

# Role of nearest-neighbor drops in the kinetics of homogeneous nucleation in a supersaturated vapor

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A theory of simultaneous nucleation and drop growth in a supersaturated vapor is developed. The theory makes use of the concept of “nearest-neighbor” drops. The effect of vapor heterogeneity caused by vapor diffusion to a growing drop, formed previously, is accounted for by considering the nucleation of the nearest-neighbor drop. The diffusional boundary value problem is solved through the application of a recent theory that maintains material balance between the vapor and the drop, even though the drop boundary is a moving one. This is fundamental to the use of the proper time and space dependent vapor supersaturation in the application of nucleation theory. The conditions are formulated under which the mean distance to the nearest-neighbor drop and the mean time to its appearance can be determined reliably. Under these conditions, the mean time provides an estimate of the duration of the nucleation stage, while the mean distance provides an estimate of the number of drops formed per unit volume during the nucleation stage. It turns out, surprisingly, that these estimates agree fairly well with the predictions of the simpler and more standard approach based on the approximation that the density of the vapor phase remains uniform during the nucleation stage. Thus, as a practical matter, in many situations, the use of the simpler and less rigorous method is justified by the predictions of the more rigorous, but more complicated theory. © 2004 American Institute of Physics. [DOI: 10.1063/1.1819871]

## I. INTRODUCTION

Since nucleation rates are extremely sensitive to the degree of supersaturation, it is important, in describing the stages of homogeneous nucleation in a supersaturated vapor, to accurately account for vapor depletion by growing droplets. One of the widespread methods for doing this involves the approximation that the metastable phase remains uniform in density as the supersaturation decays.<sup>1–5</sup> The method uses a feature characterized by the strong dependence of the nucleation rate on supersaturation. This is the fact that completion of the nucleation stage, i.e., a practical cessation of the nucleation of new drops, occurs at a relatively small (few percent under characteristic conditions) decrease of the vapor supersaturation in the system. Therefore, the accumulation of the condensing matter by every growing drop during the nucleation stage is determined essentially by the law of drop growth. The question is how many drops will be in the system at a given time  $t$ ?

The approximation of uniformity<sup>1–5</sup> assumes that the nucleation rate at  $t$  is determined by a vapor density averaged over the volume of the excess vapor. The latter can be found by subtraction of the number of molecules within the growing drops from the initial number of vapor molecules. At this point a contradiction arises. The calculations of the charac-

teristics of the nucleation stage, e.g., the total number of nucleating drops, the duration of the stage, etc., explicitly use the fact of the strong dependence of the nucleation rate on supersaturation, while at the same time the calculations neglect the continual nonuniformity of the vapor due to the growing drops. A volume averaged rate of nucleation is thus replaced by the nucleation rate at the volume averaged density of the excess vapor. Evidently, such a replacement could become a source of error with a strong (nonlinear) dependence of nucleation rate on supersaturation.

An alternate account of the vapor nonuniformity was presented in Ref. 6. The corresponding commentaries can be found in Ref. 7 where another approach to description of the nucleation stage, one that recognizes the vapor nonuniformity in the neighborhood of growing drop, is adopted. The explicit realization and the range of validity of this approach depends essentially on the regime of drop growth, e.g., on a free molecular or diffusion regime. In Ref. 7 it is assumed that the drops grow in the free-molecular regime during the whole stage of nucleation. This limitation is very restrictive and considerably narrows the range of validity of the theory in Ref. 7.

This paper broadens the approach in Ref. 7 so that it covers a wide enough class of conditions to include the case under which drops grow in the diffusion regime during the nucleation stage.

The central object under consideration is a drop that ap-

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pears to be nearest to a given initially nucleated one. Thus we will call this broadened approach to the description of the nucleation stage the “approximation of the nearest-neighbor drop.”

Formulation of the conditions under which the theory is capable of sufficiently accurate predictions for the average distance to a nearest-neighbor drop and for the average time to its appearance, will be an important part of the study in this paper. Under these conditions, the average time to the appearance of a nearest-neighbor drop provides an estimate of the duration of the nucleation stage, and the average distance to such a drop allows us to estimate the total number of drops per unit volume that will have been nucleated during the nucleation stage.

Rigor of description of the nucleation of a nearest-neighbor drop is also achieved by the use of a new accurate nonsteady solution for the vapor concentration profile around the growing drop.<sup>8</sup>

Comparison of predictions for the above mentioned theory of the nucleation stage obtained within this proposed approach with those obtained via the approximation of uniformity reveals good agreement. This agreement is rather surprising because it exists under conditions valid for the approximation of a nearest-neighbor drop. Under such conditions, every growing drop consumes the excess vapor, the majority of which was initially concentrated in the sphere around the growing drop, a sphere whose radius is equal to the average distance to a nearest-neighbor drop.

## II. VAPOR CONCENTRATION IN THE NEIGHBORHOOD OF A DROPLET

Consider a vapor-gas medium that becomes supersaturated instantaneously, so that drops growing irreversibly begin to nucleate within the medium. Imagine the following experiment. Choose the drop, which appeared first, and study the probability of the nucleation of a new drop in the neighborhood of the first one. The time of formation of the first drop will serve as the zero of time. Denote the radius of the chosen drop by  $R(t)$  and the mean free path of vapor molecules by  $\lambda$ . At the time of nucleation of the first drop, its radius evidently satisfies the inequality  $R(0) < \lambda$ . This relation will hold for other drops nucleated at other times. Under some conditions it is possible that the nucleation stage will terminate while the condition  $R(t) < \lambda$  is still valid.<sup>7</sup> In this paper we consider the other situation, in which the inequality  $R(t) \gg \lambda$  holds during the most of the nucleation stage, and the transport of vapor molecules to the drop occurs by means of diffusion. This assumes that the density of the inert gas in the system is large enough. In order to concentrate on the principal ideas of the proposed approach, the effects of the release of the latent heat of condensation, Stephan's flux, etc., are not considered. Under the restrictions on the region of applicability of the presented approach that will be formulated below, the initial pressure of the excess vapor must be of the order of 1 atm. Since the nucleation stage finishes as soon as the drops formed during it will condense even a small part (several percents) of the excess vapor, at the pressure of inert gas of 10 atm, we can disregard, with confidence, the effects of release of condensation heat. The free

path  $\lambda$  of the vapor molecules that corresponds to such a pressure of the inert gas is of the order of  $10^{-6}$  cm. At the typical value of the diffusion coefficient  $10^{-1}$  cm<sup>2</sup> s<sup>-1</sup>, in a range of  $1 - 10^{10}$  cm<sup>-3</sup> s<sup>-1</sup> of the nucleation rate, the radii of the drops will reach values of  $10^{-3} - 10^{-5}$  cm by the end of the nucleation stage. Therefore, the condition  $R(t) \gg \lambda$  is fulfilled during the major part of the nucleation stage.

We will study the probability of nucleation of a new drop, growing in the supersaturated vapor, and nearest to the one formed initially. Note that, in spite a relative smallness of the growing drop formed initially, the nonuniformity it creates in the supersaturated vapor quickly propagates via diffusion. Until the nucleation of the nearest drop, the distribution of vapor in the neighborhood of the growing drop can be assumed to be spherically symmetric. That distribution is described by the concentration  $n(r, t)$  of the vapor molecules in the vapor-gas medium in the vicinity of the growing drop. Here  $r$ , with  $(r > R)$ , is the distance from the center of the first drop. The vapor concentration  $n(r, t)$  satisfies the continuity equation into which Fick's law has been substituted, namely,

$$\frac{\partial n(r, t)}{\partial t} = \frac{D}{r} \frac{\partial^2}{\partial r^2} [rn(r, t)], \quad (1)$$

where  $D$  is the diffusion coefficient. Equation (1) is subject to the initial condition

$$n(r, 0) = n_0, \quad (2)$$

where  $n_0$  is the initial uniform vapor concentration. Equation (1) must also satisfy the boundary condition

$$n(R, t) = n_\infty, \quad (3)$$

where  $n_\infty$  is the equilibrium vapor concentration at the surface of the drop at  $r = R(t)$ . The solution of Eq. (1) must take account of the movement of the drop surface, i.e., of the time dependence of  $R$ , i.e., of the fact that with the radius  $R(t)$  of initially formed droplet changing with time. Since the density of a liquid drop is much greater than that of the vapor, the rate of change of  $R$  will be small compared to the rate of establishment of  $n(r, t)$ . The time dependence of  $R(t)$  is determined by equating the number of molecules reaching the drop via diffusion to the number of absorbed by the drop. This balance is expressed by the relation

$$\frac{dR}{dt} = v_\ell D \left. \frac{\partial n(r, t)}{\partial r} \right|_{r=R}, \quad (4)$$

where  $v_\ell$  is the volume per molecule in the drop. Equations (1)–(4) constitute the boundary value problem that must be solved for  $n(r, t)$ . Unfortunately, Eq. (4) renders the problem nonlinear so that, at the moment, only an approximate solution is available.

This approximation can be accurate if the parameter

$$\alpha \equiv [v_\ell (n_0 - n_\infty) / 2]^{1/2} \quad (5)$$

is small,<sup>8</sup> a condition that holds far below the critical temperature.

In Ref. 8 it was shown that the solution of Eqs. (1)–(4) could be approximated to the first order in  $\alpha$  by

$$n(r,t) = n_0 - \frac{2\beta t^{1/2}(n_0 - n_\infty)}{\pi^{1/2}r} \int_u^\infty \left(1 - \frac{u^2}{\tau^2}\right)^{1/2} \times \exp(-\tau^2) d\tau, \quad (6)$$

where

$$u = \frac{r - R(t)}{2(Dt)^{1/2}} \quad (7)$$

with

$$R(t) = \beta t^{1/2}, \quad (8)$$

an approximation for  $R(t)$ , also valid to the first order in  $\alpha$ , and where

$$\beta \equiv [2Dv_\ell(n_0 - n_\infty)]^{1/2} = 2D^{1/2}\alpha. \quad (9)$$

Equation (8) is a relation that has been derived by other approximate methods. However, the method in Ref. 8 maintains material balance (molecules lost from the vapor equal the number appearing in the drop) to the first order in  $\alpha$ , whereas previous methods do not.

### III. NUCLEATION IN THE NEIGHBORHOOD OF A GROWING DROP

We introduce a measure of vapor supersaturation  $\zeta(r,t)$  and of relative decrease of supersaturation  $\varphi(r,t)$  in the neighborhood of the growing drop. These are

$$\zeta(r,t) = \frac{n(r,t) - n_\infty}{n_\infty} \quad (10)$$

and

$$\varphi(r,t) \equiv \frac{\zeta_0 - \zeta(r,t)}{\zeta_0} = \frac{n_0 - n(r,t)}{n_0 - n_\infty}, \quad (11)$$

where  $\zeta_0$  is initial supersaturation of the vapor. Substitution of Eq. (6) into Eq. (11) gives

$$\varphi(r,t) = \frac{2}{\pi^{1/2}} \frac{\beta t^{1/2}}{r} \int_u^\infty d\tau \left(1 - \frac{u^2}{\tau^2}\right)^{1/2} \exp(-\tau^2). \quad (12)$$

We restrict the situation to the case of homogeneous nucleation in a vapor-gas medium, assuming the presence of foreign particles to be negligible. The nucleation rate, the number of drops formed per unit volume in the vapor-gas medium, per unit time, in the neighborhood of the initial drop, will be denoted by  $I(r,t)$ . The nucleation rate in the initial uniform vapor-gas medium with vapor concentration  $n_0$  will be denoted by  $I_0$ . This will be one of the important parameters of the theory.

Following Ref. 4, we adopt the simplified expression

$$I(r,t) = I_0 e^{-\Gamma \varphi(r,t)}. \quad (13)$$

Here,  $\Gamma$  is a dimensionless parameter characterizing the dependence of the free energy of the critical drop on the vapor supersaturation at its initial value  $\zeta_0$ . In the capillary approximation this parameter is given by the expression

$$\Gamma = \frac{4\pi v_\ell^2}{3} \left\{ \frac{2\sigma}{k_B T \ln[n_0/n_\infty]} \right\}^3 \frac{n_0 - n_\infty}{n_0}. \quad (14)$$

Here  $k_B$  is the Boltzmann constant and  $\sigma$  is the liquid-vapor surface tension,  $\Gamma$  is approximately equal to the number of molecules in the critical drop and is a large parameter of the theory.

As is shown in Ref. 4, Eq. (13) has a high relative accuracy at  $\varphi(r,t) \leq 1/\Gamma$ . When  $\varphi(r,t) = 1/\Gamma$ , the nucleation rate  $I(r,t)$  is  $e$  times less than  $I_0$ . As  $\varphi(r,t)$  increases, exceeding the value  $1/\Gamma$ , with a decrease of the distance to the growing drop, the accuracy of Eq. (13) decreases, but the nucleation rate  $I(r,t)$  also becomes small. Therefore, at  $\varphi > 1/\Gamma$ , the use of Eq. (13) does not reduce the accuracy of further calculations based on this expression.

The quantities  $\alpha$ ,  $I(0)$ ,  $\Gamma$  are interconnected by thermodynamics, but in our investigation it will be convenient to consider them as independent parameters.

### IV. VARIOUS NEAREST NEIGHBOR RELATIONS

According to the definition of the nucleation rate, the quantity

$$dp = dt \int_R^r dr' 4\pi r'^2 I(r',t) \quad (15)$$

is the average number of new droplets formed, in the infinitesimal time interval  $dt$ , in a spherical layer between  $R$  and  $r$  surrounding the initial drop. Standard probability theory, based on the smallness of  $dp$  allows  $dp$  to be regarded as the probability of formation of a single new drop in time  $dt$  in this spherical layer.

Thus the quantity  $1 - dp$  is the probability that, in time  $dt$ , no new drop will form in the layer. Since  $dp \ll 1$ , it follows that

$$1 - dp \cong \exp(-dp). \quad (16)$$

The probability that, in a finite time  $t$  after the appearance of the initial drop, no new drop will appear in the layer, is equal to the product of elementary probabilities, Eq. (16). Let us denote this probability as  $P(r,t)$ . Since the product of exponentials in Eq. (16) is equal to the exponential of the sum of exponents of the exponentials multiplied, then for the probability  $P(r,t)$ , we have

$$P(r,t) = \exp\left[-\int_0^t dt' \int_{R(t')}^r dr' 4\pi r'^2 I(r',t')\right]. \quad (17)$$

The more rigorous derivation of Eq. (17) is given in Appendix A. As time increases

$$P(r,t) \rightarrow P(r), \quad (18)$$

where  $P(r)$  is the probability that no new drops will ever appear in the layer. From Eqs. (17) and (18) it follows that

$$P(r) = \exp\left[-\int_0^{(r/\beta)^2} dt' \int_{R(t')}^r dr' 4\pi r'^2 I(r',t')\right]. \quad (19)$$

The finite upper limit, rather than  $\infty$ , appears in the integral in the exponent in Eq. (19) in order to exclude the nonphysical case  $R(t') > r$ . Eq. (19) indicates that the probability  $P(r)$  decreases with an increase of  $r$ . This is physically rea-

sonable, since as the volume of the spherical layer is increased, the greater is the probability that a new drop will be nucleated in it.

We now introduce the probability density  $f(r,t)$  for the formation of a new drop, nearest to the initial drop, in time  $dt$  and in a spherical shell of thickness  $dr$ . Then the product  $f(r,t)dr dt$  is the probability of formation of the nearest drop in time  $dt$  in the spherical shell of radius  $r$  and thickness  $dr$ . Since  $dt$  and  $dr$  are infinitesimal, standard probability theory shows that  $I(r,t)4\pi r^2 dr dt$  is also equal to the average number of drops forming in time  $dt$  in the spherical shell. Is the probability of formation of a single new drop in time  $dt$  within this spherical shell.

There are two related quantities associated with the idea of the nearest drop that merit discussion. These are (1)  $f(r,t)$  related to the probability that the nearest-neighbor forms in the shell  $dr$  in time  $dt$ , and (2)  $\psi(r,t)$  the probability density that the nearest drop will be found in  $dr$  at time  $t$ . A discussion of these quantities is as follows:

(1) The formation of the nearest drop in time  $dt$  in a spherical layer  $dr$  implies that, during time  $t$  no other drop has formed within the sphere of radius  $r$  and that, furthermore, in order for the drop formed in  $dr$  during  $dt$  to remain the nearest one, no other drop must form within the sphere of radius  $r$  after the time  $t+dt$ . The first condition is realized with the probability  $P(r,t)$ . It follows from Eqs. (17) and (19) that the second condition is realized with the probability  $p(r,t)=P(r)/P(r,t)$ . Perhaps it is a bit simpler to see this by recognizing that  $p(r,t)$  is the probability (conditional on the fact that no drop has formed in the sphere at time  $t$ ) that no new drop forms in the sphere of radius  $r$  after time  $t$ , so that  $P(r)=P(r,t)p(r,t)$  which is only a rearranged form of the prior equation. Thus, the fact that the probability density  $f(r,t)$  refers to a drop that remains a nearest one over all time is guaranteed by the use of the quantity  $P(r)$ , which is the probability that there are never any drops in the volume lying "below" the spherical shell  $4\pi r^2 dr$ . Thus, for the probability density  $f(r,t)$  we have

$$f(r,t)=4\pi r^2 P(r)I(r,t) \quad [r>R(t)]. \quad (20)$$

By using Eq. (19), it is easy to show that the normalization requirement for  $f(r,t)$ , namely,

$$\int_0^\infty dt \int_{R(t)}^\infty dr f(r,t)=1 \quad (21)$$

is satisfied.

Integrating the probability density  $f(r,t)$  with respect to  $t$  from 0 to  $(r/\beta)^2$  [in accordance with Eq. (9)] or over  $r$  from  $\beta t^{1/2}$  to  $\infty$ , one obtains, respectively, the probability density  $f(r)$  for the formation of the nearest drop at the point  $r$  and the probability density  $f(t)$  for the formation of the nearest drop at any  $r$  at time  $t$ . Thus

$$f(r)=\int_0^{(r/\beta)^2} f(r,t)dt, \quad (22)$$

$$f(t)=\int_{R(t)}^\infty f(r,t)dr. \quad (23)$$

As expected, Eqs. (22) and (23) assure the necessary normalization conditions.

(2) The probability density  $\psi(r,t)$  that the nearest drop will be found at the distance  $r$  at time  $t$  is clearly

$$\psi(r,t)=4\pi r^2 P(r,t) \int_0^t I(r,t')dt' \quad [r>R(t)]. \quad (24)$$

By using Eq. (17), it is easy to show that  $\psi(r,t)$  is normalized, i.e.,

$$\int_0^\infty dt \int_{R(t)}^\infty dr \psi(r,t)=1. \quad (25)$$

### V. DETAILED STATISTICAL-KINETIC RELATIONS CHARACTERIZING THE FORMATION OF THE NEW DROP

It is of primary interest to calculate the mean distance  $\bar{r}$  to the nearest drop and the mean time  $\bar{t}$  to the formation of the nearest drop. Using the general definition of the mean distance contained in Eqs. (22), (20), (19), (13), and (12) we obtain

$$\begin{aligned} \bar{r} &\equiv \int_0^\infty r f(r) dr \\ &= \int_0^\infty dr \exp\left\{-\int_0^{(r/\beta)^2} dt \int_{\beta t^{1/2}}^r dr' 4\pi r'^2 I_0\right. \\ &\quad \left.\times \exp\left[-\Gamma \frac{2\beta t^{1/2}}{\pi^{1/2} r'} \int_u^\infty d\tau \left(1-\frac{u^2}{\tau^2}\right)^{1/2} \exp(-\tau^2)\right]\right\}, \end{aligned} \quad (26)$$

where

$$u = \frac{r' - \beta t^{1/2}}{2(Dt)^{1/2}}.$$

The derivation of Eq. (26) is presented in Appendix B. We also show herein how the Eq. (26) can be reduced to the form

$$\bar{r}=0.92r_0, \quad (27)$$

where the characteristic length scale  $r_0$  is given by

$$r_0 = \left[ \frac{5D\alpha^2}{2\pi I_0 \eta} \right]^{1/5}. \quad (28)$$

The parameter  $\eta$  in Eq. (28) is defined as

$$\eta = \int_1^\infty dx x^{-3} \exp[-F(x)], \quad (29)$$

where

$$\begin{aligned} F(x) &= \frac{2}{\pi^{1/2}} \frac{\Gamma\alpha(x-1)}{x} \int_1^\infty dy (1-y^{-2})^{1/2} \\ &\quad \times \exp\{-[\alpha y(x-1)]^2\}. \end{aligned} \quad (30)$$

The mean time  $\bar{t}$  to the formation of the nearest drop can be calculated in a manner similar to that used for the mean distance  $\bar{r}$ . The final expression for  $\bar{t}$  is

TABLE I. The values of  $\eta$  and  $\chi$  by representative values of the parameters  $\Gamma$ ,  $\alpha$ . The values in the cells should be multiplied by the factor indicated in the second row.

$\Gamma$	$\alpha$	0.005	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.10
50	$\eta \times 10^{-3}$	0.58	0.78	1.23	1.74	2.29	2.89	3.52	4.88	6.36
	$\chi \times 10^{-6}$	1.42	2.02	3.73	6.25	9.71	14.2	19.9	35.3	56.7
75	$\eta \times 10^{-3}$	0.30	0.45	0.79	1.19	1.63	2.11	2.63	3.76	5.00
	$\chi \times 10^{-6}$	0.34	0.57	1.30	2.50	4.29	6.76	10.0	19.3	32.7
100	$\eta \times 10^{-3}$	0.20	0.32	0.60	0.93	1.31	1.73	2.19	3.19	4.30
	$\chi \times 10^{-6}$	0.12	0.25	0.67	1.42	2.59	4.27	6.55	13.2	23.2

$$\bar{t} = 0.9 t_0 \frac{\chi}{\alpha^2 \eta}. \quad (31)$$

The numerical factor 0.9 in Eq. (31) is the value of the expression

$$5 \int_0^\infty d\omega \omega^6 \exp(-\omega^5) \approx 0.9.$$

The characteristic time scale  $t_0$  and parameter  $\chi$  are given by the following expressions:

$$t_0 = \frac{r_0^2}{4D}, \quad (32)$$

$$\chi = \int_1^\infty dx x^{-5} \exp[-F(x)]. \quad (33)$$

Remarkably and conveniently, in accordance with Eqs. (29), (30), and (33), the parameters  $\eta$  and  $\chi$  depend on neither the nucleation rate  $I_0$  nor the diffusion coefficient  $D$ . Numerical values of  $\eta$  and  $\chi$  needed for following numerical analysis were calculated for the representative values of the parameters  $\Gamma$ ,  $\alpha$  and are presented in the Table I.

Using  $\psi(r, t)$  specified by Eq. (24), the mean distance  $\bar{r}$  at time  $t$  to the nearest drop can be found as

$$\bar{r}(t) \equiv \int_{\beta t^{1/2}}^\infty r \psi(r, t) dr. \quad (34)$$

Using Eqs. (24), (17), (12), and (13),  $\bar{r}(t)$  is calculated by the same way as the mean distance  $r$ . In order to write the final expression compactly, it is convenient to introduce a length scale  $\rho_0$  and a time scale  $\tau_0$  with the help of expressions

$$\rho_0 = \left[ \frac{D \alpha^2}{2 \pi I_0} \right]^{1/5}, \quad (35)$$

$$\tau_0 = \frac{\rho_0^2}{4D \alpha^2}. \quad (36)$$

Denote by  $\bar{\rho}(\tau)$  the dimensionless mean distance  $\bar{r}(t)/\rho_0$  as a function of dimensionless time  $\tau = t/\tau_0$ . For  $\bar{\rho}(\tau)$  we find

$$\begin{aligned} \bar{\rho}(\tau) = & \tau^{1/2} + \int_{\tau^{1/2}}^\infty d\rho \\ & \times \exp \left\{ -\rho^5 \int_0^{\tau^{1/2}/\rho} dz z^4 \int_1^{1/z} dx x^2 \exp[-F(x)] \right\}. \end{aligned} \quad (37)$$

This expression is more complicated than Eqs. (27)–(30). However, calculations with Eq. (37) are still possible with the help of usual mathematical programs such as MAPLE. As we show below, Fig. 1 shows plots of  $\bar{\rho}(\tau)$  as a function of  $\tau$  at typical values of the parameter  $\Gamma$  and at representative values of  $\alpha$ . The plots demonstrate an expected behavior of  $\bar{\rho}(\tau)$ . At small  $\tau$ , the nearest drop can be nucleated far from the first drop, since it is not likely that a nearer prior drop will be formed in a large volume surrounding the first drop. Interdependence of the drops is absent. All the curves coincide. At large  $\tau$  the dimensionless mean distance  $\bar{\rho}(\tau)$  attains its minimum value  $\bar{\rho} = \bar{r}/\rho_0$  since the opposite physical situation will prevail. This value is different for different curves. However, the limiting value of  $\bar{\rho}$  depends rather weakly on the parameters  $\alpha$  and  $\Gamma$ .

## VI. THE LIMITS OF APPLICABILITY OF THE THEORY

The results that have been presented are entirely reasonable if the drops formed outside the sphere of the radius  $r$  during the time interval  $0 < t \leq \bar{t}$ , do not, in essence, influence the vapor concentration within the sphere. This condition will obviously be satisfied if the first drop is not able to

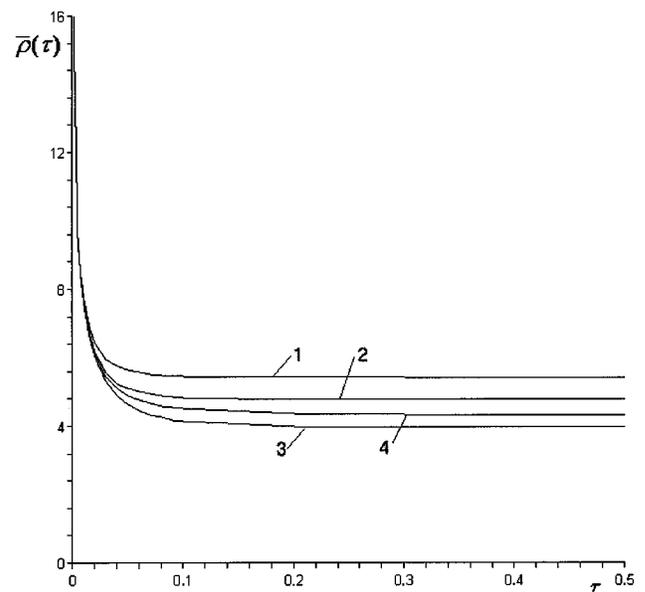


FIG. 1. The dependence of  $\bar{\rho}(\tau)$  on  $\tau$ . Curves 1, 2, and 3 correspond to  $\Gamma=100$ , and  $\alpha=0.03, 0.05$ , and  $0.10$ . Curve 4 corresponds to  $\Gamma=50$ ,  $\alpha=0.05$ .

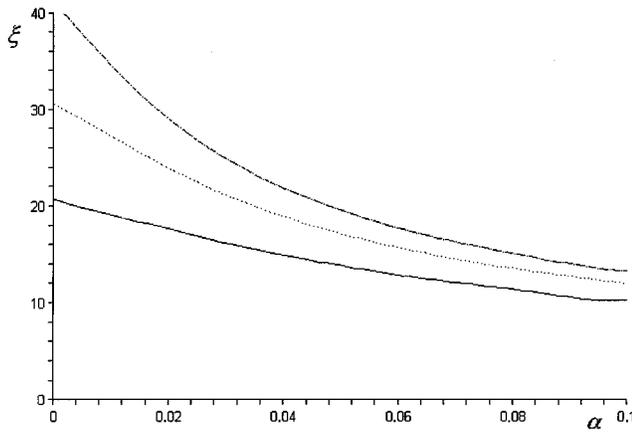


FIG. 2. The dependence of  $\xi$  on  $\alpha$ . Curves 1–3 correspond to  $\Gamma=50, 75,$  and  $100,$  respectively.

significantly influence the state of the vapor outside the sphere during  $\bar{t}$ . We can offer two measures of the achievement this situation. One is the ratio  $\delta_D$  of diffusion length  $2\sqrt{D\bar{t}}$  to the distance  $\bar{r}$

$$\delta_D = \frac{2\sqrt{D\bar{t}}}{\bar{r}}. \tag{38}$$

The other is the ratio  $\delta_v$  of the decrease of the number of vapor molecules within the sphere of radius  $\bar{r}$  at time  $\bar{t}$  to the number of molecules constituting the first drop at time  $\bar{t}$ . Thus

$$\delta_v = \frac{3v_\ell \int_{R(\bar{r})}^{\bar{r}} dr r^2 [n_0 - n(r, \bar{t})]}{R^3(\bar{t})}, \tag{39}$$

and from Eqs. (27), (31), and (38) we have for  $\delta_D$

$$\delta_D = \frac{1}{\alpha} \left( \frac{\chi}{\eta} \right)^{1/2}. \tag{40}$$

For the analysis of Eq. (39) it is convenient to introduce the ratio

$$\xi = \frac{\bar{r}}{R(\bar{t})} = 0.97 \left( \frac{\eta}{\chi} \right)^{1/2}, \tag{41}$$

where Eq. (9) has also been taken into account. The quantity  $\xi$  is itself of special interest. Introducing the solution Eq. (6) into Eq. (39), and using Eqs. (9), (27), (31), and (41) we obtain

$$\delta_v = \frac{12}{\pi^{1/2}} \alpha^3 \int_1^\xi dx (x-1) \int_1^\infty dy (1-y^{-2})^{1/2} \times \exp\{-[\alpha y(x-1)]^2\}. \tag{42}$$

As can be seen from Eqs. (40)–(42), (29), (30), and (33), the quantities  $\delta_D$ ,  $\delta_v$ , and  $\xi$  do not depend on the nucleation rate  $I_0$  or the diffusion coefficient  $D$ . Remarkably (and usefully), they depend only on parameters  $\Gamma$  and  $\alpha$ . Figure 2 shows the dependence of  $\xi$  on  $\alpha$  for different values of  $\Gamma$ . Figure 3 illustrates the dependencies of the quantities  $\delta_D$ ,  $\delta_v$ .

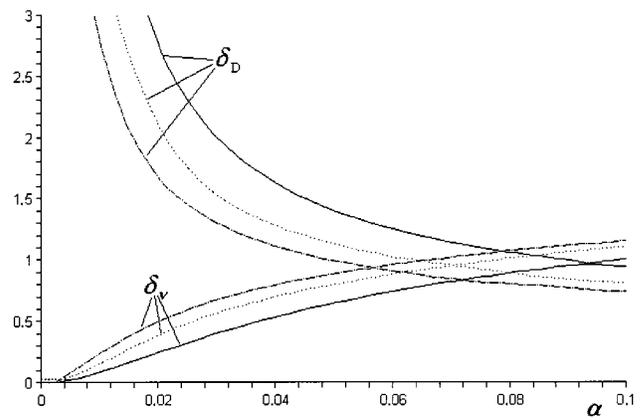


FIG. 3. The dependencies of parameters  $\delta_D$  and  $\delta_v$  on  $\alpha$ . Solid lines correspond to  $\Gamma=50$ , dotted lines to  $\Gamma=75$ , and dashed lines to  $\Gamma=100$ .

As can be seen from Fig. 3 the conditions needed for applicability of our approach,

$$\delta_D \lesssim 1 \tag{43}$$

or

$$\delta_v \approx 1 \tag{44}$$

are both satisfied if  $\alpha$  is greater than some  $\alpha_0$ , that depends on  $\Gamma$ . This  $\alpha_0$  does not depend on  $I_0$  and decreases with an increase of  $\Gamma$ . As seen from Fig. 3, as a good value for  $\alpha_0$  with  $\Gamma=50$ , we can take  $\alpha_0=0.1$ , and with  $\Gamma=75$  and  $\Gamma=100$ , good values of  $\alpha_0$  should be, respectively, 0.05 and 0.03.

### VII. ESTIMATES FOR THE TOTAL NUMBER OF DROPS AND THE DURATION OF THE NUCLEATION STAGE

It is useful to introduce a quantity  $q$  given by

$$q = \frac{4\pi}{3} \bar{r}^3 I_0 \bar{t}. \tag{45}$$

From the definition of the nucleation rate, if drop growth did not deplete the vapor,  $q$ , would represent the average number of drops that would be formed in the volume  $\bar{V}$  of a sphere of the radius  $\bar{r}$  during the time  $\bar{t}$ . Using Eqs. (27) and (31) we find

$$q \cong 0.57 \frac{\chi}{\eta^2}. \tag{46}$$

As can be seen from Eqs. (29) and (33),  $q$ , very usefully, does not depend on the nucleation rate  $I_0$  nor on the diffusion coefficient  $D$ . In Fig. 4 plots showing the dependence of  $q$  on  $\alpha$  are presented.

It is apparent from Fig. 4, that there exists a wide range of  $\alpha$  in which  $q$  is close to unity. This means that even if initially there was no drop in  $\bar{V}$ , it is highly probable that one could appear in it during  $\bar{t}$ . The formation of one drop consumes enough vapor to prevent the formation of another in this volume. In contrast the influence of the growing drop within  $\bar{V}$  can be neglected outside of  $\bar{V}$  (in the regime of applicability of our approach). Therefore, since, on the aver-

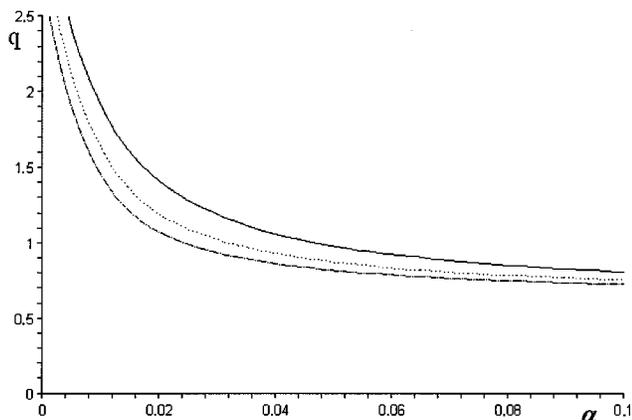


FIG. 4. The dependencies of quantity  $q$  on  $\alpha$ . Solid line corresponds to  $\Gamma=50$ , dotted lines to  $\Gamma=75$ , and dashed lines to  $\Gamma=100$ .

age, only one drop is formed in a volume  $\bar{V}$ , a good estimate of  $N$  the number of drops formed per unit volume of vapor gas will be

$$N = \bar{V}^{-t}. \quad (47)$$

On the temporal side, the average time  $\bar{t}$  to the formation of the neighboring drop provides an estimate of the duration of the nucleation stage since, when this time has elapsed, the vapor will have been sufficiently depleted to preclude any further nucleation. It should be indicated that the theory of Ref. 8 substantially strengthens the rigor of the present analysis since it maintains material balance between the vapor and the growing drop and provides a more accurate description of the time dependent supersaturation in the neighborhood of the drop.

Using Eq. (27), one finds that

$$N = \left( \frac{4\pi}{3} \bar{r}^3 \right)^{-1} \cong 0.31 \left[ \frac{2\pi I_0 \eta}{5D\alpha^2} \right]^{3/5}. \quad (48)$$

### VIII. COMPARISON WITH THE RESULTS BASED ON THE APPROXIMATION OF UNIFORM VAPOR DENSITY

Homogeneous nucleation of drops in a vapor-gas medium following the instantaneous establishment of supersaturation was studied earlier.<sup>1-5</sup> In these studies it was assumed that the vapor density remained uniform throughout the nucleation stage. In these studies, some variation of the chief characteristics of nucleation occurred because of the use of different criteria for the duration of the nucleation stage, so that this variation was no fundamentally significant. Based on the assumption of vapor uniformity, the following results were obtained for  $N_0$  the total number of drops formed per unit volume of the system and for  $t_0$  the duration of the nucleation stage (the present notation is used) in the diffusion regime of drop growth,<sup>9</sup>

$$N_0 = \frac{1}{4} \left( \frac{15}{\pi\alpha\Gamma} \right)^{2/5} \left( \frac{I_0}{D} \right)^{3/5}, \quad (49)$$

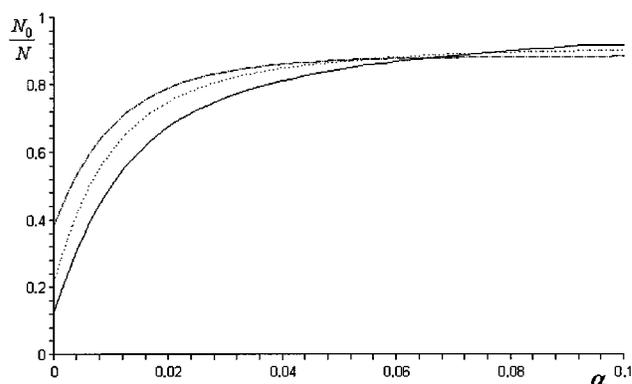


FIG. 5. The dependencies of ratio  $N_0/N$  on  $\alpha$ . Solid line corresponds to  $\Gamma=50$ , dotted line to  $\Gamma=75$ , and dashed line to  $\Gamma=100$ .

$$t_0 = \frac{1}{4} \left( \frac{15}{\pi\alpha\Gamma} \right)^{2/5} \frac{1}{I_0^{2/5} D^{3/5}}. \quad (50)$$

Let us compare the estimates Eqs. (48), (49), and (31), and (50) under the conditions of applicability of Eqs. (48) and (31). Form the ratios

$$\frac{N_0}{N} \cong 1.31 \left( \frac{\alpha^4}{\Gamma^2 \eta^3} \right)^{1/5}, \quad (51)$$

$$\frac{t_0}{\bar{t}} \cong 2.3 \left( \frac{\alpha^4 \eta^7}{\Gamma^2 \chi^5} \right)^{1/5}. \quad (52)$$

First, note that both ratios depend on neither the nucleation rate  $I_0$  nor the diffusion coefficient  $D$ . These ratios are plotted in Figs. 5 and 6. They show remarkable agreement (with  $\alpha > \alpha_0$ ) between the results of both approaches.

This agreement is unexpected. The approximation of uniformity with  $\alpha > \alpha_0$  violates the principal assumption of the theory of the present paper, namely that each drop consumes vapor molecules in its immediate neighborhood. However, a formal explanation can be advanced for the observed agreement. In the framework of the approach involving the assumption of uniformity, the nucleation stage ends when the relative decrease of supersaturation is of about  $1/\Gamma$ . On this basis, it can be shown that the present theory predicts an average decrease of supersaturation in the volume  $\bar{V}$  dur-

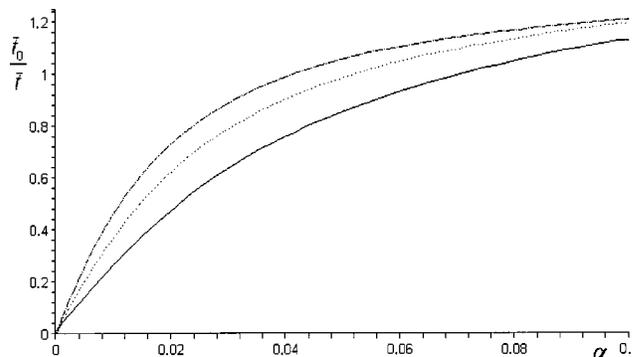


FIG. 6. The dependencies of ratio  $t_0/t$  on  $\alpha$ . Solid line corresponds to  $\Gamma=50$ , dotted line to  $\Gamma=75$ , and dashed line to  $\Gamma=100$ .

ing the time  $\bar{t}$  that is approximately the same as that predicted by the theory based on uniformity. Thus one can assume that the theory based on uniformity is applicable under the same conditions as that developed in the present paper.

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**APPENDIX A: GOVERNING EQUATION FOR THE PROBABILITY  $P(r, t)$**

Let us formulate and solve the differential equation for the probability  $P(r, t)$ . Assume that the time increment  $dt$  is infinitely small, so that the average number of drops

$$dp = dt \int_{R(t)}^r dr' 4\pi r'^2 I(r', t), \tag{A1}$$

appearing during the time  $dt$  within the spherical shell between  $R(t)$  and  $r$  will be much less than unity. Then  $dp$  can be regarded as the probability of formation of a new drop in time  $dt$  within the spherical layer. Thus the quantity

$$1 - dp = 1 - dt \int_{R(t)}^r dr' 4\pi r'^2 I(r', t) \tag{A2}$$

is the probability that no new drops will be formed in the layer in time  $dt$ . According to the sense of the probability  $P(r, t)$ , for  $P(r, t + dt)$ , we can write

$$P(r, t + dt) = P(r, t) \left[ 1 - dt \int_{R(t)}^r dr' 4\pi r'^2 I(r', t) \right]. \tag{A3}$$

From Eq. (A3), it follows that

$$\frac{\partial P(r, t)}{\partial t} = -P(r, t) \int_{R(t)}^r dr' 4\pi r'^2 I(r', t). \tag{A4}$$

Solving the differential equation (A4) with the natural initial condition

$$P(r, 0) = 1, \tag{A5}$$

we come to Eq. (17).

**APPENDIX B: CALCULATION OF THE MEAN DISTANCE TO THE NEAREST-NEIGHBOR DROP**

Let us explain the origin of Eqs. (26) and (27). From Eq. (19), with the aid of Eq. (8), according to which  $R(t') = \beta t'^{1/2}$ , we obtain

$$\frac{dP(r)}{dr} = -P(r) 4\pi r^2 \int_0^{(r/\beta)^2} dt I(r, t). \tag{B1}$$

Taking into account Eqs. (20), (22), and (B1), let us transform the expression for the mean distance to the nearest neighbor drop  $\bar{r}$  as

$$\begin{aligned} \bar{r} &\equiv \int_0^\infty dr r f(r) = \int_0^\infty dr r P(r) 4\pi r^2 \int_0^{(r/\beta)^2} dt I(r, t) \\ &= - \int_0^\infty r dP(r) = \int_0^\infty P(r) dr. \end{aligned} \tag{B2}$$

Substituting the expression for the function  $P(r)$  from Eq. (19) to the right-hand side of Eq. (B2) and taking into consideration Eqs. (8), (12), and (13), we come to Eq. (26).

To obtain Eq. (27), consider the exponent of the exponential in the integral in the right-hand side of Eq. (26). Denote this exponent as

$$\begin{aligned} H(r) &\equiv - \int_0^{(r/\beta)^2} dt \int_{\beta t^{1/2}}^r dr' 4\pi r'^2 I_0 \\ &\times \exp \left[ -\Gamma \frac{2\beta t^{1/2}}{\pi^{1/2} r'} \int_u^\infty d\tau \left( 1 - \frac{u^2}{\tau^2} \right)^{1/2} e^{-\tau^2} \right]. \end{aligned} \tag{B3}$$

In Eq. (B3), in place of  $r'$ , introduce a new variable of integration  $x$  defined by  $r' = \beta t^{1/2} x = 2D^{1/2} \alpha t^{1/2} x$ . Taking into account that  $u = (r' - \beta t^{1/2})/2(Dt)^{1/2}$ , we find

$$\begin{aligned} H(r) &= -4\pi I_0 \beta^3 \int_0^{(r/\beta)^2} dt \int_1^{r/\beta t^{1/2}} dx t^{3/2} x^2 \\ &\times \exp \left\{ -\Gamma \frac{2}{\pi^{1/2} x} \int_{\alpha(x-1)}^\infty d\tau \right. \\ &\times \left. \left[ 1 - \frac{\alpha^2(x-1)^2}{\tau^2} \right]^{1/2} e^{-\tau^2} \right\}. \end{aligned} \tag{B4}$$

In the right-hand side of Eq. (B4), we introduce new variable of integration  $z$  in favor of  $t$  by means of  $t = z^2 r^2 / \beta^2$ . Then we obtain

$$\begin{aligned} H(r) &= -\frac{8\pi I_0}{\beta^2} r^5 \int_0^1 dz z^4 \int_1^{1/z} dx x^2 \\ &\times \exp \left\{ -\Gamma \frac{2}{\pi^{1/2} x} \int_{\alpha(x-1)}^\infty d\tau \left[ 1 - \frac{\alpha^2(x-1)^2}{\tau^2} \right]^{1/2} e^{-\tau^2} \right\}. \end{aligned} \tag{B5}$$

In principal, Eq. (B5) already has the structure that is necessary for the further calculations because the whole dependence on  $r$  is expressed by the factor  $r^5$  in the right-hand side of Eq. (B5). This equation allows an simplification that is important for the numerical calculations. The inversion of the order of integration over  $z$  and  $x$  when

$$\int_0^1 dz \int_0^{1/z} dx \rightarrow \int_1^\infty dx \int_0^{1/x} dz,$$

enables us to perform the integration over  $z$  in explicit form and, then, for Eq. (B5), we have

$$\begin{aligned}
 H(r) = & -\frac{8\pi I_0}{5\beta^2} r^5 \int_1^\infty dx x^{-3} \\
 & \times \exp\left\{-\Gamma \frac{2}{\pi^{1/2} x} \int_{\alpha(x-1)}^\infty d\tau \left[1 - \frac{\alpha^2(x-1)^2}{\tau^2}\right]^{1/2} e^{-\tau^2}\right\}. \quad (\text{B6})
 \end{aligned}$$

For convenience of numerical calculations, in Eq. (B6), it is worth transforming variables that eliminate  $\tau$  in favor of  $y$ . This is  $\tau = \alpha(x-1)y$ . After such transformation, using Eqs. (28)–(30) and taking into account  $\beta = 2D^{1/2}\alpha$ , for  $H(r)$  we have

$$H(r) = -\left(\frac{r}{r_0}\right)^5. \quad (\text{B7})$$

Substituting Eq. (B7) instead of the expression in the exponent of the exponential in the right-hand side of Eq. (26), we come to

$$\bar{r} = \int_0^\infty dr \exp\left[-\left(\frac{r}{r_0}\right)^5\right]. \quad (\text{B8})$$

From Eq. (B8), it follows Eq. (27) in which the numerical factor is the value of the integral:

$$\int_0^\infty d\xi e^{-\xi^5} \approx 0.92. \quad (\text{B9})$$

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