Heterogeneous condensation in dense media

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A theoretical description of heterogeneous nucleation kinetics is presented. This description takes into account the perturbation of the vapor phase initiated by the growing droplets. The form of the density profile around the growing droplet is analyzed and some special approximations are given. Then the process of nucleation in the whole system is described. As a result all the main characteristics of the process are determined analytically.

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I. INTRODUCTION

Among the numerous examples of first order phase transitions the case of condensation stands out because of its relative simplicity. This case is well investigated experimentally and is traditionally regarded as the base for application of new theoretical methods. The classical theory of condensation (see, for example, [1]) gives solid ground for further theoretical constructions. Numerous modifications and reconsiderations (see, for example, [2]) allow one to consider that the case of condensation is well analyzed both theoretically and experimentally.

One cannot state that all problems in the derivation of the stationary nucleation rate are completely solved, but the nucleation rate dependence on supersaturation is reliable at least in its general features. Certainly, there exist some unknown factors involved in the smooth dependence on the parameters of external conditions, but they are not very important in the current consideration.

One has to stress that essentially all investigations so far were intended to determine the rate of nucleation and have not presented the global picture of the phase transition. Theoretical descriptions of the global evolution appeared later than the classical theory of nucleation and they were not so numerous as those intended to get the stationary nucleation rate. One can extract many aspects of the global picture of the phase transition. When there is a sufficient quantity of aerosol in the system (i.e., there are already existing droplets formed on impurities) the evolution description does not require the process of droplet formation to be taken into account. This radically simplifies the problem, and this case was investigated in [3]. The total number of droplets there is already known from external conditions. Here this value will be the matter of investigation.

We shall determine the number of droplets and their size spectrum by solving the complex nonlinear problem. Because of the difficulties of this problem, only some numerical calculations have been presented earlier [4,5]. The scheme of calculations presented in [5] allowed the authors to establish in [4] some dimensionless combinations which essentially simplify the numerical procedure used there and allow rather complex numerical calculations. The sectional model presented in [6] simplifies the calculations once more and allows both nucleation and coagulation to be taken into account. Here we do not consider the process of coagulation,

assuming that the probability of this process is very low and it can be observed only long after the end of nucleation.

We have to stress that here we are going to present an analytical theory which does not require computer simulations except for some calculations of universal constants. This has to be done only once. The period of nucleation (i.e., the appearance of new droplets) is difficult to describe analytically and ordinarily one has to suggest some model approximation to estimate the influence of the vapor consumption by the existing droplets. Sometimes this influence is not important and it is shown in [7] that this situation is rather widespread in laminar tube flows. In [7] the theory for this case was given and the methods of describing the global evolution were presented completely.

An analytical method to describe most of the nucleation process was presented in [8] on the basis of the balance equation for some characteristic time scales. The form of the size spectrum was postulated and the parameters of this form were associated with characteristic time scales. Then some special equations to obtain these time scales were formulated, which gives a way to get all the main characteristics of the nucleation process.

Here we are going to determine the form of the size spectrum explicitly taking account of the profile of vapor density around every droplet. The great importance of the problem of vapor exhaustion around the droplet was stressed by Reiss in [9], where the stationary profiles around droplets were obtained. Approximation of the stationary profiles was necessary in [9] to get the rate of droplet growth. It will be shown that to describe the kinetics of nucleation it is essential to use nonstationary profiles of the vapor density around the droplet instead of quasistationary ones. The appearance of contradiction between the approach in [9] and that used below is explained by the fact that in [9] only distances near the droplet were considered. To get the rate of growth it is sufficient to consider only relatively small distances. Below we shall be interested in some large distances which have the scale of the mean distance between droplets.

To start our consideration one has to fix external conditions. We shall analyze condensation after the instantaneous creation of initial supersaturation, which is very often used in experiments. The theoretical investigations of this case are also rather numerous. Among them one can extract the descriptions of metastable phase decay by Wakeshima [10], by Segal' [11], and by Kuni and Grinin [12]. The process of

condensation that occurs during a smooth variation of external conditions is considered in [13]. Nevertheless, all the mentioned theoretical descriptions of a global picture of condensation kinetics have ignored an important feature of this process, namely, the exhaustion of a metastable phase near the growing embryo of a new phase has not been taken properly into account. Certainly, this exhaustion is partially taken into account in the expression for the rate of embryo growth in the continuous model (i.e., in the diffusion regime of embryo growth). This effect has been analyzed in both stationary and nonstationary aspects in many publications mainly in the field of mechanics of continuous media. But the presence of a gap in the metastable phase density near a droplet will act on the rate of new droplet formation. This effect was not taken into account in all the mentioned previous theoretical descriptions of global evolution during a first order phase transition. But, as shown in [14], this gap can lead to large numerical effects in the description of the whole process.

The reason that this effect has not been considered before is rather trivial. Even under a spatially homogeneous consumption of the metastable phase the descriptions were rather difficult to solve [13]. The condensation process has usually been described in the free molecule regime of droplet growth where there will be no such gap. This was a serious restriction of the theoretical description.

In some publications devoted to construction of a global picture of the phase transition (see, for example, [15]) the regime of droplet growth was the diffusion regime. This requires consideration of the gap in the density near the growing droplet but the vapor consumption was regarded as homogeneous in space. Since this effect is very important one cannot present a reliable description without taking it into account. Here we shall give a more realistic picture of the phase transition which takes this gap into account but allows an analytical solution.

Qualitatively the picture of the condensation process is rather simple. A process of nucleation (i.e., formation of supercritical embryos of a liquid phase) leads to vapor exhaustion, which stops the process of nucleation, but the supercritical embryos continue to consume the vapor phase. All the surplus material of the metastable phase will be accumulated in the embryos of a new phase. One can say that the process of condensation is now completed.[1]

A global picture of homogeneous condensation with explicit account of the density profiles was presented in [14], where very large numerical effects were observed, but ordinarily the process of nucleation occurs on heterogeneous centers.[2] This fact radically complicates the theoretical description due to the centers' exhaustion. This exhaustion has

essentially nonlinear character. For simplicity we shall assume that there is only one type of heterogeneous center and the total number of centers is fixed in time. During the nucleation process some of the heterogeneous centers become the centers of supercritical droplets that are growing irreversibly in time. But the nucleation process diminishes the number of free heterogeneous centers (those unoccupied by droplets). In some cases the total exhaustion of free heterogeneous centers interrupts the nucleation; in some cases partial exhaustion of heterogeneous centers seriously diminishes the nucleation rate. This effect has also to be taken into account in a theoretical description.

A simple analytical description of heterogeneous condensation will be presented here with a proper account of all problems mentioned above. As a result, all the main characteristics of the condensation process will be expressed through some parameters of the external conditions and through the substance parameters by explicit analytical formulas. The error of the description presented will be estimated.

The structure of the theory will be as follows. First we shall analyze the density profile around a solitary droplet and construct some approximations. This has much in common with the case of homogeneous condensation considered in [14] and will be considered briefly. Then we shall construct some models for the kinetics of the process. We have to show that these models estimate the time evolution of the system during the nucleation period from above and from below. Since these models give similar results one can state that an approximate description of the nucleation kinetics is given. The error of the description is thus estimated. When the solution has been obtained we can compare it with the formulas given by the previous approach without density profiles and see the numerical effect of the gap near the growing droplets.

The small parameter of the theory will be the inverse number of molecules inside the critical embryo of a new phase. The small value of this parameter is not a restriction of our theory—it comes from the validity of the thermodynamic approach to calculating the free energy of the critical embryo. There is no other reliable way to calculate the free energy except the thermodynamic approach.[3] To use the thermodynamic approach it is necessary to have at least a few dozen molecules inside the embryo.

Also, we shall require a barrier character of the nucleation. This means that every embryo has to overcome an activation barrier of a particular height to begin to grow irreversibly. This height is less than the critical energy for the homogeneously (purely fluctuationally) formed embryo but still attains several thermal units.[4] Certainly, one can imagine a situation when there is no activation barrier. Then all embryos immediately begin to grow irreversibly. The number of

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[1]Further evolution includes the consumption of some relatively small embryos by some relatively big ones. It will be seen later that when all surplus material is consumed all droplets have approximately the same size, and we do not analyze this process here. A description of the further evolution can be given with the help of the Ostwald ripening theory formulated by Lifshitz and Slezov.

[2]Also, it is simpler to observe the heterogeneous case experimentally.

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[3]All microscopic models require very complex calculations that cannot be fulfilled directly.

[4]All energylike values will be measured in thermal units.

droplets (i.e., the irreversibly growing embryos) will be equal to the total number of centers and the kinetics of the process will be relatively simple.

We shall speak only about the density profiles around the droplet and ignore the heat extraction in the nucleation process.[5] In fact, the mathematical structure of the diffusion equation resembles the structure of a heat transfer equation. So all constructions for the condensation heat extraction will be the same as for substance consumption. This effect will lead only to some renormalizations. That is why only a few remarks will be made. Some detailed results can be found in [6].

We shall consider the situation of metastable phase decay. This means that in the initial moment of time all the substance is in the vapor phase. All heterogeneous centers are free from droplets.

II. PROFILE AROUND THE SOLITARY DROPLET

Due to the external influence in the initial moment of time one can observe a homogeneous mother metastable phase with particle number density n equal to some initial value n_0. All heterogeneous centers are distributed rather homogeneously in space with the number density η_{tot}. A system of unit volume is considered.

The process of condensation can begin only when n_0 is greater than the molecule number density n_∞ in saturated vapor over a plane liquid. The power of the vapor metastability is characterized by the value of the supersaturation ζ defined as

$$\zeta = \frac{n}{n_\infty} - 1 .$$

The initial value of the supersaturation is denoted by ζ_0.

Almost immediately there will be formed around every center an equilibrium embryo which has ν_e molecules. The value of ν_e is relatively small[6] and there is no need to consider the density profile around the equilibrium embryos.[7]

During the condensation process the number of free heterogeneous centers η decreases due to the exhaustion of the free heterogeneous centers,

$$\eta = \eta_{\text{tot}} - N,$$

where N is the number of supercritical embryos, which will be called the droplets. Despite the simple form of the last relation the effect is very complex because N depends on time in a very complex manner.

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[5]The validity of this assumption can be ensured by using a passive gas.

[6]In comparison with the characteristic number of molecules inside the droplet during the nucleation period.

[7]In fact the gap is rather small and will disappear rather fast. This leads to a slight variation of the equilibrium embryo characteristics. This variation will act on the gap in reverse, but the final relaxation will be rather rapid.

The effects of the density profile will be essential also for account of the heterogeneous centers' exhaustion and one cannot directly apply the results of [13]. One has to determine the effect of the influence of the centers' exhaustion even for the density profile of a solitary droplet.

We shall call the approach where the law of embryo growth is found from the continuous model but there is no account of the profile around the droplets the ''additive approach'' (AA). Then one can formulate the following evident statement.

Statement 1. The duration of the nucleation period[8] and the characteristic sizes of the droplets at the end of the nucleation period are greater than those calculated in the AA.

In fact, the existence of the density profile means that part of the substance is going to be consumed from regions where there is no droplet formation. This material is consumed from the gap instead of from unexhausted regions as is supposed in the AA.

Then having repeated all constructions[9] from [13] one can see the following.[10]

Statement 2. The characteristic size of the droplets at the end of the nucleation period is many times greater than the size of the critical embryo. The main role in vapor consumption is played by the supercritical embryos.

Statement 3. The characteristic duration of the nucleation period is many times greater than the time of relaxation to the stationary state in the near-critical region. Thus one can use the stationary rate of nucleation as a measure of the intensity of droplet formation at every current moment of time.

Because of statement 2 one has to investigate the profile around a growing droplet. The problem is whether one has to consider the interference of profiles around different droplets. To solve this problem one has to use the small parameter of the theory. From statement 3 the rate of nucleation is equal to the stationary one. This can be taken from [1],

$$I_s = Z \eta \exp(-\Delta F),$$

where ΔF is the height of the activation barrier (in thermal units), η is the number of free heterogeneous centers (unoccupied by the supercritical embryos), and Z is the Zeldovic factor. The Zeldovic factor is a smooth function of the supersaturation that is given by

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[8]The period of nucleation is the period of relatively intense formation of droplets. It can be proved that the end of this period is well defined due to the cutoff of the intensity of droplet formation.

[9]In [13] the AA was formulated for external conditions of dynamic type. For the situation of decay the required hierarchical inequalities can be proved in the same way. Note that in [13] there is no special reference to the types of condition when the required estimates are proved.

[10]A barrier character of the nucleation is required here. This means that the magnitude of the activation barrier height has the same order as the free energy of the homogeneous critical embryos (it might be three on four times smaller).

$$Z = \frac{W}{\pi^{1/2} \Delta \nu_e \Delta \nu_c},$$

where W is a kinetic factor, $\Delta \nu_c$ is the half-width of the near-critical region, and $\Delta \nu_e$ is the width of the equilibrium region. During the nucleation period the value of Z can be considered as as constant.

Due to its rather small size it is reasonable to use for the critical embryo the free molecule regime of substance exchange.[11] In this regime the expression for the nucleation rate is well known. One has also to note that the critical embryo is in equilibrium (but an unstable one) with the metastable phase, which implies no profiles of vapor density, and the regime of substance exchange has to be the free molecule one.

Under the free molecule regime W can be calculated as

$$W = 3 \frac{\zeta + 1}{\tau} \nu_c^{2/3} \alpha,$$

where ν_c is the number of molecules inside the critical embryo, α is the condensation coefficient,

$$\tau \sim 12 [(36 \pi \nu_l^2)^{1/3} n_\infty \nu_T]^{-1}$$

is the characteristic time, ν_l is the volume per one molecule in the liquid phase, and ν_T is the mean thermal velocity of a molecule.

The value of $\Delta \nu_c$ is the half-width of the near-critical region and it can be rewritten as

$$\Delta \nu_c = \sum_{\nu \leq (\nu_c + \nu_e)/2} \exp(-F_c + F_\nu) \pi^{-1/2},$$

where ν is the number of molecules inside the embryo, F_ν is the free energy of the embryo of ν molecules, and F_c is the free energy of the critical embryo. In the continuous approximation it can be estimated as[12]

$$\Delta \nu_c = \left| \frac{2}{\delta^2 F / \delta \nu^2} \right|^{1/2}_{\nu = \nu_c}.$$

The value of $\Delta \nu_e$ can be estimated as

$$\Delta \nu_e = \sum_{\nu \leq (\nu_e + \nu_c)/2} \exp(-F_\nu + F_e)$$

where F_e is the free energy of the equilibrium embryo. Both $\Delta \nu_c$ and $\Delta \nu_e$ are rather smooth functions of the supersaturation.

One can see that I_s is a very sharp function of the supersaturation. This means that a relatively small decrease of the supersaturation leads to an interruption of droplet formation.

At least for $\zeta > \zeta_0/2$ one can show that $d^2\zeta/dt^2 > 0$ and there is no long tail of the size spectrum at small intensity of droplet formation. This means that an interruption of the intensive droplet formation leads to an interruption of new droplet formation. So the relative decrease of supersaturation during the nucleation process is small. One can arrive at the following statement.

Statement 4. During the nucleation period the relative variation of supersaturation is small.

The last statement shows that there is no need to consider the interference of profiles in order to change the rate of droplet growth (and only the rate of growth).

On the basis of the expressions mentioned and the smallness of the relative decrease of supersaturation one can see the validity of the approximation

$$I_s(\zeta) = I_s(\zeta_0) \exp[\Delta F(\zeta_0) - \Delta F(\zeta)]$$

for the nucleation period. Moreover, one can linearize the height of the activation barrier over the supersaturation and get

$$I_s(\zeta) = I_s(\zeta_0) \exp\left(-\left. \frac{d\Delta F(\zeta)}{d\zeta} \right|_{\zeta = \zeta_0} (\zeta - \zeta_0) \right). \quad (1)$$

The validity of the last approximation depends on the particular type of heterogeneous center but it is valid for the majority of heterogeneous center types. For example, this validity can be directly proved for ions.

One can explicitly calculate the derivative in the last expression,[13]

$$\frac{d\Delta F}{d\zeta} = -\frac{1}{\zeta + 1} (\nu_c - \nu_e).$$

The smooth character of the last expression shows the validity of Eq. (1) once more.[14]

Then Eq. (1) can be rewritten as

$$I_s(\zeta) = I_s(\zeta_0) \exp\left(\Gamma \frac{\zeta - \zeta_0}{\zeta_0} \right), \quad (2)$$

where

$$\Gamma = -\zeta_0 \left. \frac{d\Delta F}{d\zeta} \right|_{\zeta = \zeta_0} = \frac{\zeta_0}{\zeta_0 + 1} [\nu_c(\zeta_0) - \nu_e(\zeta_0)].$$

The real value of Γ is very large.[15] Certainly, one can consider the possibility of compensation between ν_c and ν_e in

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[11]Since the characteristic size of the droplet during the nucleation is many times greater that the critical size it is quite reasonable to use the diffusion regime of growth for the characteristic droplets.

[12]$\Delta \nu_e$ is usually smaller than $\Delta \nu_c$ and an explicit summation for $\Delta \nu_c$ is quite reasonable.

[13]Here we assume the vapor to be an ideal gas and suppose the possibility of presenting the free energy of critical and equilibrium embryos as an analytical function of the inverse embryo radius.

[14]A concrete value of the free energy derivative is not essential.

[15]Since the value of ν_c in going to infinity here the value of Γ is also going to infinity.

the expression for Γ. Then one has to mention that due to the barrier character of nucleation at least $\nu_c - \nu_e \geqslant \Delta \nu_c$. Having estimated $\Delta \nu_c$ as the homogeneous value $\Delta \nu_c \sim \nu_c^{2/3}$ one can see that $\Gamma \gg 1$ in any case.

The small value of Γ^{-1} will be very important in further constructions.

We see that the essential dependence on supersaturation occurs through the height of the activation barrier. This allows one to give the interpretation of the stationary rate of nucleation as the probability for the given embryo to overcome the activation barrier. After the interpretation of I_s as a probability we can apply it to an arbitrary spatial point of a spatially inhomogeneous system. To use this interpretation the natural requirement is a weak unhomogeneity of a system, namely, the volume of the regions where

$$\frac{\zeta(r) - \zeta(r + \sqrt{4Dt_s})}{\zeta(r)} \ll \Gamma^{-1}$$

is violated has to be relatively small. Here D is the diffusion coefficient, and t_s is the time of relaxation in the near-critical region, which can be estimated according to Zeldovic [1] as

$$t_s \sim \frac{\Delta \nu_c^2}{W}.$$

One can use instead of t_s the time $\Delta \nu_e Z^{-1}$, which can be interpreted as the mean time to overcome the near-critical region.

Both these estimates are valid. Actually we need them only for those regions where the intensity of the droplet formation is not too small in comparison with the initial intensity. Certainly, the required property is observed in these regions.

Now we have to turn to determining the rate of embryo growth. According to statement 2 above, the characteristic size of the droplets is rather large. Then it is more reasonable to use the diffusion regime of droplet growth. At intermediate Knudsen numbers one has to use an interpolation law for the rate of embryo growth (for example, see [17,4]). It will be important that all expressions for the embryo growth lead to an avalanche of substance consumption.

The avalanche character of substance consumption means that the quantity of substance accumulated by a droplet increases strongly in time. The most evident manifestation of the avalanche consumption can be seen in the free molecule regime of substance consumption. The weakest effect can be seen in the diffusion regime of substance consumption. The force of the iteration convergence in [13] is based on this property. The property of avalanche consumption will be extremely important in further constructions also. That is why we take the diffusion regime, to have the worst situation and to grasp errors in all possible cases.

In the diffusion regime of vapor consumption the law of growth for a droplet (i.e., for a supercritical embryo) can be written in the following way:

$$\frac{d\nu}{dt} = \kappa \zeta \nu^{1/3},$$

where

$$\kappa = \left(\tfrac{2}{3}\right)^{-1/3} 4 \pi n_\infty D \left(\frac{v_l}{2\pi}\right)^{1/3}$$

is some constant. The last expression is written in the stationary approximation. The nonstationary effects have been investigated in many publications in detail and here they are rather small (see, for example, [9]).

One can see that the rate of droplet growth is proportional to ζ. So the rate of growth can be changed only by a relative variation of ζ. Then according to statement 4 one can see the following.

Statement 5. The rate of droplet growth during the nucleation period can be approximated as a constant.

The last statement is extremely important because it allows us to analyze the profile of the density initiated by a solitary droplet.[16] Now we are going to consider this problem.

The approximately constant value of the supersaturation allows us to integrate the law of growth and to get

$$\nu(t) = \gamma t^{3/2},$$

where

$$\gamma = (4\pi)^{3/2} \left(\frac{3v_l}{4\pi}\right)^{1/2} \left(\frac{2\zeta n_\infty D}{3}\right)^{3/2}$$

and t is the duration of irreversible growth for the given droplet. Consider a spherical system of coordinates with the center in the center of the droplet. The diffusion equation is written as

$$\frac{\partial n}{\partial t} = D \Delta n$$

where Δ is the Laplace operator. The diffusion coefficient D is supposed to be approximately constant (there is a lot of a passive gas and the density of a gas mixture is approximately constant).

The boundary conditions are

$$n|_{r=\infty} = n(\infty),$$

$$n|_{r=R_d} = n_\infty,$$

where R_d is the radius of the droplet. The values n_∞ and $n(\infty)$ are known parameters. The variable r is the distance from the center of the embryo.

The stationary approximation is suitable for the rate of droplet growth. The errors are analyzed in [17] and they are small. But the stationary solution cannot give a reasonable result for the density far from the droplet. The stationary solution is

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[16]The interference of the density profiles will be analyzed later.

$$n(r) = n(\infty) - \frac{R_d}{r}[n(\infty) - n_\infty] \qquad (3)$$

and has a very long tail. This tail leads to the infinite value of

$$G = \int_0^\infty 4\pi r^2 [n(\infty) - n(r)] dr,$$

which must be the integrated excess of the substance, which must be in the droplet. This contradiction shows that it is absolutely impossible to use the stationary approximation for the density profile around the droplet. One has to introduce another approach.

One can see that if the first boundary condition is changed to

$$n|_{r=\infty} = n(\infty)(1 - \Gamma^{-1})$$

then the rate of embryo growth will not be essentially changed. But the level $n(\infty)(1 - \Gamma^{-1})$ is the level when nucleation stops. So one can see that during the nucleation period there is no interaction between droplets through a change of the growth rate. Certainly, two droplets can appear too close and act upon one another but the probability of such a coincidence is very small. That is why one can come to the principle of separate growth of droplets during the nucleation period.

Now one has to prove that at the distances $(5-10)R_d$ from the droplet one can observe a quasistationary profile. One has to note that

$$v_l/v_v \ll 1, \qquad (4)$$

where v_v is the partial molecular volume in the vapor phase. This last ratio is very small (for example, it is 0.001 for water in normal thermodynamic conditions). But unlike Γ^{-1} one cannot consider it in all cases as zero. Now one can introduce a formal parameter l which attains some large values

$$l \gg 1$$

but satisfies the condition

$$l^2 \frac{v_l}{v_v} \ll 1. \qquad (5)$$

According to Eq. (4) it is possible to do this.

In the region $r \leq lR_d$ the stationary profile is established after

$$t_h = \frac{l^2 R_d^2}{4D}.$$

It is necessary to show that

$$s \equiv \frac{R_d(t + t_h) - R_d(t)}{R_d(t)} \ll 1.$$

In fact,

$$s \approx \frac{dR_d}{dt}\frac{t_h}{R_d}$$

and

$$s \sim l^2 \frac{v_l}{v_v},$$

which is a small value according to Eq. (5). So the stationary form of the profile in the region $r < R_d l$ is proved.

Since $\Gamma \gg 1$ and at least $\Gamma \gg l$ one can see that in the region $r < lR_d$ there is no formation of new droplets. Thus this region is not interesting for the theory and one can observe only the region $r > lR_d$.

The previous notation is rather important; this property allows one to use the model with a point source. One can consider only distances greater than lR_d, but at these distances the droplet can be interpreted as a point source of vapor consumption. Certainly, the point approximation of a droplet cannot give an expression for the rate of droplet growth because the boundary condition at $r = R_d$ is absent. But the rate of growth is already known and can be used directly as a known function of time. Thus

$$\frac{dv}{dt} = \lambda t^{1/2},$$

where

$$\lambda = 2^{5/2} \pi v_l^{1/2} \zeta^{3/2} n_\infty^{3/2} D^{3/2}.$$

The action of a point source of vapor consumption can be described in a simple and suitable manner by the Green function formalism. The Green function G_r for the diffusion equation can be written in the form

$$G_r = \Theta(t) \frac{\exp(-r^2/4Dt)}{(4\pi Dt)^{3/2}}.$$

Then one can get the density profile by a simple integration,

$$n(r) = n(\infty) - \int_0^t \frac{\lambda x^{1/2}}{[4\pi D(t-x)]^{3/2}} \exp\left(-\frac{r^2}{4D(t-x)}\right) dx.$$

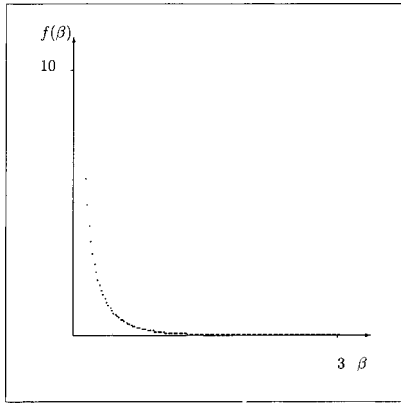After obvious transformations one can come to

$$\frac{\zeta_0 - \zeta}{\zeta_0} = \sqrt{2/\pi}\sqrt{v_l/v_v} f(\beta), \qquad (6)$$

where

$$\beta = \frac{r}{\sqrt{4Dt}}$$

and

$$f(\beta) = \int_\beta^\infty \left(\frac{1}{\beta^2} - \frac{1}{x^2}\right)^{1/2} \exp(-x^2) dx.$$

FIG. 1. The form of $f(\beta)$.

It is important that the profile dependence on t and r is now via β.

The concrete form of $f(\beta)$ is drawn in Fig. 1 in dimensionless units. One can get for $f(\beta)$ an expression through special functions:

$$f(\beta) = \tfrac{1}{2}\Gamma(\tfrac{3}{2})\exp(-\beta^2)\Psi(\tfrac{3}{2},\tfrac{3}{2};\beta^2).$$

Here Γ is the Gamma function and Ψ is the confluent hypergeometric function.

One can get the asymptotes for $f(\beta)$ at small and large values of β. At small values,

$$f(\beta) \sim \frac{\sqrt{\pi}}{2}\frac{1}{\beta}, \tag{7}$$

which corresponds to the stationary solution (3). At large values of β one arrives at

$$f(\beta) = \exp(-\beta^2)\frac{1}{2\beta^3}\int_0^\infty x^{1/2}\exp(-x)dx \sim \frac{\exp(-\beta^2)}{\beta^3}. \tag{8}$$

One can see that this asymptote differs radically from the stationary solution, namely this tail behavior gives convergence of the integral for G. Certainly, the Green function formalism ensures a precise value for G, which is introduced here as an external object.

Now we are going to construct an approximation for the nucleation rate around the growing droplet. One can see that according to Eq. (2) the behavior of the supersaturation is important when $\zeta_0 - \zeta \leq (2-3)\zeta_0/\Gamma$. When $\zeta_0 - \zeta \geq (2-3)\zeta_0/\Gamma$ the intensity of droplet formation is negligibly small. From Eq. (1) one can see that

$$I_s(\zeta(r)) = I_s(\zeta_0)\exp[-\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v}f(\beta)].$$

Then one can extract the positive parameter

$$\sigma \equiv \Gamma^2\frac{v_l}{v_v}$$

which will be important in further constructions.

Because $\Gamma \gg 1$ one can easily see that

$$\sigma \gg 1.$$

The last condition is not necessary for further constructions, but it will be rather important for manifestation of the profile effects in the nucleation process. The last condition is also the most doubtful one because $v_l/v_v \ll 1$ and one has the combination of two large parameters with generally unknown result. It is necessary to stress that the condition $v_l/v_v \ll 1$ is not as strong as $\Gamma^2 \gg 1$. In the framework of the thermodynamic description $\Gamma \gg 1$ is the main condition required and $v_l/v_v \ll 1$ is a supplementary condition that slightly simplifies the theory.

In the situation of homogeneous condensation one has a hidden contradiction between the thermodynamic description and the relatively intensive nucleation. Since in homogeneous condensation $\Delta F = F_c \sim \nu_c^{2/3}$ the limit $\nu \to \infty$ means $\Delta F \to \infty$ and the rate of nucleation goes to zero. So there is a contradiction between the thermodynamic limit in the critical embryo description and the observable rate of nucleation.[17]

In the case of heterogeneous condensation there is no such contradiction when there are some active centers of condensation. Then the height of the activation barrier has no direct connection with the number of molecules inside the critical embryo. For example, the half-width of the near-critical region estimated from the homogeneous value is $\sim \nu^{2/3}$ and goes to infinity when $\nu \to \infty$, but the free energy decreases at the boundary of the near-critical region only by one thermal unit. So in a certain sense the case of heterogeneous condensation is preferable for theoretical description.

As a compensation for this advantage one has to note that both statements 1 and 2 are based on a homogeneous estimate for the activation barrier height. These properties can be violated. But since these statements are based on very strong inequalities one can accept their validity.

Now one can analyze the profile of the intensity of droplet formation around the already formed droplet. This profile of the nucleation rate is a rather sharp function which has a steplike behavior.

To show this property we shall introduce two characteristic values of β (β_{st} and β_{fin}) by the relations

$$f(\beta_{\mathrm{st}}) = \sqrt{\pi/2}\sqrt{v_v/v_l}\frac{\exp(-\tfrac{1}{2})}{\Gamma},$$

$$f(\beta_{\mathrm{fin}}) = \sqrt{\pi/2}\sqrt{v_v/v_l}\frac{\exp(\tfrac{1}{2})}{\Gamma}.$$

In the region $\beta > \beta_{\mathrm{st}}$ the rate of nucleation essentially coincides[18] with the unperturbed value $I_s(\zeta_0)$. In the region $\zeta < \zeta_{\mathrm{fin}}$ the rate of nucleation is negligible in comparison with the unperturbed value, i.e., $I_s(\zeta(r)) \ll I_s(\zeta_0)$.

At some moment t the values β_{st} and β_{fin} are related to the space distances r_{st} and r_{fin} by the expressions

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[17]This is not very small.

[18]One can easily see the monotonic character of $f(\beta)$.

$$r_{st} = \beta_{st}\sqrt{4Dt},$$

$$r_{fin} = \beta_{fin}\sqrt{4Dt}.$$

When $\sigma \gg 1$ one can arrive at

$$f(\beta_{st}) \ll 1,$$

$$f(\beta_{fin}) \ll 1$$

and

$$\beta_{st} \gg 1,$$

$$\beta_{fin} \gg 1.$$

Then one can use the asymptote (8) and see that

$$\frac{|\beta_{st} - \beta_{fin}|}{\beta_{st} + \beta_{fin}} = \frac{1}{4\beta_{st,fin}} \ll 1,$$

$$\frac{|r_{st} - r_{fin}|}{r_{st} + r_{fin}} = \frac{1}{4\beta_{st,fin}} \ll 1.$$

The real picture of nucleation occurs on the time scale. At a fixed space point r one can introduce two characteristic times t_{st} and t_{fin} by the expressions

$$t_{st} = \frac{r^2}{4\beta_{st}^2 D},$$

$$t_{fin} = \frac{r^2}{4\beta_{fin}^2 D}.$$

Before t_{st} one cannot observe any deviation of the nucleation rate from the unperturbed value. After t_{fin} the rate of nucleation is very small.

One can get for the relative deviation

$$\delta \equiv \frac{t_{fin} - t_{st}}{t_{st,fin}}$$

the expression

$$\delta \sim \frac{1}{\beta_{st,fin}}.$$

So the relative deviation is small. Even in the situation of small σ one can show with the help of asymptote (7) that the value of δ is rather small.

The steplike behavior of the intensity profile allows one to introduce some characteristic parameter β_{eff} and to consider the region[19]

$$\beta < \beta_{eff}$$

as the exhausted region where there is no longer nucleation and the region

$$\beta > \beta_{eff}$$

as the region where the rate of nucleation is unperturbed.[20]

One has to choose β_{eff} carefully. The problem is the possibility of existence of a long tail of the density profile. To grasp the situation of small values of σ one has to introduce β_{eff} in an integral manner.

One can introduce the excess of the nucleation rate ΔI_s by the formula

$$\Delta I_s = I_s \int_0^\infty \left[1 - \exp\left(-\frac{\Gamma(\zeta_0 - \zeta(r))}{\zeta_0} \right) \right] 4\pi r^2 \, dr,$$

where I_s is the unperturbed rate of nucleation. On the basis of this expression one can get the excess of N due to the existence of the solitary profile. This value will be denoted ΔN_{sol} and can be found as

$$\Delta N_{sol} = I_s \int_0^t \int_0^\infty \left[1 - \exp\left(-\frac{\Gamma(\zeta_0 - \zeta(r))}{\zeta_0} \right) \right] 4\pi r^2 \, dr \, dt'.$$

Having used Eq. (6) one arrives at

$$\Delta I_s = 4\pi(4Dt)^{3/2} I_s$$

$$\times \int_0^\infty \{1 - \exp[-\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v} f(\beta)]\}\beta^2 \, d\beta.$$

The parameter $\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v}$ has a constant value.

The value ΔN_{sol} can be presented as

$$\Delta N_{sol} = 4\pi(4Dt)^{3/2} I_s$$

$$\times \int_0^t \int_0^\infty \{1 - \exp[-\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v} f(\beta)]\}$$

$$\times \beta^2 \, d\beta \, dt'.$$

The steplike approximation of the nucleation profile will lead to

$$\Delta I_s^0(\beta_{eff}) = 4\pi(4Dt)^{3/2} I_s \int_0^{\beta_{eff}} x^2 \, dx.$$

The value β_{eff} has to be determined from

$$\Delta I_s^0(\beta_{eff}) = \Delta I_s.$$

Certainly, the value of β_{eff} depends on $\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v}$.

The value of β_{eff} leads to

$$r_{eff} = 2\beta_{eff} D^{1/2} t^{1/2}.$$

One can state that inside the volume

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[19]At $\sigma \ll 1$ the value of β_{eff} can be greater than β_{st} and β_{fin}.

[20]In all cases $\beta_{eff} > \beta_{fin}$.

$$V_{\mathrm{eff}} = \tfrac{4}{3}\pi r_{\mathrm{eff}}^3$$

there is no nucleation and outside this volume the rate of nucleation is unperturbed. Thus one can imagine that around every solitary droplet there is an exhausted region (ER) where no nucleation is observed and around the ER there is the unexhausted region (UR) where the nucleation remains unperturbed. The whole space now is divided into two regions.

The volume V_{eff} grows in time in the following way:

$$V_{\mathrm{eff}} = \frac{32}{3}\pi\beta_{\mathrm{eff}}^3 D^{3/2} t^{3/2}.$$

In the free molecule regime V_{eff} will grow even faster. For β_{eff} one can get the simple expression

$$\beta_{\mathrm{eff}}^3 = 3\int_0^\infty \{1 - \exp[-\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v}f(\beta)]\}\beta^2\, d\beta$$

or

$$\beta_{\mathrm{eff}}^3 = 3\int_0^\infty \{1 - \exp[-\sigma^{1/2}\sqrt{2/\pi}f(\beta)]\}\beta^2 d\beta.$$

For ΔN_{sol} one can obtain

$$\Delta N_{\mathrm{sol}} = I_s(\zeta_0)\int_0^t dt'\, V_{\mathrm{eff}} = I_s(\zeta_0)\int_0^t dt'\, \tfrac{4}{3}\pi r_{\mathrm{eff}}^3.$$

One can easily integrate the last expression and get

$$\Delta N_{\mathrm{sol}} = I_s(\zeta_0)\frac{64}{15}\pi\beta_{\mathrm{eff}}^3 D^{3/2} t^{5/2}.$$

One can see that ΔN_{sol} is growing in time rather rapidly. That is, this property illustrates the feature of avalanche consumption during a first order phase transition as applied to heterogeneous nucleation.

For those situations where $\sigma \gg 1$ one can get

$$\beta_{\mathrm{eff}} \approx \beta_{\mathrm{st}} \approx \beta_{\mathrm{fin}}$$

and β_{eff} is determined by the simple equation

$$\exp(-\beta_{\mathrm{eff}}^2) = \beta_{\mathrm{eff}}^3\sqrt{v_v/v_l}\sqrt{\pi/2}\frac{1}{\Gamma}.$$

The last equation can easily be solved by iteration since $\beta_{\mathrm{eff}} \gg 1$ and $\exp(-\beta^2)$ is a very sharp function.

When the principle of separate growth was discussed some remarks were made. The reason given for the absence of interaction between droplets was the low probability of appearing too close to one another due only to the smallness of the space volume. Now one can see that the growing ER also helps to exclude interaction. The essential deviation of supersaturation from the ideal can be seen in the region $r < R_d l$. This means that the distance between the droplets with interference must be of the order $2R_d l$. Then the time distance between the moments of formation of these droplets must be shorter than

$$\Delta t_{\mathrm{init}} \sim \left(\frac{R_d l}{\beta_{\mathrm{eff}} D^{1/2}}\right)^2.$$

This time interval is many times shorter than the duration of the nucleation period.

Rather rapidly after the moment of formation every droplet forms an ER of such a size that it guarantees that the rate of growth of the given droplet cannot be perturbed by vapor consumption initiated by other droplets.

III. KINETIC MODELS OF GLOBAL EVOLUTION

Now one can construct the picture of nucleation in the whole system. The main problem is to take into account the interference of the density profiles. Interference through the rate of growth is absent, but there is a simple overlapping of profiles. This overlapping leads to deviation of the total nucleation rate over the volume from those calculated taking account of the additive excess around every droplet.

The overlapping of ER's (even when this approximate formalism is used) is very complex and cannot be directly taken into account in a precise manner. Instead of using some long expressions that cannot be explicitly calculated one can act in another manner. First some simple approximate models for the kinetics of the nucleation process will be formulated. These models estimate the nucleation characteristics from below and from above and lead essentially to similar results. So it will be shown that the complex details of ER overlaps have no strong influence on the real characteristics of the phase transition.

First one can consider the common feature of all models. This feature is concerned with the exhaustion of free heterogeneous centers.

The rate of nucleation I depends on time t and on spatial point r (the last behavior is the most complex). So it is reasonable to consider the mean (over space) value of I, denoting it by $\langle I\rangle$. For $\langle I\rangle$ one can write the expression

$$\langle I\rangle = \frac{W_{\mathrm{free}}}{W_{\mathrm{tot}}}\frac{\eta}{\eta_{\mathrm{tot}}}I_0, \tag{9}$$

where I_0 is the unperturbed rate of nucleation. Here W_{free} is the volume of the region where the rate of nucleation is unperturbed, i.e., the total UR of the whole system. The value W_{tot} is the total volume of the system (it equals unity and is written only to clarify the consideration).

Then since

$$N = \int_0^t \langle I\rangle(t')\, dt'$$

one can get

$$\eta = \eta_{\mathrm{tot}} - \int_0^t \langle I\rangle(t')\, dt'.$$

In the differential form the last relation can be written as

$$\frac{d\eta}{dt} = -\langle I\rangle$$

and with the help of Eq. (9) it can be rewritten as

$$\frac{d\eta}{dt} = -\frac{\eta}{\eta_{\text{tot}}}\frac{W_{\text{free}}}{W_{\text{tot}}}I_0.$$

After integration of the last expression one arrives at

$$\eta = \eta_{\text{tot}}\exp\left(-\int_0^t \frac{W_{\text{free}}(t')}{W_{\text{tot}}}\frac{I_0}{\eta_{\text{tot}}}dt'\right). \qquad (10)$$

One should note that the heterogeneous centers are not distributed homogeneously with respect to the ER (or UR). Only free heterogeneous centers are distributed homogeneously with respect to the ER. This fact has also to be taken into account.

The problem is to determine the value of W_{free}. In different models it will be given in different forms.

A. The model without overlap

One can write

$$W_{\text{free}} = W_{\text{tot}} - W_{\text{exh}}$$

where W_{exh} is the volume where there is no further formation of droplets. Very approximately one can present it as the sum of all ER's around all already existing droplets,

$$W_{\text{exh}} \approx \sum_i V_{\text{eff}}$$

(the sum is taken over all already formed droplets). Certainly, the last approximation is rigorous only when there is no overlap of the ER's around different droplets.

Having used the expression for V_{eff} one arrives at

$$W_{\text{exh}} = \int_0^t dt'\langle I\rangle(t')\frac{32}{3}\pi\beta_{\text{eff}}^3 D^{3/2}(t-t')^{3/2}. \qquad (11)$$

After using the expression for $\langle I\rangle$ one comes to the closed system of nucleation kinetics equations

$$W_{\text{free}} = W_{\text{tot}} - \int_0^t dt'\frac{\eta}{\eta_{\text{tot}}}\frac{W_{\text{free}}}{W_{\text{tot}}}I_0\frac{32}{3}\pi\beta_{\text{eff}}^3 D^{3/2}(t-t')^{3/2},$$

$$\eta = \eta_{\text{tot}}\exp\left(-\int_0^t \frac{W_{\text{free}}(t')}{W_{\text{tot}}}\frac{I_0}{\eta_{\text{tot}}}dt'\right) \equiv \hat{H}(W_{\text{free}}). \qquad (12)$$

Now we have to introduce the quasihomogeneous limit. When there is no essential exhaustion of the heterogeneous centers a balance equation for them is not necessary. Only the balance equation for the substance molecules has to be considered. Equation (12) has the same form as in the homogeneous case (after some proper renormalizations). That is why we shall call it the quasihomogeneous equation.

In the quasihomogeneous limit this system can be reduced to

$$W_{\text{free}} = W_{\text{tot}} - \int_0^t dt'\frac{W_{\text{free}}}{W_{\text{tot}}}I_0\frac{32}{3}\pi\beta_{\text{eff}}^3 D^{3/2}(t-t')^{3/2},$$

which can be rewritten after the obvious renormalization $t \to at$, $t' \to at'$ where $a = (I_0\frac{32}{3}\pi\beta_{\text{eff}}^3 D^{3/2})^{2/5}$ in the universal form

$$W_{\text{free}} = 1 - \int_0^t dt'(t-t')^{3/2}W_{\text{free}}.$$

One should note that in the general case the system of nucleation equations can be solved with the help of methods presented in [13]. First one can solve the quasihomogeneous equation (it is a Volterra equation[21] with a rather simple kernel which allows one to apply the Laplace transformation to solve it), and then on the base of the quasihomogeneous equation one can find the final rather precise expression using Eq. (10) as the formula for η.

Another variant is to solve numerically the universal equation for $W_{\text{free hom}}$:

$$W_{\text{free hom}} = 1 - \int_0^t dt'(t-t')^{3/2}W_{\text{free hom}}.$$

As a result one has the universal function $W_{\text{free hom}}$. Then one can find η as

$$\eta = \eta_{\text{tot}}\exp\left(-a^{-1}\int_0^t \frac{W_{\text{free hom}}(t')}{W_{\text{tot}}}\frac{I_0}{\eta_{\text{tot}}}dt'\right).$$

The last expression leads to the formula for $\langle I\rangle$:

$$\langle I\rangle = \frac{W_{\text{free hom}}}{W_{\text{tot}}}\exp\left(-a^{-1}\int_0^t \frac{W_{\text{free hom}}(t')}{W_{\text{tot}}}\frac{I_0}{\eta_{\text{tot}}}dt'I_0\right).$$

The justification for such an approach is analogous to [13]. The physical reason is very simple: when there is no exhaustion of heterogeneous centers then the solution is found precisely; when there is an essential exhaustion of centers there is no need to know W_{free} with high precision because the converging force of $\hat{H}$ is extremely high.

Now we shall take into account the effect of overlapping. This can be done rather approximately.

B. The model with chaotic overlap

The matter under discussion is the correct expression for W_{free}, which cannot be found absolutely precisely. Now a reasonable expression for W_{free} will be presented. Certainly, this will lead to a more complex equation, which will be more difficult to solve.

One can use the differential approach to write the expression for W_{free}. Having written the obvious relation

$$\frac{dW_{\text{free}}}{dt} = -\frac{dW_{\text{exh}}}{dt},$$

one has to invent an approximation for dW_{exh}/dt. Here the approximation

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[21]The nonlinear generalization.

$$\frac{dW_{\text{exh}}}{dt} \approx \frac{d\Sigma_i V_{\text{eff}}}{dt} \frac{W_{\text{free}}}{W_{\text{tot}}}$$

will be used (the sum is taken over all droplets). It corresponds to the following approach: The probability of the absence of overlap of the new parts of the ER around a given droplet with other ER's is proportional to the free volume of the system. This supposition seems to be rather reasonable.

The value $d\Sigma_i V_{\text{eff}}/dt$ can be rewritten as

$$\frac{d\Sigma_i V_{\text{eff}}}{dt} = \sum_i \frac{dV_{\text{eff}}}{dt}.$$

This can be easily expressed through $\langle I \rangle$ as

$$\sum_i \frac{dV_{\text{eff}}}{dt} = \frac{3}{2} \int_0^t dt' \langle I \rangle(t') \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t-t')^{1/2} \tag{13}$$

due to Eq. (11). Then

$$\frac{dW_{\text{exh}}}{dt} = \frac{3}{2} \int_0^t \langle I \rangle(t') \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t-t')^{1/2} dt' W_{\text{free}}(t)$$

and

$$\frac{dW_{\text{free}}}{dt} = -\frac{3}{2} \int_0^t \langle I \rangle(t') \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t-t')^{1/2} dt' W_{\text{free}}(t).$$

Having used an expression for $\langle I \rangle$ one arrives at

$$\frac{dW_{\text{free}}}{dt} = -\frac{3}{2} \int_0^t \frac{W_{\text{free}}}{W_{\text{tot}}} I_0 \frac{\eta}{\eta_{\text{tot}}} \frac{32}{3}$$
$$\times \pi \beta_{\text{eff}}^3 D^{3/2} (t-t')^{1/2} dt' W_{\text{free}}(t).$$

Together with Eq. (12) the last equation forms the closed system of nucleation equations in the second model.

The previous equation can be integrated, which gives

$$\ln W_{\text{free}} = -\int_0^t \frac{W_{\text{free}}(t')}{W_{\text{tot}}} I_0 \frac{\eta(t')}{\eta_{\text{tot}}} \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t-t')^{3/2} dt'$$
$$+ \text{const}.$$

Because of the initial conditions the value of the constant is equal to zero. Having introduced the function $F = -\ln W_{\text{free}}$, one can get for F, η the following system of equations:

$$F(t) = \int_0^t \exp[-F(t')] I_0 \frac{\eta(t')}{\eta_{\text{tot}}} \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t-t')^{3/2} dt',$$

$$\eta = \eta_{\text{tot}} \exp\left(-\int_0^t \exp[-F(t')] \frac{I_0}{\eta_{\text{tot}}} dt'\right).$$

One can see that the system of condensation equations is identical to the system of condensation equations in the AA. It was completely analyzed in [13]. Certainly, the parameters in the system will be different.

The last system can be rewritten after the obvious renormalization as

$$F(t) = \int_0^t \exp[-F(t')](t-t')^{3/2} \theta(t') dt' \equiv \hat{F}(F, \theta),$$

$$\theta(t) = \exp\left(-A \int_0^t \exp[-F(t')] dt'\right) \equiv \hat{\theta}(F),$$

where $\theta(t) = \eta(t)/\eta_{\text{tot}}$ and A is some known parameter. This system can be solved by iterations defined as

$$F_{i+1} = \hat{F}(F_i, \theta_i),$$

$$\theta_{i+1} = \hat{\theta}(F_i)$$

with $F_0 = 0, \theta_0 = 1$. For F_i, θ_i one can get the chains of inequalities

$$F_0 < F_2 \cdots < F_{2i} < \cdots < F < \cdots < F_{2i+1} < \cdots < F_3 < F_1,$$

$$\theta_1 < \theta_3 < \cdots < \theta_{2i+1} < \cdots < \theta < \cdots < \theta_{2i} < \cdots < \theta_2 < \theta_0.$$

Thus one can estimate errors in F_i and θ_i.

One can also use other methods analogous to those described in [13].

The similarity of the condensation equations in the AA and in the second model is extremely important for the transition toward the collective character of vapor consumption, which is analyzed in [13]. The physical reason for the considered model is the chaotic overlap of ER's that is, the chaotic overlap lies at the base of the approximation used here. But due to the spherical form of every ER the overlap is not absolutely chaotic. What can be done in such a situation? In the next model we shall show that the actual type of overlap is not very important.

To finish with the second model we shall show the same method of its solution as for the first model. One can also formulate the quasihomogeneous equation as

$$F_{\text{hom}}(t) = \int_0^t \exp[-F_{\text{hom}}(t')] I_0 \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t-t')^{3/2} dt'.$$

Then η can be approximately found as

$$\eta = \eta_{\text{tot}} \exp\left(-\int_0^t \exp[-F_{\text{hom}}(t')] \frac{I_0}{\eta_{\text{tot}}} dt'\right).$$

The quasihomogeneous equation can be renormalized. After the renormalization $z \to at, t' \to at'$ where

$$a = \left(I_0 \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2}\right)^{2/5}$$

one can transform the quasihomogeneous equation into the universal form

$$\ln W_{\text{free hom}}(t) = -\int_0^t W_{\text{free hom}}(t')(t-t')^{3/2} dt'.$$

C. The model with formation of droplets inside the ER

The third model will show that the role of the overlap is not so essential as might be imagined initially. Suppose that new droplets can also appear in the ER of the already existing droplets. Then instead of Eq. (13) one has to use

$$\sum_i \frac{dV_{\text{eff}}}{dt} = \frac{3}{2} \int_0^t dt' I_0 \frac{\eta(t')}{\eta_{\text{tot}}} \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2}(t-t')^{1/2}.$$

Then

$$\frac{dW_{\text{exh}}}{dt} = \frac{3}{2} \int_0^t \frac{\eta(t')}{\eta_{\text{tot}}} I_0 \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2}(t-t')^{1/2} dt' W_{\text{free}}(t)$$

and

$$\frac{dW_{\text{free}}}{dt} = -\frac{3}{2} \int_0^t I_0 \frac{\eta(t')}{\eta_{\text{tot}}} \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2}(t-t')^{1/2} dt' W_{\text{free}}(t).$$

Together with Eq. (12) the last equation forms the closed system of nucleation equations in the third model.

The material balance equation of the system can be integrated to give

$$\ln W_{\text{free}} = -\int_0^t I_0 \frac{\eta(t')}{\eta_{\text{tot}}} \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2}(t-t')^{3/2} dt' + \text{const.}$$

From the initial conditions the constant in the last equation is equal to zero. Having introduced the function $F = -\ln W_{\text{free}}$ one can get for F, η the following system of equations:

$$F(t) = \int_0^t I_0 \frac{\eta(t')}{\eta_{\text{tot}}} \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2}(t-t')^{3/2} dt',$$

$$\eta = \eta_{\text{tot}} \exp\left(-\int_0^t \exp[-F(t')] \frac{I_0}{\eta_{\text{tot}}} dt'\right).$$

This system corresponds to the first iteration in the solution of the second model by the method of iterations described in [13]. These iterations are also mentioned above. For η the whole set of iterations has been taken (see details in [13]).

One can slightly modify the model and suppose that in the expression for η one can use the same approximation for $\langle I \rangle$ as in the equation for W_{free}. Then the last system of equations will precisely correspond to the first iteration in the iteration solution. One need not analyze these models in detail following [13] but just note that all these solutions are very similar.

Now one has to explain why the third model is rather accurate. One can do it only with the help of results obtained in [16]. There was noted that when the power of the kernel $(t-t')$ is rather large the solution of the quasihomogeneous equation depends weakly on the actual value of the power. It is also important that when the power of $(t-t')$ is extremely high the ER of the given (first) droplet formed inside the ER of another (second) droplet cannot go outside the ER of that (second) droplet. The third model is absolutely adequate in this situation. The same feature can be seen directly from the results of the iteration procedure. Combining these two results, one can see that the second model is close to the first iteration (i.e., to the modified third model) in the situation with large power in the kernel where the third model is suitable.

Now it is possible to explain why the overlap is not so important as might be imagined. Since the power of the kernel is large and one can observe avalanche consumption of the vapor phase, one can see the following qualitative picture. (1) During the whole period of nucleation the total ER is small and there is no problem of overlap. (2) At the end of the nucleation period the total ER will occupy the essential part of the volume and a few moments later it occupies all the volume of the system. This process is rather rapid. It stops the nucleation. This picture shows that there is no strong influence of the overlap on the nucleation process (except for the final moments of the nucleation period). But in the final moments only a few droplets can be formed, so it is not very important to know the overlap in the final moments of the nucleation period.

The nucleation description is now complete. One can use both the second and the third models to get the nucleation description. How to solve these equations is also described here. Now we can turn our attention to a more accurate method which does not give an analytical expression for the size distribution of droplets but gives more precise universal results for all essential characteristics of the nucleation period.

D. The universal solution

The main idea of the theory presented in [13] was to consider the quasihomogeneous equation, to get a universal solution, and then on the basis of this solution to calculate the number of free heterogeneous centers. As a result one can get an expression for $\langle I \rangle$ and can calculate the total number of droplets appearing during the nucleation process.

Here we follow the same idea, but develop it further. It is not necessary to formulate the universal quasihomogeneous equation. Instead of the universal equation one can formulate a universal model.

The model will be the following.

(i) The rate of nucleation $\langle I \rangle$ can be found from

$$\langle I \rangle = I_0 \frac{W_{\text{free}}}{W_{\text{tot}}} \frac{\eta}{\eta_{\text{tot}}}.$$

(ii) With intensity I_0 the droplet appears at an arbitrary point of the system.

(iii) The value W_{free} can be found by exclusion of all ER's around the already existing droplets.

(iv) If the point is occupied by the ER of any droplet then the new droplet cannot be formed.

(v) The size r_{eff} of the ER grows in time according to

$$r_{\text{eff}} = 2\beta_{\text{eff}} D^{1/2} t^{1/2}.$$

(vi) The initial conditions are the absence of droplets and the random distribution of centers.

With the proper renormalization of time t and size r one can cancel all coefficients. Then this process will be a universal one and as a result the value of W_{free} is a universal function of time. Then one can directly apply Eq. (12) and get the number of free heterogeneous centers (after the proper renormalization).[22] This number is the main result of the approximate separation principle. All other quasi-integrals of the further evolution can be obtained in the same manner.

The modification for dynamic conditions [13] requires using instead of I_0 the value $I_0 \exp(ct)$ with some parameter c determined by external conditions and changing the lower limit 0 of integration to $-\infty$ [13]. The main constructions of the theory will be exactly the same but the forms of the characteristic curves will be radically changed.

IV. NUMERICAL RESULTS

Numerical simulation plays at least two important roles here. The first is the standard comparison with the approximate models to observe their quality. The second is more specific and is concerned with some universal dependencies in the nucleation kinetics.

In the additive approach to the nucleation kinetics it was shown that an adequate approach can be presented on the basis of the quasihomogeneous solution [13]. Despite the dynamic conditions considered in [13] this is true in the situation of metastable phase decay also. Recall the reasons for such an approach. The formal reason is the careful analysis of the iteration procedure proposed in [13]. The final result for the total number of droplets appearing in the nucleation process is given by the second iteration (see the iterations of type a in [13]) for the relative number of free heterogeneous centers. This iteration is based only on the first iteration for the supersaturation. There the value of the supersaturation is calculated without taking account of the heterogeneous centers' exhaustion. So one can see that the final result can be obtained on the basis of supersaturation in the quasihomogeneous approximation. This approximation can be more sophisticated than the first iteration, that is, it was used in [13] where the precise quasihomogeneous universal solution was chosen as the basis for the final results.

The physical reason for such behavior is rather simple. The main role in vapor consumption is played by droplets of relatively large sizes. We have already remarked on this fact. Moreover, due to the avalanche character of the vapor consumption the main role is played by the relatively large droplets that are formed in the first moments of time of the nucleation period. When the effect of center exhaustion is already essential in the first moments of the nucleation period[23] then at the end of the nucleation period all centers will already be exhausted. The result is evident—all centers will be the centers of droplets. Because of the high force of convergence in this situation this result can be obtained without any precise information about the behavior of supersaturation (even including the quasihomogeneous case). In the opposite case when the exhaustion of heterogeneous centers during the first moments of the nucleation period is not essential one can use the quasihomogeneous behavior of supersaturation.

This property can be viewed as an approximate separation of the heterogeneous and homogeneous problems. It is based only on the avalanche consumption of the metastable phase. So there are no objections to seeing this effect also with the density profiles considered here. Thus it is rather important to get the solution in the quasihomogeneous situation and to clarify whether it can be presented in a universal form.

The universal form of the quasihomogeneous solution can be easily seen in the situation with density profiles also. In the AA there was no specific space scale because the consumption took place homogeneously at all space points of the system. Here in the situation with density profiles there is an elementary space scale and one can choose the space scale to ensure that the linear size of the ER around the droplet is growing[24] as $t^{1/2}$ without any additional coefficients. The time scale has to be chosen so that in the initial free volume (equal to the total volume of the system) one can see the appearance of one droplet in the unit of time. Since the functional dependencies of the nucleation rate and of the radius of the ER on the time and on the space variables are not identical one can make such a renormalization without any problems. Thus we see that here the pseudohomogeneous case allows a universal description.

The process of exhaustion of the heterogeneous centers destroys this universality and one has to act as in [13].[25] The total number of droplets has to be approximately calculated as

$$N_{total} = \eta_{tot}\left[1 - \exp\left(-\frac{N_{hom}}{\eta_{tot}}\right)\right], \qquad (14)$$

where N_{hom} is the number of droplets appearing in the quasihomogeneous situation (with the same parameters). This formula can also be used for all approximate models described earlier.

For the numerical simulation it was convenient to consider a cubic box of side 10 units. The rate of ER growth is chosen as

$$\frac{dR}{dt} = 100t^{1/2}$$

where R is the radius of the ER. The rate of nucleation is chosen to have one attempt at new droplet formation in the system during $dt = 0.002$. The spatial position of this attempt is determined by a random procedure. It may lead to a position in one of the ER's and then no droplet will be formed. In

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[22]This will complete the quasihomogeneous approach method.

[23]More precisely one can define these ''first moments of time'' as 2/5 of the nucleation period duration (under the free molecule regime it is 1/4 of the nucleation period duration). The reason for such concrete values can be seen from the iteration procedure.

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[24]Certainly the power has to be conserved.

[25]Here we use a slightly simpler and more approximate method.

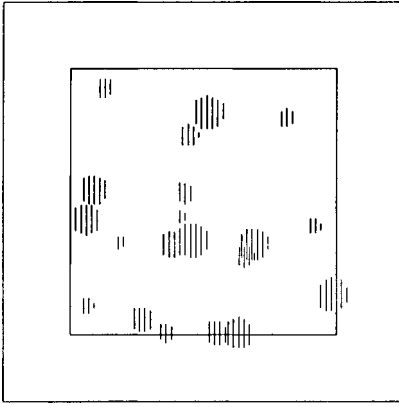FIG. 2. The cross section of the system at $t=0.5$ for the quasihomogeneous situation.

FIG. 3. The cross section of the system at $t=1$ for the quasihomogeneous situation.

the opposite situation when the point indicated is outside the ER's of all droplets already existing there will be formation of a new droplet.

One has to stress that the random procedure ordinarily used in computer simulations has one specific negative feature. In the standard numerical procedures the next random coordinate is calculated on the basis of the previous ones. So if the current coordinate lies near the center of an already existing ER then the next coordinate will also be near the center of another ER. These correlations lead to the necessity to consider a large system. In the system under consideration the number of droplets appearing in the quasihomogeneous situation will be near 500. Nevertheless the mean square fluctuation will be about 20.

The correlations mentioned are not the only source of fluctuations.[26] Careful consideration shows that the error introduced by the substitution of zero boundary conditions for periodic ones has the same power as the mean square error. This can be seen directly by numerical simulation. It is explained by the obvious fact that the characteristic overlap of profiles is about the mean profile size. We shall call this feature the property of ''moderate overlap.'' This fact can be proved analytically.

The mean value of the total droplet number is equal to 504.8 (under zero boundary conditions). This value has to be put into the previous formula.

The avalanche character of vapor consumption is illustrated by Figs. 2–4. Three different moments of time t $=0.5$, 1, and 1.5 are chosen as characteristic values. The space cross section of the system is drawn. The dashed regions correspond to the ER's of the droplets already existing. The black regions correspond to the overlap of ER's.[27]

Now the effects of exhaustion of the heterogeneous centers will be considered. The number of heterogeneous centers in this system is arbitrary. Certainly the effects of their exhaustion will be important when the number of centers is

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[26]To prevent these correlations one has to use some special random procedures.

[27]For technical reasons, this occurs only when the distance between the neighboring centers is odd.
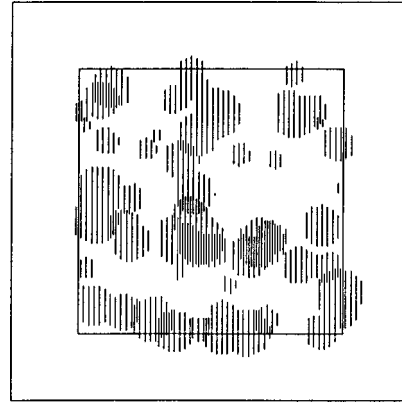
small (in comparison with $N_{hom}=504.8$). Pictures for η_{tot} $=50$ are drawn in Figs. 5–7 for $t=1.5$, 3, and 6. One can see that the number of ER's is smaller than in the quasihomogeneous case. The size of the ER's when the free volume is almost exhausted is larger than in the quasihomogeneous case. The time necessary to cover the whole volume with ER's is greater than in the quasihomogeneous case. This does not mean that the duration of the nucleation period is longer (simply, all centers will be exhausted and this means the end of nucleation). Moreover, the duration of the nucleation period in the situation with a relatively small number of heterogeneous centers will be shorter than in the quasihomogeneous case.

One can also see that the avalanche character of the vapor consumption in the whole system (not by a solitary droplet) here will be smoother than in the quasihomogeneous case. Certainly, in the quasihomogeneous case the appearance of some new ER's helps to consume the vapor phase in the avalanche manner. But in the situation with a small number of centers there is no need to consider the process carefully because the exhaustion of centers leads to the obvious result of condensation—the number of droplets equals the number of centers.

It is evident that the main object of our interest will be the quasihomogeneous case. The relative rate of nucleation in this case is shown in Fig. 8. Here the rate of nucleation is averaged over $100dt\equiv0.2$ and over 16 attempts. So the rate of nucleation here is a rather smooth function.

The relative rate of nucleation is compared in Fig. 8 with the models described above. The rate of nucleation defines the spectrum of sizes when the role of the size of the embryo is played by some characteristic that has a rate of growth independent of the size. For the diffusion regime this characteristic is the number of molecules to the power $\frac{2}{3}$.

One can see in Fig. 8 three different curves and some solitary points. The solitary points correspond to the numerical simulation of the quasihomogeneous case and the three curves correspond to the three models in the quasihomogeneous case.

The shortest spectrum is for the first model. This line is doubled. This occurs because the ideal variant of the first model is also drawn. This ideal variant corresponds to
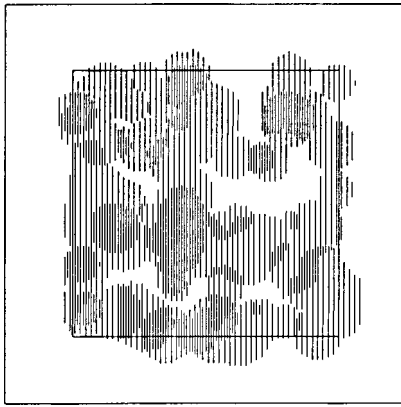
FIG. 4. The cross section of the system at $t=1.5$ for the quasi-homogeneous system.

FIG. 6. The cross section of the system at $t=3$ for $\eta_{tot}=50$.

$W_{free}/W_{total}\equiv 1$ in the subintegral function. The coincidence of the two lines means that the main role in the first model is played by the relatively large droplets that were formed at $W_{free}=W_{total}$.

The longest spectrum corresponds to the second model. This curve is very close to the intermediate curve which corresponds to the third model. The approximate coincidence of the second and third models shows that both of them are valid and the role of the relatively large droplets here is the main one. One also sees that even the first model is not too far from the real solution. This allows us to present rigorous estimates for the nucleation rate.

Now we going to present rigorous analytical estimates from below and from above for the evolution during the nucleation period. Certainly the first model is an estimate of the real process from below. It gives a number of droplets about 20% less than the numerical simulation. An estimate for the nucleation rate from above can be obtained in the following way. From the first model it follows that until $t=0.52$ (this case is essentially drawn in Fig. 2) the rate of nucleation is near the ideal value and the deviation is less than 15%. So one can say that the period $0<t<0.52$ corresponds to the absence of overlap (the first model is the estimate from above). Thus one can consider the process where the total volume is exhausted only by the ER's of the droplets appearing at $0<t<0.52$ in a random manner. The distri-
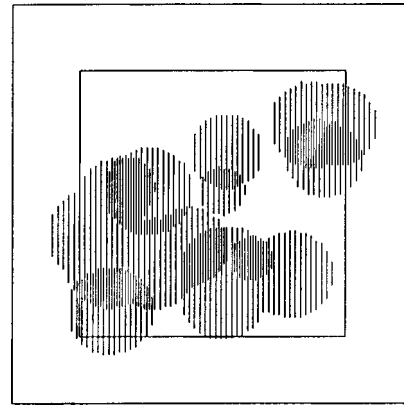
bution of the centers of the ER's of such droplets is also random. This model certainly gives an estimate from above for the nucleation process. A simple calculation shows that the total number of droplets is only 25% greater than the result of the estimate from above. As a conclusion one can state that two suitable estimates from below and above are obtained.

The proximity of the last estimate to the real solution justifies the supposition that the main role in vapor consumption belongs to the droplets of relatively large sizes appearing when the system is essentially free of ER's. This supposition can also be justified in an analytical manner.

One can see that the second and third models are rather close to the real solution but do not coincide with it. There are at least two reasons for the deviation. The first is the presence of strong correlations in a real system—if two ER's overlap in some moment of time then the power of the overlap can only grow in time. It does not have a random character as stated in the second and third models.

This effect can be taken into account in a rather simple manner. It is sufficient to consider two spheres and calculate the power of the overlap as a function of distance and time (it is a simple geometrical problem). Unfortunately the answer can be written only in a very complicated form. If we have two ER's with radii R_1 and R_2 with a distance l between their centers and $l>\max(R_1,R_2)$, then the volume of overlap is
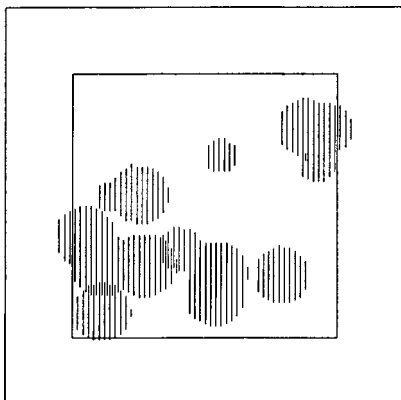

FIG. 5. The cross section of the system at $t=1.5$ for $\eta_{tot}=50$.

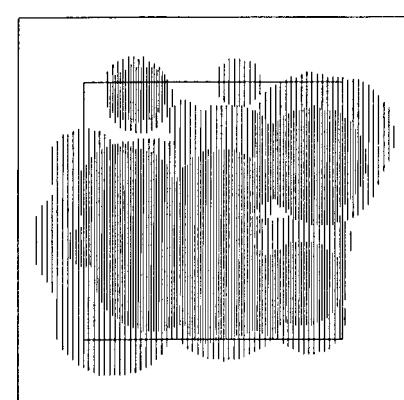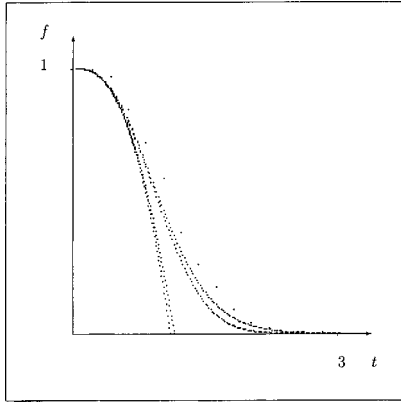FIG. 7. The cross section of the system at $t=6$ for $\eta_{tot}=50$.

FIG. 8. Comparison of different models in the quasihomogeneous situation.

$$V_{over} = \frac{2\pi R_1^3}{3}(1 - 2\cos\varphi_1 + \cos^3\varphi_1)$$

$$+ \frac{2\pi R_2^3}{3}(1 - 2\cos\varphi_2 + \cos^3\varphi_2),$$

where

$$\cos\varphi_1 = \frac{-R_2^2 + R_1^2 + l^2}{2R_1 l},$$

$$\cos\varphi_2 = \frac{-R_1^2 + R_2^2 + l^2}{2R_2 l}.$$

Certainly, this result cannot lead to a simple form of the balance equation. It will be difficult to solve it analytically.

The second reason for the deviation is the moderate overlap problem. This property means that actually there is an interaction through overlapping in an ensemble of several droplets. Earlier this property was extracted [18] in terms of a special effective length of the ER. Now we see that this property is rather general. The way to solve this problem proposed in [18] is very complicated and leads to some uncertain relations.
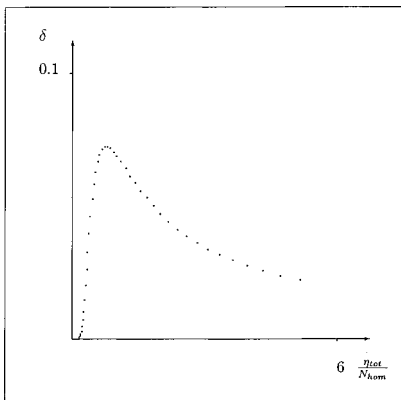

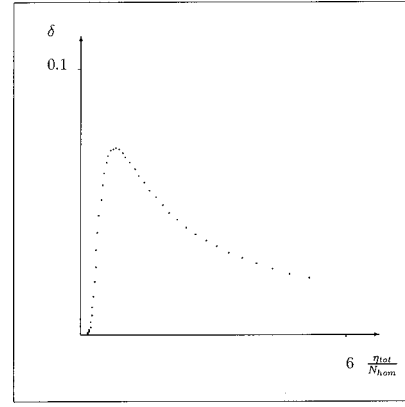FIG. 9. Relative error of the quasihomogeneous approach in the first model.

FIG. 10. Relative error of the quasihomogeneous approach in the second model.

How can one overcome all these problems? In fact, one has no need to do it analytically. A simple numerical simulation takes into account all these effects and gives a universal solution. Really we need only one number—the total number of droplets that have formed. This can be given by the numerical simulation. Then one can forget about all the mentioned difficulties.

Now one can analyze the heterogeneous case explicitly. A suitable approximation is given by Eq. (14). One has to substitute instead of N_{hom} the number of droplets given by the corresponding model.

The relative error of approximation (14) is drawn in Fig. 9 for the first model, in Fig. 10 for the second model, and in Fig. 11 for the third model. It is rather small for all models. For the third model it is practically negligible. This is because the third model is based on the approximation of chaotic overlap.

One can perform the same analysis for the numerical simulation. In Fig. 12 the relative error of (14) for numerical simulation is drawn. Here in Eq. (14) the value $N_{iom} = 504.8$ from the numerical simulation is used. The result is compared with a computer simulation of heterogeneous condensation. This simulation is rather simple. One can take the procedure for the quasihomogeneous case but place the center of the new droplet with probability η/η_{tot}. Every time this point is outside the ER we reduce η as $\eta \to \eta - 1$.

One can see that the relative error is very small. We do not use an average over many attempts (this is the reason why there is no smooth curve) to see that the error of Eq. (14) has the scale of the mean square error of the numerical simulation.[28] So there is no need to use a more sophisticated approach.

The solution of the problem is now completed. Generalization for conditions of dynamic type is absolutely analogous to [14]. The convergence due to avalanche consumption is weaker and one has to use instead of the approximation (14) a more sophisticated procedure described in [13]. The universal constants used in [13] have to be calculated by numerical simulation with the density profiles taken into account. Generalization to the arbitrary regime of droplet

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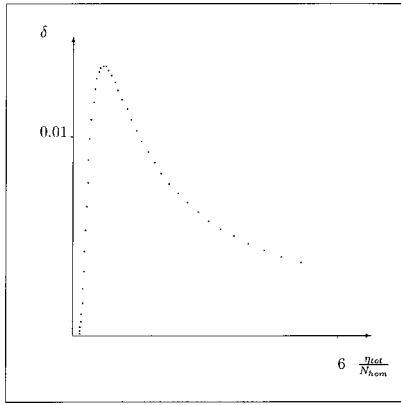[28]Here there is a system with 500 droplets.

FIG. 11. Relative error of the quasihomogeneous approach in the third model.
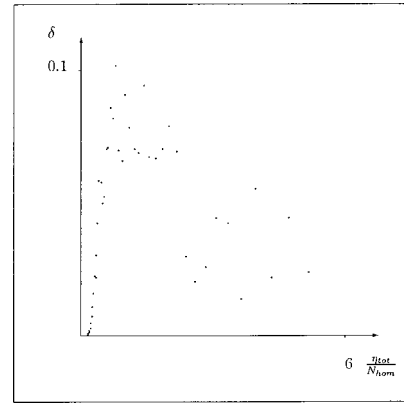

FIG. 12. Relative error of the quasihomogeneous approach in the universal simulation.

growth can be done as in [14]. The generalization is based on the similarity of the functional forms obtained here and in the AA. This similarity lies at the base of the universality property formulated in [16,18].

One can see that the theory of condensation with profiles taken into account presents a picture that is quite different from the AA. Nevertheless, in many situations the result of experiment coincides with the result of the AA. One has to explain this coincidence although it is a rather formal one. In any experiment it is more convenient to have a small system and to get many droplets. The rate of nucleation has to be taken as a rather high one. So the supersaturation is relatively high and the parameter σ^{-1} is not a real small parameter of the theory.[29] Thus as shown in [18] the AA gives the correct qualitative result despite the wrong basis of consideration. The reason lies in the fact that at small σ most of the material is in the tail of the profile. The tail of the profile is rather thin and can be taken into account by the AA. The correction term for the AA at small σ can also be found in [18].

An important feature to mention is the movement of the embryo boundaries. This problem has been widely discussed in the determination of the rate of regular growth for supercritical embryos. In different systems the effect of the boundary movement on the rate of growth is different. We note that in the theory presented here the rate of the embryo growth is an external value which is supposed to be known.[30]

Another problem is to take adequate account of the effect of boundary movement in the method of constructing the ER. If part of the volume is occupied by the liquid phase of the given embryo, one cannot use the Green function of an empty space in an absolutely precise manner. In the first part of this paper we already showed that the effect is small. Here we shall present abstract arguments for this conclusion.

To use the thermodynamic approach the initial power of the mother phase metastability has to be relatively small. Together with the Maxwell rule this leads to the following final result for the phase transition: Only a relatively small part of the system volume is occupied by the new phase. This is not in contradiction with the property that the whole volume is occupied by ER's. The final state of the system is an essentially saturated mother phase and a small volume (distributed over the whole system) occupied by a new phase. As a result one can see that the process of substance consumption (extraction) leads to saturation in a volume relatively large in comparison with the volume of the new embryo phase. The mother phase cannot be undersaturated (then the embryos would disappear). Since even the mother phase has to be spread over almost all the volume of the system, the mean distance between two neighboring embryos of the new phase is many times greater than the mean size of the embryo. Thus one can state that the embryo produces an effective perturbation over relatively large distances in comparison with the size of the embryo. To have an interruption (a relative interruption in comparison with the ideal nucleation rate) of the new phase formation, one needs a very small reduction of the power of metastability.[31] This reduction can be attained only at distances which are very large in comparison with the embryo linear size.[32] Thus one can use the point source approximation as was done in the first part of this paper and forget about the boundary movement.[33] The negligible character of the boundary movement is now proved for all possible systems.

The heat extraction and account of all other intensive parameters of the description can be performed as in [6].

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[29]It is not necessary for the consideration presented here, but it has to be small for a thermodynamic description of the critical embryo.

[30]It is really known for essentially all systems.

[31]The relative reduction has to be Γ^{-1} where $\Gamma \gg 1$ is the scale of the number of molecules in the critical embryo.

[32]Because the profile is sharper than in the stationary solution.

[33]The effect of the boundary movement on the embryo growth rate is taken into account as an external parameter.

[1] J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, New York, 1977).

[2] J. Lothe and G. M. Pound, J. Chem. Phys. **36**, 2082 (1962).

[3] C. F. Clement, Proc. R. Soc. London, Ser. A **398**, 307 (1985).

[4] D. R. Warren and J. H. Seinfeld, J. Colloid Interface Sci. **105**, 136 (1985).

[5] D. R. Warren and J. H. Seinfeld, Aerosol. Sci. Technol. **3**, 135 (1984).

[6] D. R. Warren and J. H. Seinfeld, Aerosol. Sci. Technol. **4**, 31 (1985).

[7] J. C. Barrett and T. J. Baldwin, J. Aerosol Sci. **31**, 633 (2000).

[8] J. C. Barrett, J. Aerosol Sci. **31**, 51 (2000).

[9] H. Reiss, J. Chem. Phys. **19**, 482 (1951).

[10] H. Wakeshima, J. Chem. Phys. **22**, 1614 (1954).

[11] R. B. Segal', Zh. Eksp. Teor. Fiz. **21**, 814 (1951).

[12] F. M. Kuni and A. P. Grinin, Kolloidn. Zh. **46**, 674 (1984).

[13] V. B. Kurasov, Phys. Rev. E **49**, 3948 (1994).

[14] V. B. Kurasov, Physica A **226**, 117 (1996).

[15] A. A. Melikhov, F. M. Kuni, and I. A. Smirnova, Vestn. Leningr. Univ., Ser. 4: Fiz., Khim. **2**, 13 (1986).

[16] V. B. Kurasov, *Universality in Kinetics of the First Order Phase Transitions* (Chemistry Research Institute of St. Petersburg University, St. Petersburg, Russia, 1997).

[17] N. A. Fucs, *Evaporation and Growth of Droplets in Gaseous Media* (Publishing House of Academy of Sciences, USSR, Moscow, 1958) (in Russian).

[18] V. B. Kurasov, *Development of the Universality Conception in the First Order Phase Transitions* (Chemistry Research Institute of St. Petersburg University, St. Petersburg, Russia, 1998).