually coincides with n . Hence, in the case of free molecular absorption of vapor by supercritical droplets, the quasi-steady-state of vapor also appears as the quasi-equilibrium, which is determined by the current value of the density of the number of

vapor molecules n far from the surface of the supercritical droplets.

Using equality (1.10) for the total flux $J_s \equiv 4\pi DR^2 \partial n_s(r)/\partial r|_{r=R}$ of vapor molecules to the supercritical droplet in the quasi-steady-state, we have an expression

$$J_s = 4\pi qR^2(n - n_R), \quad (1.11)$$

where the L parameter is completely absent. Evidently, J_s also determines the number of vapor molecules entering per unit of time into the absorption sphere surrounding the supercritical droplet.

Relationships (1.10) and (1.11) correspond to the accepted notions on the free molecular absorption of vapor by supercritical droplets [14].

Let us substantiate the applicability of the diffusion equation (1.2) and relevant boundary condition (1.7) at the free molecular absorption of vapor by a supercritical droplet.

Vapor molecules pass the boundary Knudsen layer $R \leq r \leq l/\alpha$ virtually without any collisions. Thus, in this layer, the vapor concentration $n(r, t)$ coincides with its value at the external layer of a surface. Then, in accordance with relationship (5.1) from [14] and kinetic considerations, we have the following expression for the flux J of the vapor molecules to the droplets,

$$J = 4\pi qR^2[n(r, t)|_{r=l/\alpha} - n_R]. \quad (1.12)$$

On the other hand, for the same flux J , according to the hydrodynamic considerations applied outside the wall boundary layer, we may write

$$J = 4\pi D \left(\frac{l}{\alpha} \right)^2 \frac{\partial n(r, t)}{\partial r} \Big|_{r=l/\alpha}. \quad (1.13)$$

Equating (1.12) and (1.13), we obtain the boundary condition

$$\begin{aligned} D \partial n(r, t) / \partial r|_{r=l/\alpha} \\ = \frac{q\alpha^2 R^2}{l^2} [n(r, t)|_{r=l/\alpha} - n_R], \end{aligned} \quad (1.14)$$

which is valid in a general non-stationary case. Outside the surface $r = l/\alpha$, the diffusion equation (1.2) is definitely valid.

Substituting (1.7) for (1.14), i.e., substituting R and q for l/α and $q\alpha^2 R^2/l^2$, respectively, in the quasi-equilibrium case instead of (1.9), we have

$$n_s(r) = n + \frac{qR^2(n - n_R)}{DL + (q\alpha R^2/l)(L - l/\alpha)} \left(1 - \frac{L}{r} \right). \quad (1.15)$$

Undoubtedly, equation (1.15) refers to the range $l/\alpha \leq r \leq L$ outside the boundary layer adjacent to the droplet. In this case, the diffusion equation (1.2) and expression (1.13) based on hydrodynamic considerations, and, hence, the boundary condition (1.14) are

valid in a greater region. As noted above, in the boundary layer adjacent to the droplet, the $n(r, t)$ concentration coincides with its value at the external surface of a layer.

From (1.3), (1.5), and (1.8) readily follows the inequality $q\alpha R^2/lD \ll 1$. According to this inequality and the aforementioned inequality $l/\alpha \ll L$, expression (1.15) is reduced to the expression (1.10) derived earlier. Accordingly, expressions (1.12) and (1.13) under quasi-steady-state of vapor are reduced to the previous expression (1.11).

Hence, the diffusion equation (1.2) and relevant boundary condition (1.7) are efficiently applicable for the determination of the quasi-steady-state concentration $n_s(r)$ outside the boundary layer adjacent to the droplet and the quasi-steady-state flux J_s of the vapor molecules to the droplets.

2. TIME OF ESTABLISHMENT OF THE QUASI-STEADY-STATE OF VAPOR AT FREE MOLECULAR ABSORPTION OF VAPOR BY SUPERCRITICAL DROPLETS

Let us find out how the local vapor concentration $n(r, t)$ approaches with time its quasi-steady-state value $n_s(r)$ under the free molecular absorption of vapor by the supercritical droplets. Apparently, this task is reduced to the elucidation of the character of the approach to zero of the deviation

$$\Delta n(r, t) \equiv n(r, t) - n_s(r) \quad (2.1)$$

of the concentration $n(r, t)$ from $n_s(r)$.

Let us first use the diffusion equation (1.2) up to the droplet surface with the relevant boundary condition (1.7). We will find out at the end of this section to what extent this fact corresponds to boundary condition (1.14).

According to equation (1.2) and the fact that $n_s(r)$ is its solution, we have for the deviation $\Delta n(r, t)$, which is defined by equation (2.1), the following equation

$$\partial \Delta n(r, t) / \partial t = (D/r) \partial^2 [r \Delta n(r, t)] / \partial r^2. \quad (2.2)$$

Further, according to boundary conditions (1.6) and (1.7) and the fact that $n_s(r)$ satisfies these conditions, we have for $\Delta n(r, t)$ boundary conditions of the following type

$$\Delta n(r, t)|_{r=L} = 0, \quad (2.3)$$

$$D \partial \Delta n(r, t) / \partial r|_{r=R} = q \Delta n(r, t)|_{r=R}. \quad (2.4)$$

Let us note right away that the time-independent solution $\Delta n(r, t) = A + B/r$ of equation (2.2), where A and B are the constants, is absent, since at boundary conditions (2.3) and (2.4), $A = 0$ and $B = 0$.

This circumstance is explained by the fact that the quasi-steady-state concentration $n_s(r)$ already involves the entire time-independent contribution to the total concentration $n(r, t)$.

Once the boundary condition (2.3) is fulfilled, the time-dependent solution of equation (2.2), which we are concerned with, has the form

$$\Delta n(r, t) = \frac{A}{r} \sin[\lambda(r-L)] e^{-\lambda^2 D t}, \quad (2.5)$$

where A is the constant, and λ is the desirable nonzero value.

The substitution of solution (2.5) into the boundary conditions (2.3) and (2.4) results in the transcendental equation for λ . We are interested in the least by the absolute value (other than zero) root λ of this equation. As is clear from (2.5), it is this root that according to equality

$$t_{rel} = 1/\lambda^2 D \quad (2.6)$$

determines the desired time t_{rel} of the establishment of the quasi-steady-state in vapor.

As may be readily shown, transcendental equation for λ has the form

$$\tan[\lambda(L-R)] = \frac{\lambda R}{1+qR/D}. \quad (2.7)$$

At $R \ll L$ and $qR \ll D$, equation (2.7) transforms into the following expression

$$\tan(\lambda L) = -\lambda R. \quad (2.8)$$

The least root by the absolute value (other than zero) λ of equation (2.8) we seek in the form

$$\lambda = (\pi - \delta)/L, \quad (2.9)$$

where the δ value, which should be determined, satisfies the constraint $0 < \delta \ll 1$. Substituting (2.9) into (2.8), we arrive at the equation

$$\tan \delta = (\pi - \delta)R/L, \quad (2.10)$$

whose solution (with a high degree of accuracy) is the combination

$$\delta = \pi R/L. \quad (2.11)$$

In view of inequality $R \ll L$, this solution confirms the constraint $0 < \delta \ll 1$ employed for its determination, whereas according to (2.9), this solution leads (with a high degree of accuracy) to the expression

$$\lambda = \pi/L. \quad (2.12)$$

The radius of the supercritical droplet R is not included into this equation.

From (2.6) and (2.12), it follows that

$$t_{rel} = L^2/\pi^2 D. \quad (2.13)$$

The process of the approach with time of the non-steady-state concentration $n(r, t)$ to the quasi-steady-state concentration distribution $n_s(r)$ is of interest only in the range $l/\alpha \leq r \leq L$ outside the boundary layer adjacent to the droplet. While working with this range, we may employ the boundary condition (1.14). As is apparent from (2.7)–(2.11), the substitution of bound-

ary condition (1.7) for boundary condition (1.14); i.e., the substitution of R and q for l/α and $q\alpha^2 R^2/l^2$, respectively, does not affect (in view of inequalities $l/\alpha \ll L$ and $q\alpha R^2/lD \ll 1$ the formula (2.12)). This fact confirms the resultant formula (2.13).

3. QUASI-STEADY-STATE OF VAPOR AT ITS DIFFUSION ABSORPTION BY SUPERCRITICAL DROPLETS

Let us now discuss the case where vapor is absorbed by supercritical droplets in the diffusion regime. This case occurs when the condition

$$R \gg l/\alpha \quad (3.1)$$

opposite to (1.5) is fulfilled.

Of course, in the case considered by equation (1.2) remains valid. However, instead of (1.6) and (1.7), we have new boundary conditions

$$n(r, t)|_{r=L} = n, \quad (3.2)$$

and

$$n(r, t)|_{r=R} = n_R, \quad (3.3)$$

where n is still the density of the number of vapor molecules far from the surface of the supercritical droplets.

According to (1.2), (3.2), and (3.3), under the quasi-steady-state, we have the solution

$$n_s(r) = n + \frac{R(n-n_R)}{L-R} - \frac{LR(n-n_R)}{L-R} \frac{1}{r}. \quad (3.4)$$

The assumption made in (3.4) about the quasi-immobility of the surface of the supercritical droplets will be discussed in Section 7.

In view of inequality $R \ll L$, from (3.4), we may obtain a simpler expression

$$n_s(r) = n + \frac{R(n-n_R)}{L} - \frac{R(n-n_R)}{r}. \quad (3.5)$$

According to (3.5), the deviation of the concentration $n_s(r)$ from n appears to be significant near the surface of a supercritical droplet. Accordingly, the quasi-steady-state of vapor differs from quasi-equilibrium state determined by the current value of the density of the number of vapor molecules n far from the surface of a supercritical droplet.

It follows from (3.5) that

$$4\pi \int_R^L r^2 n_s(r) dr = \frac{4\pi}{3} (L^3 - R^3) n - 2\pi R (L^2 - R^2) (n - n_R). \quad (3.6)$$

At $R \ll L$, this expression is reduced to the equality

$$4\pi \int_R^L r^2 n_s(r) dr \approx \frac{4\pi}{3} L^3 n. \quad (3.7)$$

According to (3.7), at the quasi-steady-state of vapor, irrespective of the deviation from the quasi-equilibrium state, the total number of the vapor molecules in the entire sphere of vapor absorption by the supercritical droplets remains virtually the same as it would be inside this sphere for the homogeneous vapor with concentration n . This circumstance is very important for the generalization of the theory proposed for the case of diffusion growth of the supercritical droplets [1, 2].

For the total flux $J_s \equiv 4\pi DR^2 \partial n_s(r) / \partial r|_{r=R}$ of the vapor molecules to the supercritical droplets under the quasi-steady-state, from (3.5), we now have the following expression

$$J_s = 4\pi DR(n - n_R), \quad (3.8)$$

where the L parameter is completely absent. Obviously, J_s also determines the number of vapor molecules entering per unit of time into the absorption sphere surrounding the supercritical droplet.

Relationships (3.5) and (3.8) correspond to the current notions on the diffusion absorption of vapor by the supercritical droplets [14].

4. TIME OF ESTABLISHMENT OF THE QUASI-STEADY-STATE OF VAPOR AT ITS DIFFUSION ABSORPTION BY SUPERCRITICAL DROPLETS

Let us elucidate how the local vapor concentration $n(r, t)$ approaches its quasi-steady-state value $n_s(r)$ at the diffusion absorption by supercritical droplets. This problem is reduced to the elucidation of the character of approaching zero by the deviation $\Delta n(r, t)$ determined by equality (2.1).

According to equation (1.2) and the fact that $n_s(r)$ is nothing other than its solution, we have for $\Delta n(r, t)$ the same equation (2.2).

Then, in compliance with boundary conditions (3.2) and (3.4) and the fact that $n_s(r)$ satisfies these conditions, the boundary conditions for $\Delta n(r, t)$ are:

$$\Delta n(r, t)|_{r=L} = 0, \quad (4.1)$$

and

$$\Delta n(r, t)|_{r=R} = 0. \quad (4.2)$$

Note again that the time-independent solution $\Delta n(r, t) = A + B/r$ of equation (2.2), where A and B are the constants, is absent, because under boundary conditions (4.1) and (4.2), $A = 0$ and $B = 0$. Of course, this circumstance is explained by the fact that the quasi-steady-state concentration $n_s(r)$ already involves the entire time-independent contribution to the total concentration $n(r, t)$.

The time-dependent solution of equation (2.2) (which is of interest to us) still has the form of expression (2.5), where A is the constant, and λ is the desired nonzero value, provided that boundary condition (4.1) is fulfilled. Correspondingly, expression (2.6) for the

time t_{rel} of the establishment of quasi-steady-state in vapor remains valid.

The compliance of boundary condition (4.2) with the solution (2.5) of equation (2.2) leads to the transcendental equation for λ . We will again be concerned with the least root by absolute value (other than zero) of this equation. Evidently, it is this root that determines the desired time t_{rel} required to establish quasi-steady-state in vapor.

As may be readily shown, the transcendental equation for λ has the form

$$\sin[\lambda(L - R)] = 0. \quad (4.3)$$

At $R \ll L$, equation (4.3) transforms into equation

$$\sin(\lambda L) = 0, \quad (4.4)$$

whose desired root λ is determined by the same expression (2.12), where the radius of the supercritical droplet R is completely absent.

Hence, it follows from (2.6) and (2.12) that the previous expression (2.13) for the time t_{rel} required to establish quasi-steady-state in vapor also remains valid for the diffusion absorption of vapor by a supercritical droplet.

Let us be convinced of the fact that time t_{rel} represented by expression (2.13) and estimation (1.1) determines (by an order of magnitude) both the time of the establishment of the quasi-steady-state in vapor in the spheres of its absorption by supercritical droplets and the time required to establish the quasi-steady-state in vapor over the entire vapor-gas medium, where supercritical droplets originated.

At a sufficiently dense "packing" of the vapor absorption spheres in the vapor-gas medium admitted by the aforementioned considerations (albeit compatible with the absence of sphere overlapping), the volume of the interlayers between the spheres is smaller than that occupied by the spheres. Then, the role of the interlayers is quite insignificant. Correspondingly, the time required to establish the quasi-steady-state in vapor in the absorption spheres is only slightly smaller than the time required to establish this state over the entire vapor-gas medium.

In addition, note that expression (1.1) overestimates the radius L of the vapor absorption sphere. Indeed, according to this estimate, the fraction of a volume $4\pi L^3 N/3$ occupied by the spheres seems to be larger than unity. Then, expression (2.13) also overestimates the time t_{rel} , hence, resulting in its approach to the time of the establishment of quasi-steady-state over the entire vapor-gas medium.

As a result, the time t_{rel} defined by expression (3.13) and estimation (1.1) actually determines the order of the value of the time required to establish the quasi-steady-state over the entire vapor-gas medium.

Note that the determination of time t_{rel} did not require the knowledge of the initial vapor concentration.

The approach (with time) of the vapor to its quasi-steady-state in the absorption sphere of vapor by the droplets under boundary conditions (3.2) and (3.3) was studied earlier [14]. However, only the limiting case $L \rightarrow \infty$ was treated in [14]; moreover, it was assumed that at the initial moment $t = 0$ the vapor concentration is uniform over its entire volume and is equal to n . According to formula (14.4) from [14] at $t \rightarrow \infty$, the asymptotics for the flux of the vapor molecules to the droplet has the form

$$J = J_s \left(1 + \frac{R}{\sqrt{\pi D t}} \right) \quad t \rightarrow \infty, \quad (4.5)$$

where the accepted notations were employed, and the quasi-steady-state flux J_s is determined by formula (3.8). Since the pattern of asymptotics (4.5) is the power (but not exponential) with respect to t , it does not assume (even for the vicinity of point $r = R$, where the flux of vapor molecules to the droplet is formed) the existence of the finite relaxation time t_{rel} . Once this time is exceeded, the vapor state becomes a quasi-steady-state. Expression (4.5) allows us to identify the characteristic time $R^2/\pi D$ and the degree of approach to the quasi-steady-state, which is sufficient in each specific case [14]. The more time t exceeds the characteristic time $R^2/\pi D$, the larger [according to (4.5)] the degree of approach to the quasi-steady-state. The fact that at infinite volume of the absorption sphere of vapor [proposed in (4.5)] there is no finite relaxation time t_{rel} following from both (4.5) and our formula (2.13), according to which at $L \rightarrow \infty$, $t \rightarrow \infty$.

The results obtained are also consistent with the power (with respect to t) approximation to the quasi-steady-state demonstrated by asymptotics (4.5). Indeed, in the limit $L \rightarrow \infty$, the nonzero roots $\lambda_j = j\pi/L$ ($j = 1, 2, \dots$) of equation (4.4) form an almost continuous spectrum of values. Out of all of these roots, only the least (by the absolute value) root was taken into account in expression (2.12). Moreover, the expression in the right-hand side of equation (2.5) transfers into the sum over $j = 1, 2, \dots$ of the identical expressions with $\lambda = \lambda_j$ and coefficients $A = A_j$ determined by the initial vapor concentration. When the initial vapor concentration is close to uniform [as assumed in (4.5)], the sum over j is reduced to the integral with respect to j . Although in the integral with respect to j and the roots $\lambda_j = j\pi/L$ in the limit $L \rightarrow \infty$ tend to vanish, this integral eventually decreases with an increase in t . Note that in accordance with (4.5), this decrease is quite slow and follows the power function (with respect to t).

In our previous discussions, we assumed that the absorption spheres of vapor by the droplets may exchange the vapor with the environment. Such a situation (which we are concerned with) is represented by boundary conditions (3.2) and (1.6) and actually takes place when the droplet ensemble is formed in the vapor-gas medium. Let us compare this situation with the ideal case, when the sphere of vapor absorption by

the droplets cannot exchange the vapor with its environment. Then, instead of (3.2) the following boundary condition

$$\partial n(r, t) / \partial r|_{r=L} = 0. \quad (4.6)$$

is fulfilled.

The solution of diffusion equation (1.2) at the boundary conditions (3.3) and (4.6), as well as at zero initial vapor concentration at the moment $t = 0$ was studied in [14]. Naturally, this work dealt with the evaporation, but not with the droplet growth. According to formula (14.22) from [14], at $t \rightarrow \infty$ the asymptotics for positive flux $I \equiv -J$ of vapor molecules from the droplet has the form

$$I = 4\pi D R^2 n_R \left[\frac{1}{R} \exp\left(-\frac{3RDt}{(L-R)^3}\right) + \frac{2}{L-R} \exp\left(-\frac{20Dt}{L^2}\right) + \dots \right] \quad t \rightarrow \infty, \quad (4.7)$$

where the accepted notations were used. When inequality $R \ll L$ [proposed in asymptotics (4.7)] is valid, its first term decays exponentially during the relaxation time $t_{rel}^{(1)} = L^3/3RD$, whereas the second term decays exponentially over a much shorter relaxation time $t_{rel}^{(2)} = L^2/20D$. At $L \rightarrow \infty$, both values of the relaxation time tend to infinity. Time $t_{rel}^{(1)}$ determines the duration of the establishment of the quasi-steady-state in vapor, when its concentration over the entire sphere of vapor absorption becomes identical and equal to concentration n_R at the droplet surface. Time $t_{rel}^{(2)}$ determines the duration of the establishment of the quasi-steady-state in vapor preceding its quasi-equilibrium state. This is consistent with the fact that time $t_{rel}^{(2)} = L^2/20D$ coincides by an order of magnitude with time t_{rel} represented by expression (2.13).

According to (4.7), the total number of vapor molecules in the sphere of its absorption (actually, its evolution) by the droplet varies with time at the physical isolation of a sphere from its environment. When relaxation time $t^{(1)} = L^3/3RD$ elapses, this number is determined by the sphere volume and the concentration achieved asymptotically over the entire sphere at the quasi-equilibrium state in vapor, and it is equal to concentration n_R at the droplet surface. On the contrary, according to (3.7), the total number of vapor molecules in the sphere of vapor absorption by the droplets varies with the time at the material contact of a sphere with its environment and on quasi-steady-state in vapor only as far as the vapor concentration at the external surface of a sphere varies, i.e., as the vapor in the vapor-gas medium is absorbed by the entire droplet ensemble presented in this medium.

The consideration of the droplet ensemble, which is actually originated in supersaturated vapor is of fundamental importance for the nucleation. The appearance of this ensemble occurs consistently with the vapor absorption of the already originated supercritical droplets and its external transport; when condensation nuclei are present, this process occurs consistently with the consumption of nuclei by already originated supercritical droplets.

The stage corresponding to effective nucleation of supercritical droplets is the most important and complex research problem concerning nucleation. It is this stage at which the ensemble of supercritical droplets appear and their size spectrum is formed. However, this stage does not imply the termination of the vapor absorption by supercritical droplets. Moreover, the vapor absorption (even in the absence of external vapor transport) proceeds during some longer periods of time and with an increasing intensity, which resulted to the rapid collapse of vapor. Nevertheless, the investigation of the stages followed by the stage corresponding to effective nucleation of the supercritical droplets is not that difficult, because the size spectrum of the supercritical droplets was determined. This study was performed in [15], and we are not concerned with it in this work. The majority of our efforts will be concentrated at the stage corresponding to the effective nucleation of supercritical droplets.

5. CHARACTERISTIC KINETIC TIMES AT THE STAGE CORRESPONDING TO EFFECTIVE NUCLEATION OF SUPERCRITICAL DROPLETS

As follows from expression (2.13), estimate (1.1), and the discussion presented at the end of a preceding section, the establishment of the quasi-steady-state in vapor in the vapor-gas medium, where supercritical droplets are originated, occurs over the time t_{rel} estimated as

$$t_{rel} \sim 1/\pi^2 DN^{2/3}. \quad (5.1)$$

At the stage corresponding to effective nucleation of the supercritical droplets (which is of interest to us), estimate (5.1) is valid at the possible prevalence of both free molecular and diffusion absorption of vapor by supercritical droplets at this stage.

We will assume below that the nucleation of supercritical droplets in vapor occurs on the macroscopic condensation nuclei that are present in vapor (actually, in the vapor-gas medium). As was noted in [1,2], the importance of considering such a situation is explained by the fact that in this case the vapor condensation may occur at rather low supersaturations. The macroscopicity of the condensation nuclei suggests that $v_n^{1/3} \gg 1$, where v_n is the number of molecules (or ions) in the condensation nucleus.

For the sake of simplicity, let us assume that the condensation nuclei are completely dissolved in the droplets originating on their surfaces, and the matter comprising nuclei is surface-inactive.

In the kinetic theory of the nucleation of supercritical droplets, the time required to establish the steady-state (actually, quasi-steady-state) regime of overcoming the activation barrier of nucleation by the droplets is a very important parameter. For this time, denoted, according to formula (5.2) from [1], by t_s , we have the expression

$$t_s \approx \left(\frac{3}{2}\right)^{7/2} \frac{\tau v_n^{4/3}}{\alpha a^2}, \quad (5.2)$$

where τ is the free time of the saturated vapor molecules. It is defined by the equality

$$\tau = 12/[(36\pi)^{1/3} v^{2/3} n_\infty v_T], \quad (5.3)$$

where $n_\infty \equiv n_{R|R \rightarrow \infty}$ is the density of the number of saturated vapor molecules. Further, a is the dimensionless surface tension of a droplet defined by the equality

$$a = (4\pi\sigma/kT)(3v/4\pi)^{2/3}, \quad (5.4)$$

where σ is the droplet surface tension; k is the Boltzmann constant; and T is the temperature of the droplets and surrounding vapor-gas medium at the stage corresponding to effective nucleation of the supercritical droplets.

The gradual creation of the metastable state in vapor is described by the law of the growth (in time) of the ideal supersaturation Φ defined by the equality

$$\Phi = (n_{tot}/n_\infty) - 1, \quad (5.5)$$

where n_{tot} is the total number of molecules of the condensing matter per unit volume of the vapor-gas medium, including molecules comprising droplets (the number n_{tot} is larger than number n by the number of vapor molecules condensed by the droplets occurring 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. Following [1, 2], let us assume power approximation

$$\Phi = (t/t_\infty)^m \quad (5.6)$$

as the law of the growth (in time) of ideal supersaturation. In this approximation, there are two independent parameters, namely, the scaling time t_∞ and the exponent m . According to power approximation (5.6), time t is taken with the reference to the moment corresponding to $\Phi = 0$. Approximation (5.6) will be significant only at the stage corresponding to effective nucleation of supercritical droplets. It was shown [2] that in this case this approximation is quite adequate. It was also demonstrated [2] how one can determine the parameters t_∞ and m of approximation (5.6) by the law of the creation of the metastable state in vapor, which was set

by the experiment. As was noted earlier [1, 2], the significance of the gradual externally controlled creation of the metastable state in vapor is explained by the fact that it may enable one to monitor the development of the condensation process.

To define time t_{rel} set by estimate (5.1) via the initial parameters of a theory, one should express the number N of the supercritical droplets originating at the stage corresponding to effective nucleation per unit volume of the vapor-gas medium via these parameters.

At this stage, upon the prevalence of free molecular absorption of vapor by supercritical droplets for the number N , we have [1, equation (4.9)]

$$N = \eta(-\infty)[1 - \exp(-1/h)], \quad (5.7)$$

where $\eta(-\infty)$ denotes the initial concentration of the condensation nuclei, i.e., 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 the vapor supersaturation, is given by the approximate relationship (4.15) [1]

$$h \approx \frac{1}{4^2} \left(\frac{2^{5/2}}{27} \right)^{(2m+3)/m} \frac{\eta(-\infty) (\alpha t_\infty)^3 a^{(6m+9)/2m}}{n_\infty (m\tau)^3 v_n^{(14m+9)/6m}}. \quad (5.8)$$

It is assumed that the constraint $R \ll l/\alpha$, corresponding to the prevalence of free molecular absorption of vapor by supercritical droplets at the stage corresponding to effective nucleation, is fulfilled (we do not round off the numerical factors in order to follow them more easily).

Extending the kinetic theory developed in [1] to the case, where the diffusion absorption of vapor becomes prevalent at the stage corresponding to effective nucleation of supercritical droplets, we may be convinced that expression (5.7) remains valid in this case as well. However, the dimensionless parameter h still describing the dependence of the activation energy of nucleation on the vapor supersaturation will be given, instead of (5.8), by the approximate relationship

$$h \approx \frac{81\pi^{1/2}}{24^{1/4}32} \left(\frac{2^{5/2}}{27} \right)^{3(m+1)/2m} \times \frac{\eta(-\infty) \left(\frac{t_\infty}{m\tau_D} \right)^{3/2} a^{(3m+9)/4m}}{n_\infty (m\tau_D)^{3/2} v_n^{(7m+9)/12m}} \quad (R \gg l/\alpha), \quad (5.9)$$

where τ_D is the time characteristic for the prevalence of the diffusion absorption of vapor, which is determined by equality

$$\tau_D = (3/8\pi)(4\pi/3v)^{1/3}/Dn_\infty. \quad (5.10)$$

The number of originating supercritical droplets is the most important kinetic characteristic of the entire condensation process. Relationships (5.7)–(5.9) allow

us to determine this number; therefore, these relationships alone are of great significance.

As follows from (5.7) at $h \gg 1$ and $h \ll 1$, we have

$$N = \eta(-\infty)/h \quad (h \gg 1), \quad (5.11)$$

$$N = \eta(-\infty) \quad (h \ll 1). \quad (5.12)$$

According to (5.11), in the case of $h \gg 1$, the supercritical droplets consume only a small fraction of the initial number of condensation nuclei (each droplet consumes one nuclei). On the contrary, according to (5.12), at $h \ll 1$, the supercritical droplets absorb virtually the entire initial amount of the condensation nuclei. Limiting situations $h \gg 1$ and $h \ll 1$ are of interest in view of both their comparative simplicity and physical obviousness, as well as due to the fact that at the linear dependence of parameter h on $\eta(-\infty)$ demonstrated by relationships (5.8) and (5.9), these situations occur within the entire practical range of the variation of the initial nuclei concentration $\eta(-\infty)$ much more often than the intermediate situation where $h \sim 1$.

Under the kinetic theory of the nucleation of supercritical droplets, the important factor is also the duration Δt of the stage corresponding to effective nucleation of supercritical droplets. At the prevalence of free molecular absorption of vapor by supercritical droplets at this stage, for the typical limiting situations $h \gg 1$ and $h \ll 1$, we have the approximate relationship for the ratio of Δt to time t_s [1, expression (2.7)]

$$\frac{\Delta t}{t_s} = \frac{1}{2^{3/2}} \left(\frac{2^{5/2}}{27} \right)^{(m+1)/m} \frac{\alpha t_\infty a^{(4m+3)/2m}}{m\tau v_n^{(4m+1)/2m}} \quad (5.13)$$

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

Once it is represented directly for time Δt , according to (5.2), this relationship is expressed as

$$\Delta t = \frac{6^{1/2}}{8} \left(\frac{2^{5/2}}{27} \right)^{1/m} \frac{t_\infty a^{3/2m}}{m v_n^{(4m+3)/6m}} \quad (5.14)$$

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

Extending the developed theory [1] to the case where the diffusion absorption of vapor becomes prevalent at the stage corresponding to the effective nucleation of supercritical droplets, one may be convinced that relationships (5.13) and (5.14) remain valid in this case as well. The fact that the overcoming of the activation barrier of nucleation by the droplets occurs (despite the macroscopicity of condensation nuclei) virtually everytime at the free molecular absorption of vapor [3] was significant for this conclusion.

Finally, the characteristic time of the variation of the supercritical droplets radius is also important for the kinetic theory of nucleation of supercritical droplets. Obviously, this time denoted by t_R is determined by the equality

$$t_R = R/\dot{R}. \quad (5.15)$$

The point over R denotes the derivative with respect to time.

The relation between time t_R and time Δt will be revealed in the next Section.

6. THE RELATION BETWEEN THE CHARACTERISTIC TIME OF THE VARIATION OF THE RADIUS OF SUPERCRITICAL DROPLETS AND THE DURATION OF EFFECTIVE NUCLEATION OF SUPERCRITICAL DROPLETS

Let us denote the number of molecules of a matter condensed in a droplet by v . As was shown earlier [5], at the macroscopicity of the condensation nuclei and the high solubility of matter comprising the nuclei in droplets, the solution will already be rather dilute with respect to the droplets overcoming the activation barrier of nucleation. Evidently, this solution will be more dilute in the droplets that have overcome this barrier. Then, for supercritical droplets with a high degree of accuracy, we have

$$v = 4\pi R^3/3v. \quad (6.1)$$

Whatever the regime of exchange for condensing matter between a droplet and vapor is, we may always pass from variable v to variable ρ , which is the function of v . For all supercritical droplets (actually, for quite large supercritical droplets) providing approximate equality

$$n - n_R \approx n - n_\infty, \quad (6.2)$$

this variable increases with time t at a rate independent of ρ (as well as of v) and is determined only by the vapor supersaturation. Relation (6.2), i.e., the assumption about the neglect of the curvature of the supercritical droplet surface at the stage corresponding to their effective nucleation, will be substantiated in Section 8.

Let us introduce variable ρ , which is convenient for the description of supercritical droplets. From expressions (1.11) and (3.8) with allowance for (6.1) and (6.2) and the fact that the J_s value represents the rate of growth \dot{v} of the number of molecules v with time, we may see that the convenient variable ρ is defined by the equalities

$$\rho = v^{1/3} \quad (R \ll l/\alpha), \quad (6.3)$$

$$\rho = v^{2/3} \quad (R \gg l/\alpha). \quad (6.4)$$

Here, the normalization of variable ρ selected in (6.3) and (6.4), at which ρ^3 or $\rho^{3/2}$ determines the number of molecules v in the $R \ll l/\alpha$ or $R \gg l/\alpha$ cases, is insignificant. It is only of importance that in these cases variable ρ is proportional to the radius of the supercritical droplets and to the surface area.

According to (6.1), (6.3), and (6.4), we obtain

$$\dot{R}/R = \dot{\rho}/\rho \quad (R \ll l/\alpha), \quad (6.5)$$

$$\dot{R}/R = \dot{\rho}/2\rho \quad (R \gg l/\alpha). \quad (6.6)$$

Naturally, at the stage corresponding to effective nucleation of supercritical droplets, the droplets, which most intensely absorb the vapor molecules or consume the initial amount of the condensation nuclei in the vapor-gas medium, seem to be the most significant; eventually, these droplets suppress the effective nucleation of the supercritical droplets. The "size" of these droplets at the axis of the introduced variable ρ fits approximately into the middle of the total width $\Delta\rho$ of the size spectrum for all effectively nucleating supercritical droplets.

Hence, we have an estimate

$$\rho \sim \Delta\rho. \quad (6.7)$$

Let us emphasize that only at the ρ -axis, where the rate of growth for all supercritical droplets is identical, we may identify the width $\Delta\rho$ of the size spectrum of supercritical droplets as a time-independent variable.

Taking into account that the rate $\dot{\rho}$ is uniquely determined by the vapor supersaturation, which (as was shown in [1]) remains virtually unchanged at the stage corresponding to effective nucleation of supercritical droplets, we have the approximate equality

$$\Delta\rho \approx \dot{\rho}\Delta t. \quad (6.8)$$

Taking advantage of estimate (6.7) and equality (6.8) as well as in view of definition (5.15) and relations (6.5) and (6.6), we obtain the estimate

$$t_R \sim \Delta t, \quad (6.9)$$

which determines the desired relation between the characteristic time t_R and the time Δt at the stage corresponding to effective nucleation of the supercritical droplets.

The characteristic value of vapor supersaturation corresponding to the stage of effective nucleation of supercritical droplets irrespective of the vapor absorption regime was determined under the condition of the macroscopicity of the condensation nuclei [1]. Then, the rate $\dot{\rho}$ in relationship (6.8) may be readily obtained using (1.11), (3.8), and (6.2)–(6.4) for the cases when either free molecular or diffusion absorption of vapor by the supercritical droplets become prevalent. Consequently, relationship (6.8) together with relation (5.14) make it possible in both cases to determine (at typically almost complete or rather low consumption of the initial amount of condensation nuclei by supercritical droplets) the width $\Delta\rho$ of the size spectrum of the supercritical droplets. These considerations are alone of great importance and will be needed in the next Section.

7. HIERARCHY OF CHARACTERISTIC KINETIC TIMES AT THE STAGE CORRESPONDING TO EFFECTIVE NUCLEATION OF SUPERCRITICAL DROPLETS

In order to overcome the activation barrier of nucleation by the droplets during the entire stage corresponding to effective nucleation of the supercritical droplets at the steady-state (actually, quasi-steady-state) regime, the condition

$$t_s \ll \Delta t \tag{7.1}$$

should be fulfilled. Disclosing this condition with the aid of (5.13), we obtain at $h \gg 1$ and $h \ll 1$ the inequality

$$\frac{1}{2^{3/2}} \left(\frac{2^{5/2}}{27} \right)^{(m+1)/m} \frac{\alpha t_\infty a^{(4m+3)/2m}}{m \tau v_n^{(4m+1)/2m}} \gg 1. \tag{7.2}$$

The inequality (7.2) is valid at the prevalence of both free molecular or diffusion absorption of vapor by the supercritical droplets at the stage corresponding to their effective nucleation.

In order to relate the remaining conditions of the applicability of the kinetic theory with condition (7.1), let us express the scaling time t_∞ via the $\Delta t/t_s$ ratio using equation (5.13). Then we have

$$t_\infty \approx 2^{3/2} \left(\frac{27}{2^{5/2}} \right)^{(m+1)/m} \frac{m \tau v_n^{(4m+1)/2m} \Delta t}{\alpha a^{(4m+3)/2m} t_s} \tag{7.3}$$

($h \gg 1$ or $h \ll 1$)

for both limiting regimes of the absorption of vapor by the supercritical droplets.

To retain the state of vapor around the supercritical droplets in a quasi-steady-state during the entire stage corresponding to effective nucleation of supercritical droplets, the condition

$$t_{rel} \ll \Delta t, \tag{7.4}$$

should be fulfilled. According to (5.1), this condition is reduced to the inequality

$$\pi^2 D n^{2/3} \Delta t \gg 1. \tag{7.5}$$

When the free molecular absorption of vapor becomes prevalent at the stage corresponding to effective nucleation of the supercritical droplets, condition (7.5) at $h \gg 1$ is written with the aid of (5.8), (5.11), (5.14), and (7.3) as

$$\frac{3^{3/2}}{2^{13/6}} \pi^2 D n_\infty^{2/3} \tau \frac{1}{\alpha v_n^{10/9}} \frac{t_s}{\Delta t} \gg 1 \tag{7.6}$$

and at $h \ll 1$ with the aid of (5.12), (5.14), and (7.3) as

$$\left(\frac{3}{2} \right)^{7/2} \pi^2 D \eta^{2/3} (-\infty) \frac{\tau v_n^{4/3}}{\alpha a^2} \frac{\Delta t}{t_s} \gg 1. \tag{7.7}$$

When the diffusion absorption of vapor becomes prevalent at the stage corresponding to the effective

nucleation of supercritical droplets, condition (7.5) is written at $h \gg 1$ with the aid of (5.9)–(5.11), and (7.3) as

$$\frac{3^{5/3} \pi}{2^{7/2}} \frac{1}{(n_\infty v)^{1/3}} \frac{1}{a^{1/2} v_n^{5/18}} \gg 1 \tag{7.8}$$

and at $h \ll 1$ with the aid of (5.12), (5.14), and (7.3) as inequality (7.7). The $\Delta t/t_s$ ratio did not enter into inequality (7.8).

While formulating condition (7.5) reported earlier in [1, 2], we omitted factor π^2 , which weakens this condition by approximately an order of magnitude. The π^2 factor was taken into account in inequalities (7.6)–(7.8), disclosing condition (7.5).

The significance of the π^2 factor for condition (7.5) is especially pronounced in inequality (7.8), disclosing this condition at $h \gg 1$ and at the prevalence of diffusion absorption of vapor by the supercritical droplets at the stage corresponding to their effective nucleation. Indeed, this inequality may actually be compatible with the condition of the macroscopicity of condensation nuclei ($v_n^{1/3} \gg 1$) only because the π^2 factor of condition (7.5) was accounted for in the inequality (7.8).

In order to retain the quasi-immobile state of the supercritical droplet surfaces during the entire stage corresponding to effective nucleation of supercritical droplets, we should fulfill the condition

$$t_{rel} \ll t_R. \tag{7.9}$$

This condition was not treated in [1, 2]. According to estimate (6.9) made for the time t_R , condition (7.9) is identical to inequality (7.4).

Conditions (7.1) and (7.4) as well as estimate (6.9) [providing the identity of condition (7.9) for condition (7.4)] reveal the hierarchy of four characteristic kinetic times (t_s , t_{rel} , Δt , and t_R) needed for the description of the stage corresponding to effective nucleation of the supercritical droplets. Although the compatibility of conditions (7.1) and (7.4) imposes some constraint on the value of the t_s/t_{rel} ratio, we cannot make any general statement about this value. If condition (7.1) is fulfilled much better than condition (7.4), $t_s/t_{rel} \ll 1$. On the contrary, when condition (7.1) is fulfilled much worse than condition (7.4), $t_s/t_{rel} \gg 1$.

The hierarchy disclosed for the characteristic kinetic times allows us to understand the complex multistep mechanism of the stage corresponding to effective nucleation of the supercritical droplets.

In the present consideration of the stage corresponding to effective nucleation of the supercritical droplets, we confined ourselves to two limiting regimes of vapor absorption by supercritical droplets. Let us reveal the implementation conditions of these regimes.

In order to make the free molecular absorption of vapor prevalent at the stage corresponding to effective nucleation of the supercritical droplets, it is required

that inequality (1.5) should be predominant. Thus, to this end, the condition

$$\Delta\rho/\rho_l \ll 1, \quad (7.10)$$

should be fulfilled. In this condition, according to (1.4), (6.1), and (6.3), ρ_l is estimated as

$$\rho_l \sim \alpha^{-1} (n_\infty + n_g)^{-1} v^{-1}. \quad (7.11)$$

Here, it is assumed that $n \approx n_\infty$ under the condition of the smallness of the supersaturation of vapor condensing at the macroscopic nuclei. Taking into account the discussion presented at the end of preceding section and using relationship (7.3), we may show that

$$\Delta\rho \approx \frac{3^{1/2} v_n^{5/6} \Delta t}{2 a^{1/2} t_s} \quad (h \gg 1 \text{ or } h \ll 1). \quad (7.12)$$

This relation is consistent with relationships (2.6) and (2.13) reported in [2]. Then, disclosing condition (7.10) with the aid of (7.11) and (7.12), we arrive at inequality

$$\frac{3^{1/2}}{2} \alpha (n_\infty + n_g) v \frac{v_n^{5/6} \Delta t}{a^{1/2} t_s} \ll 1 \quad (h \gg 1 \text{ or } h \ll 1). \quad (7.13)$$

In order to make the diffusion absorption of vapor prevalent at the stage corresponding to the effective nucleation of supercritical droplets, it is necessary that inequality (3.1) should be predominant at this stage. Thus, to this end, condition

$$\Delta\rho/\rho_l \gg 1, \quad (7.14)$$

should be fulfilled. In this condition, according to (1.4), (6.1), and (6.4), ρ_l is already estimated as

$$\rho_l \sim \alpha^{-2} (n_\infty + n_g)^{-2} v^{-2}. \quad (7.15)$$

Taking into account the discussion presented at the end of preceding section and taking advantage of relationship (7.3), we may show that

$$\Delta\rho \approx \frac{3^{1/2} \tau v_n^{5/6} \Delta t}{2 \alpha \tau_D a^{1/2} t_s} \quad (h \gg 1 \text{ or } h \ll 1). \quad (7.16)$$

Then, disclosing condition (7.14) with the aid of (7.15) and (7.16) and accounting for estimate

$$(\tau/\tau_D)(n_\infty + n_g) v \sim (8/3)(4\pi/3)^{1/3}, \quad (7.17)$$

followed from (1.3), (1.4), (5.3), and (5.10), we arrive at inequality

$$\frac{2^{8/3} \pi^{1/3}}{3^{5/6}} \alpha (n_\infty + n_g) v \frac{v_n^{5/6} \Delta t}{a^{1/2} t_s} \gg 1 \quad (h \gg 1 \text{ or } h \ll 1). \quad (7.18)$$

In addition, in the consideration of the stage corresponding to effective nucleation of supercritical droplets, we confined ourselves to two limiting situations

$h \gg 1$ and $h \ll 1$, corresponding to complete or rather low consumption of the initial amount of condensation nuclei by the supercritical droplets. Let us demonstrate how to disclose the conditions of the implementation of these situations.

As follows from (5.8) and (7.3), at the prevalence of free molecular absorption of vapor by the supercritical droplets for parameter h , we have the following expression

$$h \approx \frac{27 \eta(-\infty) v_n^{11/3}}{4 n_\infty a^3} \left(\frac{\Delta t}{t_s} \right)^3 \quad (h \gg 1 \text{ or } h \ll 1), \quad (7.19)$$

which is consistent with relationships (2.6) and (2.10) from [2]. It follows from (5.9) and (7.3) that at the prevalence of diffusion absorption of vapor by the supercritical droplets for parameter h , we have the expression

$$h \approx \frac{81 \pi^{1/2} \eta(-\infty)}{2^{7/2} 3^{1/4} n_\infty} \left(\frac{\tau}{\alpha \tau_D} \right)^{3/2} \frac{v_n^{29/12}}{a^{9/4}} \left(\frac{\Delta t}{t_s} \right)^{3/2} \quad (h \gg 1 \text{ or } h \ll 1). \quad (7.20)$$

Expressions (7.19) and (7.20) allow us to readily disclose the conditions of the implementation of the limiting situations $h \gg 1$ and $h \ll 1$ for the prevalence of both free molecular or diffusion absorption of vapor by the supercritical droplets. We do not report these conditions because of the obviousness of the inequalities resulted from (7.19) and (7.20). Note only that these conditions impose additional [to inequality (7.7)] constraints on the initial concentration values $\eta(-\infty)$ of condensation nuclei admitted by the theory.

8. JUSTIFICATION OF THE NEGLECT OF THE SUPERCRITICAL DROPLET SURFACE CURVATURE AT THE STAGE CORRESPONDING TO EFFECTIVE NUCLEATION

Let us justify relationship (6.2) discussed in Section 6. According to the Gibbs-Kelvin formula, we have

$$n_R = n_\infty \exp\left(\frac{2\sigma v}{kTR}\right), \quad (8.1)$$

$$n = n_\infty \exp\left(\frac{2\sigma v}{kTR_c}\right), \quad (8.2)$$

where index c denotes the values referring to the supercritical droplets under chemical equilibrium with the vapor having concentration n .

It follows from (8.1) and (8.2) that the relative error of relationship (6.2) does not exceed the R_c/R value. Then, in order for relationship (6.2) to be valid, it is sufficient that the approximate inequality

$$R \geq (3-5)R_c \quad (8.3)$$

be fulfilled.

It was shown [3] that the potential barrier of the droplet formation is overcome by the droplets virtually

everytime during the free molecular vapor absorption despite the macroscopicity of the condensation nuclei. The height of the potential barrier corresponds to the critical droplet. Then, it follows from inequalities (1.5) and (3.1) that at the diffusion absorption of vapor by the supercritical droplets that their radii are manifold larger than the radius of the critical droplets. In this case, approximate inequality (8.3) will be reliably fulfilled. Consequently, relationship (6.2) is also valid. Therefore, below, we confine ourselves to the case where the free molecular absorption of vapor by the supercritical droplets prevails at the stage corresponding to their effective nucleation.

In this case, the variable ρ suitable for the description of the supercritical droplets is given by equality (6.3). Taking into account that the variable ρ is proportional to the radius R of the supercritical droplets, we may see that the approximate inequality (8.3) is equivalent to the approximate inequality

$$\rho \geq (3-5)\rho_c. \quad (8.4)$$

The proportionality between ρ and r follows from (6.1) and (6.3) and was already mentioned in Section 6.

The characteristic values of variable ρ at the stage corresponding to the effective nucleation of the supercritical droplets are given by estimate (6.7). In order to make inequality (8.4) and, hence, relationship (6.2) be valid at this stage, it is sufficient to fulfill the condition

$$\Delta\rho/\rho_c \gg 1. \quad (8.5)$$

With a high degree of accuracy, we have at the macroscopicity of the condensation nuclei and their complete solubility in the droplets and the surface inactivity of a matter comprising nuclei [5, relationships (6) and (17)]

$$v_c \approx (9v_n/2a)^{3/2}. \quad (8.6)$$

In view of equality (6.3), it follows from (8.6) with a high degree of accuracy that

$$\rho_c \approx (9v_n/2a)^{1/2}. \quad (8.7)$$

Using (7.12) and (8.7), we arrive at

$$\Delta\rho/\rho_c \approx (v_n^{1/3}/6^{1/2})(\Delta t/t_s) \quad (8.8)$$

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

Relationship (8.8) indicates that at the macroscopicity of the condensation nuclei (at $v_n^{1/3} \gg 1$) the fulfillment of condition (8.5) is definitely provided by condition (7.1).

The speculations reported in this section confirm the significance of the passage from the scaling time t_∞ (the initial parameter of a theory) to the theoretically convenient value $\Delta t/t_s$, which is responsible for the fulfillment of condition (7.1). This passage was performed using relationship (7.3).

9. JUSTIFICATION OF THE SMALLNESS OF THE SUPERCRITICAL DROPLET RADIUS AS COMPARED TO THE RADIUS OF THE SPHERE OF VAPOR ABSORPTION BY THE DROPLETS

Let us demonstrate that inequality $R \ll L$, employed in Sections 1-4, is fulfilled at the stage corresponding to effective nucleation of the supercritical droplets.

Let us first consider the case of $h \gg 1$. From (5.11), (7.12), and (7.19) at the prevalence of free molecular absorption of vapor by the supercritical droplets, we have

$$N(\Delta\rho)^3 \approx (9/2)n_\infty\zeta_{th}/\Gamma \quad (h \gg 1). \quad (9.1)$$

From (5.11), (7.16), and (7.20) at the prevalence of the diffusion absorption of vapor by supercritical droplets, we have

$$N(\Delta\rho)^{3/2} \approx (3^{1/2}4/\pi^{1/2})n_\infty\zeta_{th}/\Gamma \quad (h \gg 1). \quad (9.2)$$

Here

$$\zeta_{th} = 2(2a)^{3/2}/27v_n^{1/2}, \quad (9.3)$$

$$\Gamma = (24/6^{1/2})v_n^{2/3}. \quad (9.4)$$

Parameter ζ_{th} represents the threshold value of vapor supersaturation [5], above which the creation of droplets on condensation nuclei is barrierless.

Evidently, the width of the supercritical droplet size spectrum $\Delta\rho$ also determines the largest size of the supercritical droplets at the ρ -axis achieved at the end of the stage corresponding to their effective nucleation. Consequently, at this stage, the inequality $\rho < \Delta\rho$ is valid. Accounting for this fact and the inequalities $\zeta_{th} \ll 1$ and $\Gamma \gg 1$ resulted from (9.3) and (9.4) under the condition of the macroscopicity of the condensation nuclei and using (6.1), (6.3), and (6.4), we conclude on the basis of relationships (9.1) and (9.2) that

$$NR^3 \ll 1 \quad (h \gg 1). \quad (9.5)$$

This inequality is valid irrespective of the fact which of the two alternative limiting regimes of the vapor absorption by the supercritical droplets prevails at the stage corresponding to their effective nucleation.

Inequality (9.5) and estimate (1.1) convince us of the validity of the inequality $R \ll L$ at $h \gg 1$.

Let us now consider the opposite case, $h \gg 1$. Let us introduce the auxiliary parameter \tilde{N}

$$\tilde{N} = \eta(-\infty)/h \quad (h \gg 1 \text{ or } h \ll 1). \quad (9.6)$$

As is apparent from (9.6) and (5.11), at $h \gg 1$, the value \tilde{N} coincides with the number of droplets N . However, at $h \ll 1$, the \tilde{N} value has a purely formal meaning.

Since it is obvious that the analytical dependences of the \tilde{N} value on the initial parameters of a theory at

both $h \gg 1$ and $h \ll 1$ are the same as those for the number of droplets N at $h \gg 1$, the relationships

$$\tilde{N}(\Delta p)^3 \approx (9/2)n_\infty \zeta_{th}/\Gamma, \quad (9.7)$$

and

$$\tilde{N}(\Delta p)^{3/2} \approx (3^{1/2}4/\pi^{1/2})n_\infty \zeta_{th}/\Gamma \quad (9.8)$$

will be valid together with relationships (9.1) and (9.2). However, unlike relationships (9.1) and (9.2), these relationships are valid not only at $h \gg 1$, but also at $h \ll 1$.

Repeating the same speculations as for the derivation of inequality (9.5) from relationships (9.1) and (9.2), based on (9.7) and (9.8), we obtain the inequality

$$\tilde{N}R^3 \ll 1 \quad (h \gg 1 \text{ or } h \ll 1), \quad (9.9)$$

which is valid despite the fact that it is unclear which of the two alternative limiting regimes of the vapor absorption by the supercritical droplets prevails at the stage corresponding to their effective nucleation.

At $h \ll 1$, from definition (9.6) follows the inequality

$$\tilde{N} \gg \eta(-\infty) \quad (h \ll 1). \quad (9.10)$$

In view of (9.9), it readily follows that

$$\eta(-\infty)R^3 \ll 1 \quad (h \ll 1). \quad (9.11)$$

According to (5.12), the initial concentration $\zeta(-\infty)$ of the condensation nuclei coincides with the number of droplets N at $h \ll 1$. Then, from (9.11), the inequality

$$NR^3 \ll 1 \quad (h \ll 1) \quad (9.12)$$

follows.

The inequality (9.12) and estimate (1.1) predetermine the validity of inequality $R \ll L$ at $h \ll 1$.

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