Kinetics of nucleation with decreasing rate of growth

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HIGHLIGHTS

- Formation of embryos with the slow rate of growth is considered analytically.
- The form of spectrum of the embryos sizes is approximately derived.
- The property of effective size for embryos with the slow rate of growth is shown.
- The head and the asymptotic tail for the spectrum of the embryos sizes are determined.
- Two basic initial approximations of iteration procedure are presented.

ARTICLE INFO

ABSTRACT

Extension of analytical description of the stage of nucleation to the case of the slow growth rates of the embryos growth has been constructed. The metastable phase consumption by the already formed embryos affects the nucleation rate which leads to the non-linear evolution. The power exponentials which are smaller than that for the diffusion growth are chosen as the model laws of the embryos growth. All main characteristics of the nucleation period including the form of the embryos sizes spectrum are found. Analytical description of nucleation in the closed systems as well as in the open systems with the metastable phase influx is presented. It is shown that the relative errors of this description are small.

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1. Introduction

To see the real picture of the first order phase transition it is necessary to consider kinetics of this process. The most used physical model of the first order phase transition is the case of condensation of a supersaturated vapor into a state of liquid droplets. The classical theory of nucleation [1,2] describes the appearance of embryos in this case. This theory is the base of kinetics of phase transformation [3,4]. We shall borrow the terminology from this case. So, the supercritical embryos of a new phase are droplets, the mother phase is the vapor phase, etc. The rate of embryos appearance is supposed to be a known smooth function of metastability in the system. But the metastability is unknown function of time. To get this function one has to formulate the system of condensation equations and then to solve it. This is the goal of the investigation below for the decreasing rate of the embryos growth.

One of the main features which allowed to present the analytical constructions in Refs. [3,4] was a property of the avalanche consumption of a mother phase by droplets. This property means that the intensity of absorption of vapor by a droplet rapidly increases with the growth of the droplet size.

For example, in the free molecular regime of the substance consumption one can see that the absorption intensity W^+ is proportional to the surface area of a droplet, i.e. to a square of radius R. When an embryo grows in time t under the constant power of metastability then $W^+ \sim t^2$ and the number of molecules ν accumulated by a droplet grows proportionally to t^3. The big value of the power exponential 3 allows to use in Refs. [3,4] some iteration procedures.

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In the diffusion regime of growth $\nu \sim t^{3/2}$. This growth is not so rapid but is quite sufficient for the application of methods from Ref. [3]. But there one cannot use the mean-field approach which implies that the power of metastability is considered as a value averaged over the whole volume. One has to account in this case the positions of embryos [5]. Only the situation of the free molecular growth and the situation of the diffusion regime were described in theoretical models of the nucleation kinetics.

There exist enough situations in nature when the rate of the droplets growth decreases in time. Situation with the decreasing rate of growth takes place in the processes of cementation, structural transformations, morphological transitions, etc. In the wonderful pictures of agates and malachites one can see the patterns appear due to the decreasing rate of growth of every initial embryo (and the variation of external influence). The reaction of environment of a growing object (for example, reaction of a human body on tumor) leads to the decrease of the rate of growth of a new object.

We can turn our attention to the situation of standard nucleation. One can see that the nucleation on soluble nuclei in the general formulation with several saddle points and several channels of nucleation and some fast and flow components also can lead to effective deceleration of the embryos growth. Here the condensation of the fast component leads to exhaustion of this component and as a result to the decrease of the rate of growth of the embryos with dominating other components.

The universality of the size spectrums in the avalanche regimes of growth [4] leads to a certain monotony in the properties of materials formed in these regimes. The goal to get new properties justifies the analysis of nucleation with the decreasing rate of growth of embryos.

The standard iteration methods do not work in the situation of the decreasing rate of growth of the new phase embryos. This situation requires a special consideration which will be given below.

We shall consider two types of external conditions which are widely spread both in theoretical and practical investigations. The first type is a situation of decay which takes place in the closed systems. Metastability is created in the system very quickly and later there is no external influence. The evolution of metastability is fully determined later by the consumption of vapor by droplets.

The second type of external conditions are the dynamic conditions. The smooth behavior of external influence in time takes place here. It means that the power of metastability is created gradually in time. Without the embryos formation and growth the supersaturation would increase. One can also speak here about such generalization as an open system with the effective metastable phase influx (if there was no formation of embryos the supersaturation would grow in time).

Here one can see a competition between the action of external conditions and the consumption of metastability. Both the formation of droplets and the process of the droplets growth consume vapor with a growing intensity and metastability begins to fall. The process of nucleation stops and one can see the formed spectrum of the embryos sizes. The analytical theory for this type of external conditions will be also constructed.

Here we shall use the exponential powers for the law of the embryos growth. The application of exponential powers is explained by the absence of any dimensional parameter. The diffusion regime and the free molecular regime have also this form. Namely

$$\nu = t^\alpha \tag{1}$$

with a parameter α. Exponential powers are smaller than that for the diffusion growth. The dependencies with $0 < \alpha < 1$ will be referred as the slow rates of growth. We shall namely this case. Dependencies with $1 < \alpha < 3/2$ are considered by the same methods as $0 < \alpha < 1$.

On the base of $\nu = t^\alpha$ it is very easy to introduce $z = \nu^{1/\alpha}$ to measure the time as the size of an embryo born in some characteristic moment (ordinary initial moment) of time.

We investigate the case of the homogeneous phase transition. Transition from the homogeneous case to the heterogeneous case can be investigated analogously to Ref. [3]. In Ref. [3] it is shown that the homogeneous case can be effectively used as the base for consideration of the heterogeneous case. The same approach can be used here.

2. Evolution equations

Situation with the slow rate of growth is more complex than the avalanche consumption because here not only the droplets with relatively big sizes are the main consumers of vapor. Here all droplets take place in consumption of vapor. But here one can see a simplifying feature which states that now there is no necessity to consider the density profiles or profiles of the power of metastability [5,4]. The characteristic scale of the diffusion blurring is

$$R_{diff} \sim \sqrt{t - t'} \tag{2}$$

where t is the current moment of time, t' is the time of the substance consumption. This estimate goes from the expression for the Green function of the diffusion equation. The Green function is a Gaussian and in the argument of exponent there stands $R^2/(t - t')$. So, we come to some characteristic space size R_{diff} of diffusion blurring. The same is valid for the thermal blurring initiated by the thermal effects of nucleation. So, when $\alpha < 3/2$ the diffusion blurring makes the density profile more smooth. In the characteristic region of localization of the profile there will be many droplets and we come to the collective regime of vapor consumption (see Refs. [5,4]).

Procedure of derivation of the evolution equation is absolutely analogous to Ref. [3], one has only to substitute the power 3 or 3/2 by α. The statement about the leading role of the supercritical embryos in the substance balance used in Ref. [3] is

so strong, that it remains valid for $0 < \alpha < 3/2$ (one can simply write the analogous inequality for the arbitrary α and then it becomes clear that it is valid for all necessary values of α). The case $\alpha = 0$ can be investigated explicitly (due to simple conservation laws) without this assumption. This consideration will be done separately below.

The case $\alpha = 0$ has a simple physical sense. When $\alpha = 0$ in the system there appeared embryos with a fixed size which do not grow.

The statement about the applicability of the quasistationary approximation for the rate of nucleation (the rate of appearance of droplets) [3] can be also proven here. Both mentioned statements take place when $\alpha > 0$ in conditions of applicability of the macroscopic description of the critical embryo.

The power of metastability will be described by the value of the supersaturation

$$\zeta = (n - n_\infty)/n_\infty \tag{3}$$

where n is the molecular number density of the mother phase, n_∞ is the same value but for the phase equilibrium.

The evolution equation for the decay conditions can be written as

$$G(z) = A \int_0^z (z - x)^\alpha \exp(-G(x)) dx \tag{4}$$

with a positive parameter A. Here G is the scaled number of molecules in a liquid phase, z is the size of the droplet which was born at the very beginning of the nucleation process (the size means here the variable with the law of growth independent on the value of this variable). The rate of nucleation is proportional to the exponent of the free energy of the critical embryo. It is possible to prove [3] that the free energy of the critical embryo can be linearized on deviation of the supersaturation. This approximation is rather accurate [3]. Then the rate of nucleation is proportional to the relative deviation in the supersaturation. The relative deviation of the supersaturation is proportional to the number of molecules in a new phase. To cancel the coefficient of proportionality in the argument of exponent we measure G in a special scale. The derivation is absolutely analogous to Ref. [3] and it is skipped here over. The spectrum of the embryos sizes is

$$f \sim \exp(-G). \tag{5}$$

The value f is on one hand the spectrum of embryo sizes and on the other hand the stationary rate of nucleation. Really, it is so because the size z is equivalent to the time t and then the rate of nucleation and the height of the size spectrum are one and the same value. Namely this equivalence allows to close the system of condensation equations.

In the situation of dynamic conditions we can linearize the supersaturation in the absence of nucleation (i.e. the ideal supersaturation) as the function of time (or as the function of z) like it is done in Ref. [3]. The supersaturation in the absence of nucleation is simply the result of the external influence and the last notation means that we can linearize the external influence on the system during the period of intensive formation of embryos as a function of time. The possibility of such linearization is explained by the relative shortness of the period of intensive formation of embryos in comparison with other periods of the condensation process. In the situation of the slow growth the period of intensive formation of embryos will be longer than in the situation with the avalanche growth but the mentioned linearization is still possible. Then we come to

$$G = A \int_{-\infty}^z (z - x)^\alpha \exp(bx - G) dx \tag{6}$$

with the additional parameter b of the mentioned linearization. Here the spectrum of the embryos sizes is

$$f \sim \exp(bx - G). \tag{7}$$

In the derivation of these equations we have used the following approximation for the stationary rate of nucleation

$$f_s(\zeta) = f_s(\zeta_0) \exp(\Gamma(\zeta - \zeta_0)) \tag{8}$$

as a function of the supersaturation ζ where index 0 characterizes the base of decomposition. Here $-\Gamma$ is the derivative of the free energy of a critical embryo formation over ζ. One can show that Γ has the scale of the number of molecules in critical embryo. Instead of the classical theory of nucleation one can use here any other approach which ensures (8) with $\Gamma \gg 1$.

We need the validity of this approximation only at some relatively short range of supersaturation where $\exp(\Gamma(\zeta - \zeta_0))$ changes only e times. Certainly it takes place for the classical theory of nucleation.

The last equation takes place because the main dependence of the nucleation rate on supersaturation occurs through the dependence of the critical embryo free energy on the supersaturation and this dependence can be linearized.

3. Decay of metastable state

Eq. (4) after the evident scaling $z \to A^{1/(\alpha+1)}z$, $x \to A^{1/(\alpha+1)}x$ leads to

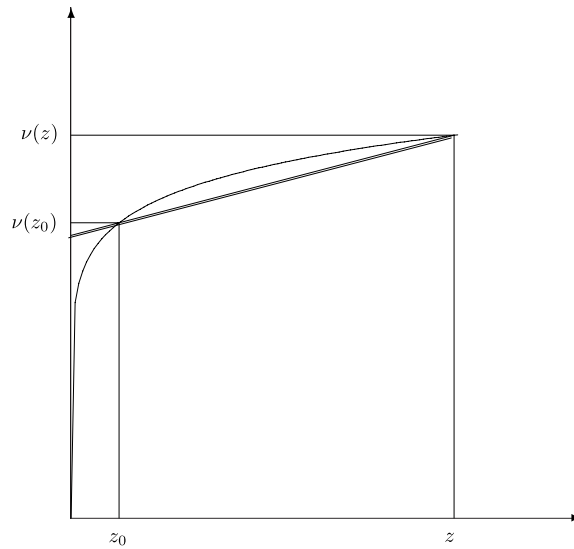$$G = \int_0^z (z - x)^\alpha \exp(-G) dx \tag{9}$$

Fig. 1. Linear approximation of the size of growth. As an example a power $\alpha = 1/8$ has been chosen. The bold line presents the approximation, the curved line is precise solution.

without parameters.[1] Then G is the universal function and the zero momentum $M_0 = \int_0^\infty \exp(-G(x))\,dx$ is the universal constant. Since M_0 is the coefficient in the asymptotically leading term $M_0 z^\alpha$ in the expression for G after the end of nucleation then the universal constant M_0 accumulates all information necessary for further evolution.

One can determine the duration of nucleation period δz by relation

$$N(\delta z) = N(\infty)(1 - \epsilon) \tag{10}$$

with some small parameter ϵ (here $N(z)$ is the number of droplets appeared before z). Since z is equivalent to the time it is possible to speak about the number of droplets appeared before z. More rigorously $N(z)$ is the number of droplets appeared before the moment of time when the size of the droplet appeared at the initial moment of time will attain the value of z.

The last equation is simply a definition of duration of the period of intensive nucleation. It is necessary to do artificially since the size spectrum has a small infinite tail, which is quite integrable.

Since the rate of nucleation decreases rather rapidly one can get for the reasonably small $\epsilon \approx 0.05 \div 0.1$ the characteristic value of δz which corresponds to the duration of the nucleation period. Since the rate of growth is known one can recalculate the value δz in the time of duration of the period of intensive nucleation. The value of the droplets number

$$N(z) \sim \int_0^z \exp(-G)\,dx \tag{11}$$

is also the universal function and δz as the root of equation with no parameters will be the universal constant.

Now we shall construct the form of the spectrum of embryos sizes explicitly. The iteration procedure analogous to Ref. [3] is not effective. To propose another iteration procedure we shall get an important property typical for the regime of the slow growth.

The property of the effective size of growth

The law of the vapor consumption by a separate droplet is shown in Fig. 1. For every moment z (or $t(z)$) we can find the boundary z_0 with two properties

- $z_0 \ll z$
- $\nu(z) - \nu(z_0) \ll \nu(z)$

One can see that for $z_0 = \alpha z/p$, $p \sim 2 \div 3$ both properties are satisfied.

It means that the qualitative picture is the following: rather soon a droplet accumulates the main quantity of vapor and later the further accumulation is not too important. Certainly, the moment z_0 of effective accumulation grows in time. There is no unique recipe to choose z_0, one can speak about the characteristic interval of possible values of z_0. Any choice from this interval is possible.

This picture allows to suggest the following initial approximation:

For every z one can imagine that practically immediately after creation of a droplet the number of molecules of a given droplet (with coordinate z) attains the value $\nu(z_0)$ and then the droplet does not grow rapidly.

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[1] Except α.

One has to stress that for different z the values z_0 are also different. But for some rather short time interval like the interval of time corresponding to the formation of the back side of the head of the spectrum of the droplets sizes one can speak about the characteristic constant z_0.

The mentioned property allows to use the approximation with $\alpha = 0$ as the initial approximation. The solution in this case has a simple explicit form.

One has to note that this property is no more than an approximation. But it is used here only as the initial step in the iteration procedure. Further steps will give better results.

To get an approximate but simple picture one can see the property of a real collective consumption of vapor:

Practically all droplets (except the small ones with the sizes less than z_0) consume vapor in approximately equal quantities.

This property is really the collective consumption of vapor. Earlier [5] this terminology was used simply for the vapor consumption in a fixed point by many droplets with different intensities of the vapor consumption. Now droplets consume vapor in equal quantities and we speak about the equal collective consumption.

The case $\alpha = 0$ can be solved analytically, because it can be reduced to the ordinary differential equation of the first order. This leads to

$$\exp(-G) = \frac{1}{1+z}. \tag{12}$$

The last equation leads to the infinite number of droplets appeared in the process of nucleation. We come to an error. This error is initiated by the use of approximation (8) which is valid only at the small supersaturations. Really, at $G = n - n_\infty$ the rate of nucleation has to be zero, but approximation (8) gives the finite value of the nucleation rate at any G.

We are not interested in the long tail $\sim z^{-1}$ of the spectrum of the embryo sizes because this tail cannot be directly seen in experiment. Integral values in this situation can be explicitly calculated without knowledge of the tail. Really, the total number of droplets can be easily obtained, it is convenient to get it even in initial variables by the following procedure:

The case $\alpha = 0$ corresponds to a fixed number v_{fin} of a number of molecules inside the droplet. This quantity does not depend on time (in the scaled units $v_{fin} = 1$). In this case some evolution occurs since here we introduce the quantity v_{fin} of the number of molecules. Certainly, this evolution is rather trivial.

The total number of droplets can be calculated very easy[2]

$$N_{total} = \frac{n - n_\infty}{v_{fin}}. \tag{13}$$

We can choose the cut-off of the spectrum of the embryos sizes at the size where $N(z) \sim \text{const} + \int^z (1+z)^{-1} dz$ equals to N_{total}.

Iteration procedure

One can see that even in the case of small positive α the spectrum of the embryos sizes is concentrated in the fixed region. This allows to use the iteration procedure

$$G_{i+1} = \int_0^z (z - x)^\alpha \exp(-G_i) dx. \tag{14}$$

Here the lower index denotes the number of iteration. As the initial approximation we choose the analytical solution for $\alpha = 0$, i.e.

$$G_0 = -\ln(x + 1). \tag{15}$$

This differs from consideration of the situations with the avalanche regimes of growth, where $G_0 = 0$.

This iteration procedure is simply postulated. One can easily prove that it converges to the real solution. The effectiveness of this procedure will be seen from our final results.

The first iteration can be easily calculated. We have

$$G_1 = \int_0^z (z - x)^\alpha \frac{1}{1 + x} dx \tag{16}$$

or

$$G_1 = -\frac{z^{\alpha+1}}{z+1} \Phi\left(-\frac{z}{z+1}, 1, \alpha + 1\right) \tag{17}$$

where

$$\Phi(z, s, v) = \sum_{k=0}^{\infty} \frac{z^k}{(v + k)^s} \tag{18}$$

is the standard special function.

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2 More accurate is to write $N_{total} v_{fin} = n - n_\infty + 2a/3 v_{fin}^{1/3}$ where a is renormalized surface tension.
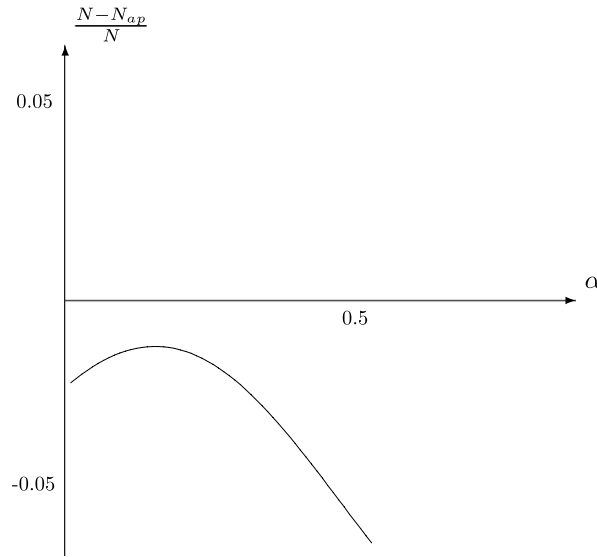
Fig. 2. Relative error in the total number of droplets as a function of α.

The spectrum of the embryos sizes $\exp(-G_1)$ can be considered as a good approximation. This property can be shown both analytically and numerically. The relative error in the number of droplets, i.e. in

$$N(z) = \int_0^z \exp(-G(x))\mathrm{d}x \qquad (19)$$

is less than 0.05 for $\alpha < 0.5$. The last integration can be fulfilled by means of the steepest descent method with a maximum at the boundary point.

The values α from $1/2$ up to $3/2$ can be considered analogously but on the base of iterations started from solution with $\alpha = 1$. This solution can be found analytically, since the evolution equation can be reduced to the automorphic second order ordinary differential equation. Then it is necessary to take one iteration step and then to integrate $\exp(-G_1)$ over time to get the number of droplets. The last integration can be fulfilled by means of the steepest descent method. Here one can make the explicit extraction of the rectangular zone for $\alpha > 1$.

Fig. 2 shows the relative error in the total number of droplets as a function of α. The integration is taken up to $z = 10$ which is absolutely sufficient for any case except $\alpha \approx 0$ and in the case $\alpha = 0$ the error is zero (certainly with the artificial cut-off which is necessary to have the finite values of characteristics). The deviation from zero at small α is initiated only by a finite step of integration. One can see that the relative error is rather small. This fact can be shown both numerically and analytically.

Fig. 3 shows the characteristic forms of the spectrum of the embryos sizes. Two cases are shown: $\alpha = 0.2$ and $\alpha = 1$. One can see two pairs of curves coinciding at the origin and coming close at big values of arguments. Every pair is the precise solution and the corresponding approximation. The case $\alpha = 1$ has the analytical solution, but one can see that even in this case our approximation works good. In this case the back side of the spectrum of the embryos sizes is more sharp than for $\alpha = 0.2$. One can also notice the relative insensibility of the form of the spectrum of the embryos sizes to concrete choice of α for small α. This feature is in the direct correspondence with the property of effective size of growth.

The process of the vapor consumption by all droplets leads to reconsideration of characteristic size of consumers in the statements about the quasi-stationarity of the nucleation rate and about the size of the main consumers of vapor [5]. But even with these modifications both statements can be proven (and in the dynamic conditions also) analytically.

4. Dynamic conditions

The simple scaling $z \to zA^{1/\alpha}, x \to xA^{1/\alpha}$ brings Eq. (6) to

$$G = \int_{-\infty}^z (z - x)^\alpha \exp(bx - G)\mathrm{d}x \qquad (20)$$

and allows to cancel parameter A. But it is not too simple to cancel parameter b because earlier [4] the condition, which allows to cancel this parameter was the following: The point of decompositions has to be chosen as the maximum of the supersaturation (or as the maximum of f).
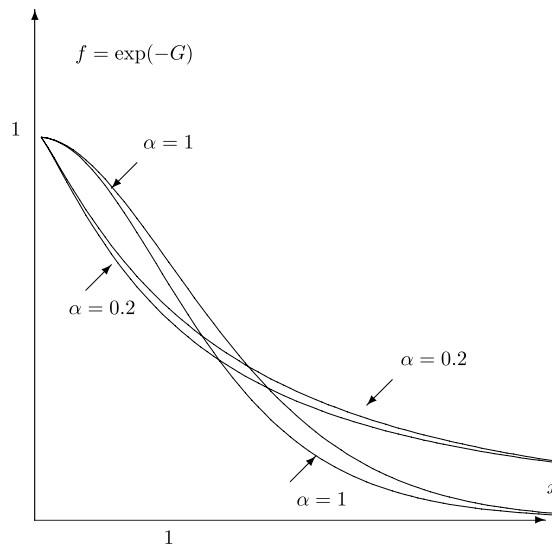
Fig. 3. Forms of the spectrum of the embryos sizes in the closed system. Examples of $\alpha = 0.2$ and $\alpha = 1$ are shown.

In situation with $\alpha = 0$ one cannot satisfy this condition. Moreover, the spectrum f increases in time. But in this case we can get the analytical solution. The analytical solution in the case $\alpha = 0$ is the following

$$f = \exp\left(bx - \ln\left(\frac{\exp(bx)}{b} + 1\right)\right) \equiv f_0. \tag{21}$$

This solution can be seen after differentiation of the evolution equation

$$\frac{dG}{dx} = \exp(bx - G(x)). \tag{22}$$

One can easily integrate this equation

$$\int \exp(G)dG = \int \exp(bx)dx \tag{23}$$

and come to (21).

One can formulate the alternative: When $\alpha > 0$ one can see the maximum of f and when $\alpha = 0$ the explicit analytical solution has been presented.

For $\alpha > 0$ one can put condition on the point of maximum. Then the standard way of derivation is possible. For $\alpha \neq 0$ we have the universal solution depended on α. This solution satisfy the following universal equation

$$-\ln(f) + \alpha \int_{-\infty}^{0} (z - x)^{\alpha-1} f(x) dxz = \int_{-\infty}^{z} (z - x)^{\alpha} f(x) dx. \tag{24}$$

The idea here is absolutely analogous to the already investigated situations [3].

Iteration steps

Now we shall present some methods to get the explicit form of the spectrum of the embryos sizes. The main feature which has to be taken into account is the long infinite tail of the spectrum of the embryos sizes for $\alpha = 0$. The explicit form in this case for $b \sim 1$ is drawn in Fig. 4. One can see that this curve is slightly blurred because here an approximation which will be discussed later is also drawn.

The most interesting region here is the region of the rapid increase of f. If we choose $b = 1$ we get this region at $x \sim 0$. We can see that it is reasonable to put $b \sim 1$ for all α.

One can note an important feature: "For $\alpha > 0$ the spectrum of the embryos sizes f lies lower than the spectrum f_0 in the case $\alpha = 0$". Having used the property of the effective size of growth one can come to conclusion that the maximum of f lies near $x = 0$ when $b = 1$. Then one can put $b = 1$ for all cases with the small values of α.

We shall use f_0 as the initial approximation in the following iteration procedure

$$G_{i+1}(z) = \int_{-\infty}^{z} (z - x)^{\alpha} \exp(bx - G_i(x)) dx \tag{25}$$
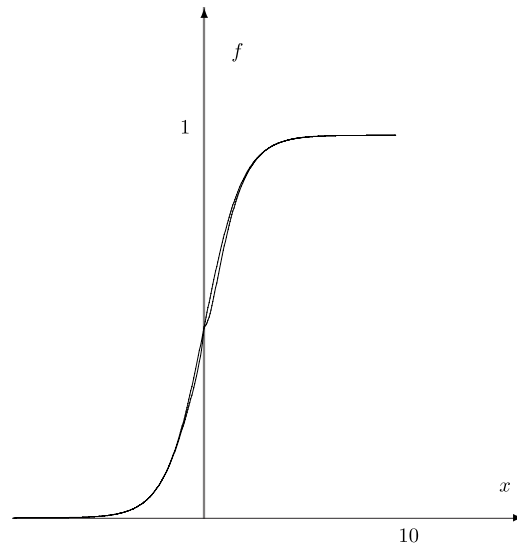
$$G_0 = -\ln(f_0) + bx. \tag{26}$$

Fig. 4. Forms of the spectrum of the embryos sizes and the corresponding approximation for $\alpha = 0$ (here $b = 1$).

The first iteration is

$$G_1(z) = \int_{-\infty}^{z} (z - x)^{\alpha} \left(\frac{\exp(bx)}{b} + 1 \right)^{-1} \exp(bx) dx. \tag{27}$$

To calculate G_1 one can act in two ways. The first way is to invent an approximation for $(z - x)^{\alpha}$. The behavior of this function is drawn in Fig. 1. We see that this function can be well approximated by a straight line as it is drawn in Fig. 1. This approximation allows the analytical calculation of G_1, since the integral can be reduced to

$$\int \frac{1}{(x + c_1)^2 - c_2} dx \tag{28}$$

and to

$$\int \frac{\ln(x + c_3)}{(x + c_4)^2 - c_5} dx = \frac{1}{2c_5} \arctan \left(\frac{c_5 x}{c_4^2 + c_5^2 + c_4 x} \right) \ln[(c_3 - c_4)^2 + c_5^2] - \frac{1}{2c_5} Cl_2(2\Theta + 2\Phi)$$

$$+ \frac{1}{2c_5} Cl_2(2\Theta_0 + 2\Phi) - \frac{1}{2c_5} Cl_2(\pi - 2\Theta) + \frac{1}{2c} Cl_2(\pi - 2\Theta_0). \tag{29}$$

Here

$$\tan \Theta = \frac{x + c_4}{c_5} \qquad \tan \Theta_0 = \frac{c_4}{c_5} \qquad \tan \Phi = \frac{c_3 - c_4}{c_5} \tag{30}$$

and

$$Cl_2(z) = - \int_0^z \ln \left(2 \sin \left(\frac{x}{2} \right) \right) dx \tag{31}$$

is the Clausen integral.

The second method which suggests an approximation for f_0 seems to be more attractive. This approximation is the following

$$f_0 \equiv \frac{1}{1 + \exp(-x)} \approx f_{ap} \tag{32}$$

where

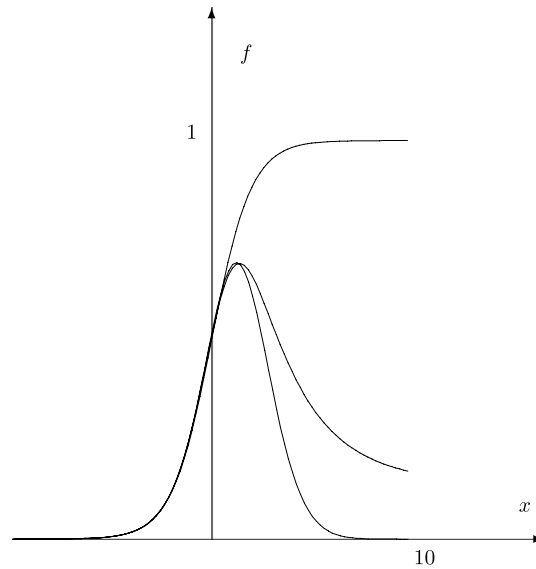$$f_{ap} = \exp(x) - \exp(2x) + \frac{1}{2} \exp(3x) \tag{33}$$

for $x < 0$ and

$$f_{ap} = 1 - \exp(-x) + \frac{1}{2} \exp(-2x) \tag{34}$$

for $x > 0$.

Fig. 5. Forms of the spectrum of the embryos sizes in the first iteration in dynamic conditions. The upper curve is the zero approximation f_0. The lower curve is the first iteration. Between these lines lies the real solution at $\alpha = 0.5$.

Namely this approximation together with the precise solution is drawn in Fig. 4. At $x = 0$ there is no difference between the precise result and the approximation. With the help of this approximation all integrals can be calculated in terms of Gamma-function.

When the first approximation G_1 is calculated we see that the function $f_1 = \exp(x - G_1)$ which is the spectrum of the embryos sizes in the first approximation has one maximum $f_{1\,max}$ at $x_{1\,max}$. In the region $x < x_{1\,max}$ this function approximates the spectrum of the embryos sizes with a high precision. We also have $x_{max} \approx x_{1\,max}$, where x_{max} is the coordinate of a real maximum and $f_{max} \approx f_{1\,max}$ where f_{max} is the amplitude of the spectrum of the embryos sizes. These facts can be proven analytically. The form of the spectrum of the embryos sizes for characteristic values of α is drawn in Fig. 5.

The spectrum of the embryos sizes in the first iteration rapidly turns to zero, but the precise spectrum of the embryos sizes has a very long tail. It is necessary to correct this discrepancy. When α is growing then $x_{1\,max}$ goes away from x_{max}; $f_{1\,max}$ goes away from f_{max} and $f_0(x_{1\,max})$ goes away from $f_{1\,max}$. But even when $\alpha = 0.5$ (this is the realistic boundary of our constructions because for $\alpha > 0.5$ one can use the decompositions starting from $\alpha = 1$) the difference between $f_0(x_{1\,max})$ and $f_{1\,max}$ is small. This allows to suggest the cut-off of the zero approximation $f_{0\,cut}$ which is

$$f_{0\,cut}(x) = f_0(x) \tag{35}$$

for $x < x_{1\,max}$ and

$$f_{0\,cut}(x) = f_0(x_{1\,max}) = f_{1\,max} \tag{36}$$

for $x > x_{1\,max}$.

On the base of this initial approximation one can reproduce all constructions and get the spectrum of embryos sizes $\hat{f}_1$ in the first approximation, which lies higher than the "previous first approximation". It is drawn in Fig. 6.

One can analytically show that the first advanced iteration describes the form of the hill satisfactory. But there remains the long tail and it is absolutely impossible to describe this tail on the base of the iteration method because the duration of this tail is very long. Then one can propose some asymptotic methods to solve this problem.

Asymptotics

We shall construct solution for $x \gg 1$. It is possible to write approximately the evolution equation as

$$G(z) = \int_0^z (z - x)^\alpha \exp(x - G(x)) dx \tag{37}$$

instead of

$$G(z) = \int_{-\infty}^z (z - x)^\alpha \exp(x - G(x)) dx. \tag{38}$$

Now we shall use the property of effective size of growth. Since the amplitude of the spectrum of the embryos sizes is not changed too quickly one can take the size $(z - x)^\alpha$ out of the integral and speak about the mean size $\bar{\rho}$ of $(z - x)^\alpha$. Then

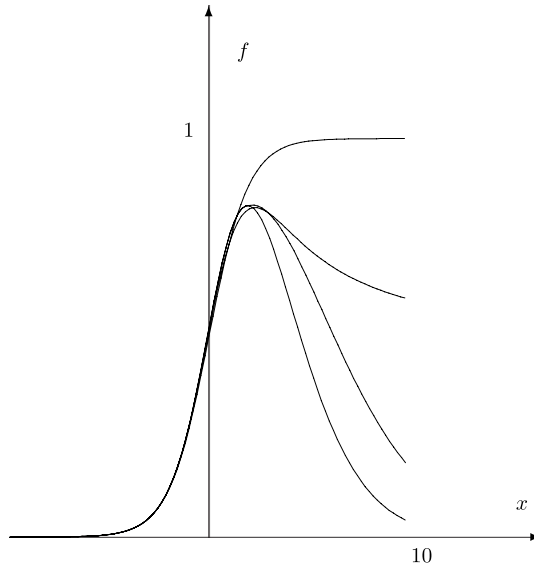$$G(z) = \bar{\rho} \int_0^z \exp(x - G(x)) dx. \tag{39}$$

Fig. 6. Forms of the spectrum of the embryos sizes in the first modified iteration at $\alpha = 0.2$. Here the upper curve is the zero approximation. The lower curve is the initial first iteration. Between these curves lie the modified first iteration and the precise solution. The modified first iteration lies between precise solution and the initial first iteration.

For $\bar{\rho}$ one gets the following expression

$$\bar{\rho} = \frac{\int_0^z (z-x)^\alpha dx}{\int_0^z dx} = \frac{z^\alpha}{\alpha+1} \approx z^\alpha. \tag{40}$$

Having differentiated G over z one has to notice that the introduced function $\bar{\rho} = z^\alpha$ is a slow function and there is no need to differentiate it. Then

$$\frac{dG}{dz} = z^\alpha \frac{d}{dz} \int_0^z \exp(x - G(x))dx = z^\alpha \exp(z - G(z)). \tag{41}$$

After the integration we come to

$$\int \exp(G)dG = \bar{\rho} \int \exp(x)dx + \text{const} \tag{42}$$

and

$$G = \ln(1 + \bar{\rho}\exp(z)). \tag{43}$$

This solution has an asymptotic

$$G \to \ln(\bar{\rho}) + z. \tag{44}$$

This asymptotic leads to the following expression for the spectrum of the embryos sizes

$$f \sim \exp(x - G) = \exp(z - \ln(\bar{\rho}) - z) = (\bar{\rho})^{-1} \tag{45}$$

and finally

$$f \sim \frac{1}{z^\alpha}. \tag{46}$$

Here one can introduce the arbitrary shift γ and the arbitrary amplitude β. Then

$$f \sim \frac{\beta}{(z-\gamma)^\alpha}. \tag{47}$$

These parameters can be determined by the requirement of the smoothness of the spectrum of the embryos sizes at the boundary between the advanced first iteration and the asymptotic. Now we shall choose this boundary.

At $z = 0$ the spectrum of the embryos sizes begins to grow, at $z = z_{\max}$ it attains maximum. It is reasonable to imagine the hill to be symmetric and to say that at $z = 2z_{\max}$ the hill is over. Namely at this point we can speak about the beginning of the asymptotic.
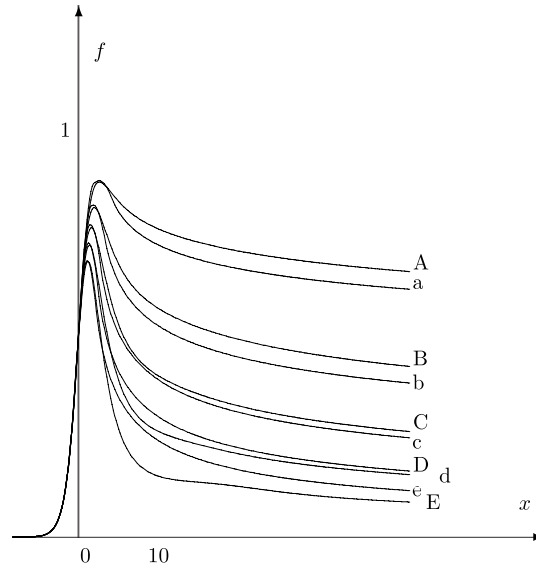
Fig. 7. Forms of the spectrum of the embryos sizes. The pair A, a corresponds to $\alpha = 0.1$. The pair B, b corresponds to $\alpha = 0.2$. The pair C, c corresponds to $\alpha = 0.3$. The pair D, d corresponds to $\alpha = 0.4$. The pair E, e corresponds to $\alpha = 0.5$.

Conditions

$$\frac{d\hat{f}_1}{dz} = -\alpha \frac{\beta}{(z - \gamma)^{\alpha+1}} \tag{48}$$

and

$$\hat{f}_1 = \frac{\beta}{(z - \gamma)^{\alpha}} \tag{49}$$

at $z = 2z_{\max}$ give the following expressions

$$\gamma = 2z_{\max} + \alpha\hat{f}_1(z_{\max})/(d\hat{f}_1/dz)|_{z=z_{\max}} \tag{50}$$

$$\beta = \hat{f}_1(z_{\max})(z - \gamma)^{\alpha}. \tag{51}$$

The characteristic forms of the spectrum of the embryos sizes and analytical approximations are drawn in Fig. 7. The letters A–E denote the pairs of curves corresponding to different α from 0.1 to 0.5 with a step 0.1. The capital letters mark the precise numerical solutions. They lie near approximate solutions (low-case letters).

The accuracy of the theory can be estimated by the error in the droplets number

$$\epsilon = \frac{|N - N_{ap}|}{N}. \tag{52}$$

Here N is the precise value found from the numerical solution and N_{ap} is the number of droplets found from the presented approximation.

In Fig. 8 the maximum of ϵ over z is drawn as a function of α. One can see that it is rather small. Here the maximal value of z is chosen to be 30.

Now we shall analyze the accuracy of calculations. In Fig. 9 the relative error for $N(z)$ at some final value is drawn. Certainly, the words "the final values" are illegal, because it is clear that for $\alpha < 1$ the finite number of droplets cannot satisfy the balance of substance. So, we need to throw away the tail, which is thin but still infinite (it contains infinite number of droplets).

In consideration of the extremely long asymptotic tails we have to take care about the accurate behavior of the asymptotic. The boundary between the iteration solution and the asymptotic solution will be put in a special point z_{bound}.

To get z_{bound} we shall fix the beginning of the nucleation process more precise. On the base of iterations we get $f_{\max}$. Then we get the value f_{st} of the amplitude at the beginning of nucleation as $f_{st} = f_{\max}/\exp(1)$. Then we can get the coordinate z_{st} of the beginning of the nucleation process as $z_{st} = \ln(f_{st})$. Then z_{bound} will be calculated according to the old recipe but with a new time of beginning of the nucleation process
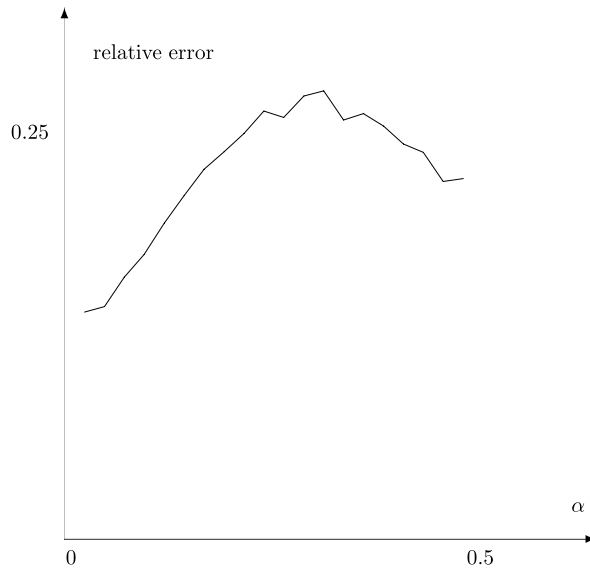
$$z_{bound} = z_{st} + 2(z_{\max} - z_{st}). \tag{53}$$

Fig. 8. Maximal errors of ϵ over z as a function of α.
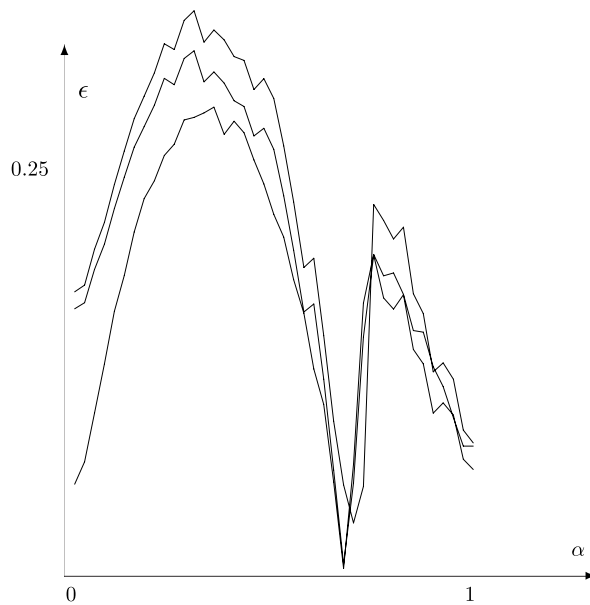

Fig. 9. Relative errors for different lengths and steps of calculation. The length is 70, the step is 0.05. Explanations can be found in text.

In Fig. 9 the values of the droplets number are compared at the "final" value z_{fin}. Two values $z_{fin} = 50$ and $z_{fin} = 70$ are chosen here. The value of ϵ is drawn. One can see three broken lines. The shapes of two of them are approximately the same at small α. These lines are the relative errors in the droplets number for different z_{fin}. It is clear that the dependence on z_{fin} at such values is very smooth and we practically attain the limit case (precisely speaking, it cannot be done). The step in calculations dx was chosen as d$x = 0.05$. The third line at small α lies below and has a more smooth shape at α near 1. It is the same ϵ for $z_{fin} = 50$ but calculated with a step d$x = 0.025$. This curve is drawn to demonstrate the error of calculations. It is not too far from the two mentioned curves. So, the necessary accuracy is attained.

Now one can analyze the behavior of the error. The decrease of $|N - N_{ap}|$ at $\alpha \approx 0.7$ is caused simply by the compensation of different sources of errors, the value $N - N_{ap}$ changes sign at $\alpha \approx 0.7$. More interesting fact is the reduction of the error at $\alpha \sim 1$. The reasons are the following: Every spectrum of the embryos sizes has a tail and a head. The head is rather short and can be described with the help of the iteration method. The tail has to be described by the asymptotic. The main source of error is the absence of the account of the influence of the surplus substance appeared in the head of the spectrum of the embryos sizes on the asymptotic. When we are going to the extremely long tails this influence will disappear.
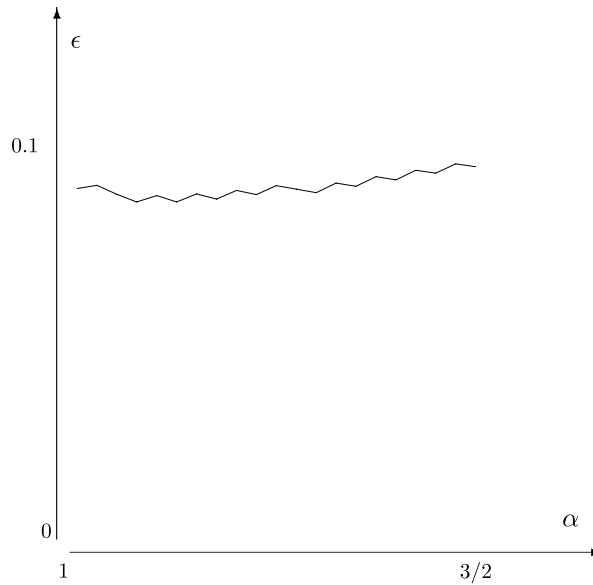
Fig. 10. Relative errors for pure iterations. The length is 50, the step is 0.05.

When α attains 1 the quantity of the droplets in the tail at the intermediate values of z is small in comparison with the quantity of droplets in the head. So, it is reasonable to take into account only the head with the help of iterations. (Certainly, now the number of droplets will be counted on the base of iterations not only until z_{bound} but also for $z > z_{bound}$.) So, now

$$N_{ap} = \int_{-\infty}^{\infty} \tilde{f}_1(x)dx \tag{54}$$

$$\tilde{f}_1 = \exp(x - \tilde{g}_1) \tag{55}$$

$$\tilde{g}_1 = \int_{-\infty}^{z} (z - x)^{\alpha} \hat{f}_0(x) \tag{56}$$

$$\hat{f}_0 = \max f_1 \tag{57}$$

for $x > x_{\max 1}$ and

$$\hat{f}_0 = f_1 \tag{58}$$

for $x < x_{\max 1}$. Here $\max f_1$ is the maximal value of f_1 and $x_{\max 1}$ is the corresponding argument. To get these values it is necessary to calculate

$$f_1 = \exp(x - g_1) \tag{59}$$

$$g_1 = \int_{-\infty}^{z} (z - x)^{\alpha} f_0(x) \tag{60}$$

where f_0 is the analytical solution corresponding to $\alpha = 0$.

The result is drawn in Fig. 10. Here the relative error ϵ at $z = 50$ is presented. The step of calculations was $dz = 0.05$. We see that even for $\alpha = 3/2$ the result is good even without asymptotic and even with initial approximation corresponding to $\alpha = 0$. For $\alpha > 3/2$ the result is presented in Ref. [4]. All situations are considered now.

We have stressed that for all α except the very small ones the initial approximation chosen as the analytical solution for the case $\alpha = 1$ is better than the initial approximation corresponding to $\alpha = 0$. Then the accuracy of further iterations will be also better. Now we shall present the analytical solution for $\alpha = 1$. The evolution equation is

$$g = \int_{-\infty}^{z} (z - x) \exp(x - g(x))dx. \tag{61}$$

For $\phi = -x + g$ this equation is

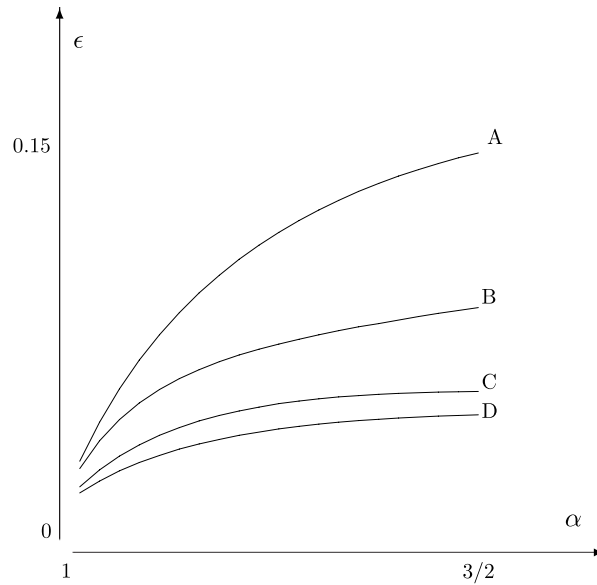$$\phi + z = \int_{-\infty}^{z} (z - x) \exp(-\phi(x))dx. \tag{62}$$

Fig. 11. Relative errors for pure iterations for moderate α. The meaning of curves is given in text. The length of calculations is 50, the step is 0.05. Basic power to start iterations is 1.

Having differentiated the last equation two times we get

$$\frac{d^2\phi}{dz^2} = \exp(-\phi). \tag{63}$$

This automorphic second order differential equation can be integrated. Let ϕ be the argument u, $d\phi/dz$ be the function y. Then $d^2\phi/dz^2 = ydy/du$. Integration gives

$$-\frac{y^2}{2} = \exp(u) + c_1. \tag{64}$$

From the boundary conditions we get

$$c_1 = -\frac{1}{2}. \tag{65}$$

Then

$$d\phi/dz = \sqrt{c_1 - 2\exp(\phi)}. \tag{66}$$

Integration gives

$$\int \frac{d\phi}{\sqrt{c_1 - 2\exp(\phi)}} = x + c_2. \tag{67}$$

The integral here can be taken which gives the expression for the spectrum of the embryos sizes in this case. The constant c_2 can be taken from the limit behavior $\phi \to -x$ when $x \to -\infty$.

This solution is very fruitful for description of situations with α close to 1. Results are given in Fig. 11 which is analogous to Fig. 10 but with another initial approximation. One can see here the curve A, which demonstrates the error of the first iteration in the direct iteration method. Here

$$N_{ap} = \int_{-\infty}^{\infty} f_1(x)dx \tag{68}$$

$$f_1 = \exp(x - g_1) \tag{69}$$

$$g_1 = \int_{-\infty}^{z} (z - x)^{\alpha} f_0(x) \tag{70}$$

and f_0 is the analytical solution corresponding to $\alpha = 1$.

We see that the error is even greater than the error in Fig. 10. This effect occurs because the head of the spectrum (the amplitude, not the shape) is seriously diminished. This effect is the same as we have seen for the smaller exponential powers. This decrease is the main source of error. So, we need to reexamine the initial approximation.

The first way is to act in a style like it was done with the advanced iterations. Here

$$N_{ap} = \int_{-\infty}^{\infty} \tilde{f}_1(x)dx \tag{71}$$

$$\tilde{f}_1 = \exp(x - \tilde{g}_1) \tag{72}$$

$$\tilde{g}_1 = \int_{-\infty}^{z} (z - x)^{\alpha} \hat{f}_0(x) \tag{73}$$

$$\hat{f}_0 = \max f_1 \tag{74}$$

for $x > x_{\max 1}$ and

$$\hat{f}_0 = f_1 \tag{75}$$

for $x < x_{\max 1}$. Here $\max f_1$ is the maximal value of f_1 and $x_{\max 1}$ is the corresponding argument. Then

$$f_1 = \exp(x - g_1) \tag{76}$$

$$g_1 = \int_{-\infty}^{z} (z - x)^{\alpha} f_0(x) \tag{77}$$

and f_0 in (77) is the analytical solution corresponding to $\alpha = 1$. The error is given by the curve B.

We can act also in a slightly another way. We can scale the number g of molecules in the liquid phase to have the approximately equal amplitudes. One can calculate the constants

$$q(\alpha) = \int_{-\infty}^{0} \exp(-x)x^{\alpha}dx \tag{78}$$

and instead of g consider g/q (both for current α and for $\alpha = 1$). This corresponds to the approximate equality of $g(\alpha)$ and $g(\alpha = 1)$ at $z = 0$. The error of this approach is presented by the curve C. One can see that the error is seriously diminished.

One can also require the approximate equality in derivatives of g as the functions of x at t_* as it is considered in the balance for establishing of t_* (see Ref. [3]). Then the constants q will be

$$q(\alpha) = \alpha \int_{-\infty}^{0} \exp(-x)x^{\alpha-1}dx. \tag{79}$$

The error is shown by the curve D. It is seen that the error is practically the same. This insensibility corresponds to the property of approximate universality observed in Ref. [4]. Now we see that this approximate universality goes also for the case of intermediate $1 < \alpha < 3/2$.

Here the values of q were calculated on the base of the ideal supersaturation, i.e. on the base of $\exp(x)$. The results will be even better if we take q calculated on the base of solution at $\alpha = 1$.

One cannot calculate here the iterations analytically, but can act in a manner presented in Ref. [3]. Certainly, the leading term here will be zN where z is the coordinate of the maximum of the peak of the spectrum of the embryos sizes, N is the total number of droplets.

The situation of decay is much more simple and we can use the standard iteration solution given by formulas

$$N_{ap} = \int_{0}^{\infty} f_1(x)dx \tag{80}$$

$$f_1 = \exp(-g_1) \tag{81}$$

$$g_1 = \int_{0}^{z} (z - x)^{\alpha} f_0(x)dx \tag{82}$$

where f_0 is the analytical solution corresponding to $\alpha = 1$. The error is drawn in Fig. 12. It is small. The slight decrease of the error when α grows is caused only by the finite step of numerical calculation.

All presented solutions can be improved to take into account the approximative manner of simplifications necessary for the derivation. We must mention some corrections which have to be done at the tails of the spectrum of the embryos sizes. Since the asymptotic are derived here in a simple algebraic way, one can enlarge the account of the specific features in asymptotic.

In consideration at the long tails one has to take into account the higher derivatives of the free energy of critical embryo. This account is rather simple since we know the general solution. It can be done both by the iteration approach and by the perturbation technique.

Also the validity of the linearization of the ideal supersaturation can be broken at the long tails. But there will be also no difficulties to correct the asymptotic for deviations from the linear case.
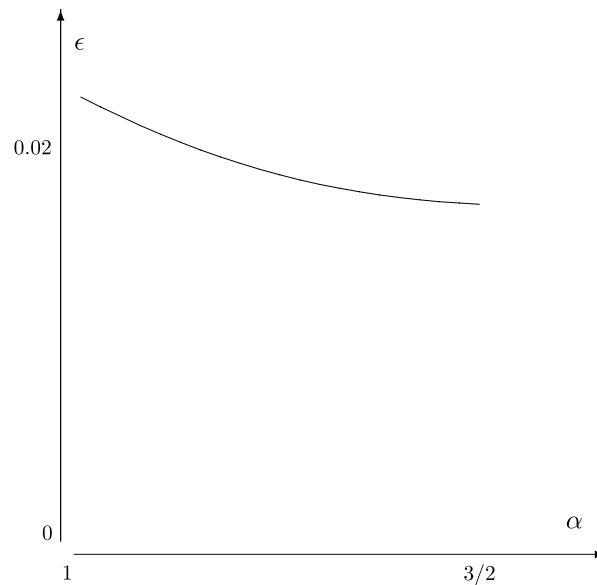
Fig. 12. Relative errors for pure iterations in the situations of decay for moderate α. The length is 50 units. The step of calculations is 0.05. Basic power to start the iteration procedure is 1.

As the result one has to conclude that the complete analytical description for the process of the new phase embryos formation is given. Not only the behavior of the supersaturation is found but it is found with such a high precision which ensures the high relative precision of determination of the nucleation rate (however, the formula for the stationary nucleation rate as a function of a supersaturation is supposed to be known). The high relative accurateness is illustrated in many figures. It is possible to get the analytical estimates for the smallness of the error in the total number of embryos by approach analogous to [3] but it leads to some long formulas and is skipped here over. This is not a difficult problem. The true goal is to get the good solution for the intensity of the new embryos formation and it is attained here.

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Research Article

Gibbs Thermodynamics of the Renninger-Wilemski Problem

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The Renninger-Wilemski problem in nucleation is analyzed. The Gibbs dividing surfaces method with external parameters is used to enrich the initial model. It is shown that both the traditional (Doyle) model and the Renninger-Wilemski model are not complete ones and, namely, the Gibbs dividing surface approach can solve this problem. It is shown that the application of the Gibbs approach also requires some model constructions. The simplified Gibbs model is proposed. It is shown that the simplified Gibbs model gives for the height of activation barrier the same numerical results as the Renninger-Wilemski model.

1. Introduction

Although the principles of thermodynamics are well grounded, there exist many narrow questions in applications. One of such questions belongs to the new phase embryos formation. Despite the fact that the free energy of the new phase embryo can be calculated in frames of equilibrium thermodynamics, there remain many questions of account of specific conditions for the critical embryo appearance.

There is no need to demonstrate the actuality of nucleation taking place practically overall. The importance of nucleation initiates investigations from Wilson's experiments [1–3] up to modern investigations. Thermodynamic aspects of investigations occupy an important place in this field considering not only the fundamental question of stationarity (see to clarify it, e.g., [4, 5]), but also the problems of smallness of characteristic embryos and corrections appeared because of its sizes and shapes [6]. The results given by thermodynamics immediately lead to quantitative description of kinetics [7] and can be included into consideration of some rather complex aggregates with very specific properties [8]. This consideration is based mainly on thermodynamics of small embryos. Here we will discuss, namely, some important specific features of the small embryos thermodynamics.

The bright demonstration of specific features of thermodynamic aspects is the Renninger-Wilemski problem which occupies an important place in the nucleation of multicomponent liquids. An abbreviated version of this problem sounds as follows:

> (i) Is it necessary to take the derivative of the surface tension on concentration to determine the characteristics of a critical droplet?

From the first glance this problem sounds so simple that the answer seems to be evident. But it took a dozens of years to clarify this problem.

This problem arises from the very beginning of investigations of the multicomponent nucleation since the pioneer paper written by Reiss [9], but until the paper of Renninger et al. [10] this problem was somehow in a shadow. The classical theory of nucleation [11, 12] is standing somehow aside of this question. The reason of this shadow is the rather weak dependence of the surface tension on concentration in the intermediate region of concentrations for the dominating majority of mixtures. The physical nature of this weakness is the enrichment of the surface layer with the surface-active molecules. When it is easy to find in the bulk of an embryo a molecule of the surface-active substance then it is profitable to catch it and to put in the surface. Roughly speaking only an entropy of mixing has to be paid here. The energy profit in this situation is a surface with a surface-active substance. So, the surface tension appears to be a relatively smooth function of concentration. Only when it is difficult to find such a molecule in a bulk liquid one has to pay some

relatively essential work to find it and the surface tension begins to depend on concentration essentially. But the last situation occurs at small concentrations and this case should be preferably described as a one-component nucleation with some impurities.

The mentioned weak dependence allows many authors in 1950–80s to ignore the fact of dependence of the surface tension on concentration, although there exist some investigations like that by Mirabel and Katz [13]. In [13] the correction for the Young-Laplace formula with the derivative of the surface tension on concentration was presented. This correction is rather doubtful.

The statement that it is necessary to forbid to differentiate the surface tension was announced by Renninger and coauthors in [10] criticizing mainly Doyle [14] and Mirabel and Katz [13]. Before [10] the situation was the following: there exists the expression for the free energy, it is clear that the free energy of the critical embryo is the free energy at the saddle point, and it is clear that to get the coordinates of the saddle point it is necessary to take the free energy partial derivatives and to put them to zero, but no special attention was paid for the question what to do with the derivative of the surface tension on the solution concentration.

It was Doyle [15] who presented contrary to [10] the arguments for the traditional version with the differentiation of the free energy on concentration having justified his initial approach in [14]. Later Wilemski clarified the problem in [16, 17] and one could say after [16, 17] that the phenomenological recipe required that it was necessary to forbid to differentiate the surface tension. This seemed to be the final conclusion in this question. Since that time the problem is called the Renninger-Wilemski (RW) problem and seemed to be the closed problem in thermodynamics.

This problem was revitalized in 2003 by Reiss and Reguera [18, 19] who showed by a refinement of some connections for derivatives of chemical potentials in droplet the alternative variant of derivation of equations which are similar to those used by Dole. One can say that technically the publication [18, 19] was the top of analysis of this problem. But the Gibbs approach has not been considered in [18, 19]. It was announced in [18, 19] that the Gibbs approach [20] "is of course the most sophisticated and general, but its application requires more information than is available in macroscopic thermodynamic observables." Meanwhile the recent investigations on thermodynamics of complex systems successfully operate with the quantities of excesses which is typical for the Gibbs dividing surfaces conception.

One has to mention that already after Wilemski in the field of multicomponent nucleation many models use the elements of the Gibbs dividing surface method but in their proper constructions. Instead of application of thermodynamics with some parameters of the model these papers try to build their "true" constructions without any choice of parameters. Here one can mention the approach of Debenedetti [21], the model of Nishioka and Kusaka [22], and the approach of Laaksonen et al. [23] which was analyzed also in [24]. All these models have the features of the Gibbs dividing surface method, but all of them propose some specific relations to close the system of equations. All of them announced the

recipe for determination of the critical embryo characteristics as the only "true" one although the Gibbs model is principally a model with external parameters.

Here we will analyze both traditional models (the Doyle model and the Renninger-Wilemski model) and show that both of them are not self-consistent. The alternative model as realization of the Gibbs dividing surface method will be presented. In the last part it will be shown how to simplify this approach.

2. Initial Remarks

To determine the coordinates of the critical embryo one can follow at least two ways.

 (i) The first way is to construct some expression (namely, the expression in the capillary approximation) for the total free energy of the critical embryo formation and then to determine the coordinates of the critical embryo as the coordinates of the free energy saddle point by differentiating and putting the derivatives to zero.

(ii) The second way is to use the general relations coming from the differential analysis such as the Laplace-Young formula and the Gibbs-Thomson formula for the equilibrium (critical) droplet and to put into these formulas some concrete models for necessary values.

When the expression for the free energy is precise then both approaches have to give one and the same result. The trouble is that everything we can suggest is no more than an approximation. In fact these approaches historically led to two different results and this discrepancy has now the name of the Renninger-Wilemski problem (for such a terminology see [18, 19]). Now it is clear that both results can be derived in both approaches but historically Renninger et al. [10] used the second approach and their opponent Doyle [15] used the first one. Following the history of the question we will speak about RW-model and about D-model correspondingly. Certainly, this classification is rather artificial.

The question of thermodynamic derivations of the surface characteristics was the subject of numerous investigations. The thermodynamic definition of the surface tension is discussed in [25]. Thermodynamics of a surface layer is analyzed in [26].

At first it is necessary to present the formal thermodynamic derivation in order to see where the hidden suppositions about the structure of the system under consideration have been done. Here we follow the manner of [18, 19] because, namely, that derivation opened the possibility to see different approaches in frames of the differential formalism. Certainly some essential modifications will be introduced.

Since in the system where the embryo is born the variables T (temperature) and V (volume) are supposed to be fixed, one has to use the Helmholtz free energy

$$F = U - TS. \tag{1}$$

Really, according to principles of thermodynamics,

$$dF = -SdT - pdV. \tag{2}$$

We suppose that the terms $\sum_i \mu_i N_i$ (μ_i are the chemical potentials, N_i are the numbers of particles, and index i numerates the components) are included into thermodynamic potentials[1].

One has to split U and S into contributions from the liquid phase (index l) and the vapor phase (index v)[2]. Then

$$U = U_l + U_v, \qquad S = S_l + S_v, \qquad V = V_l + V_v,$$

$$dU_v = TdS_v - p_v dV_v + \sum_i \mu_{vi} dN_{vi},$$

$$dU_l = TdS_l - p_l dV_l + \sum_i \mu_{li} dN_{li}. \tag{3}$$

Since

$$dV_l = -dV_v, \qquad dN_{vi} = -dN_{li} \tag{4}$$

we come to

$$dU = TdS - (p_l - \widehat{p_v}) dV_l + \sum_i (\mu_{li} - \mu_{vi}) dN_{li}. \tag{5}$$

Here the symbol $\frown$ indicates that the pressure is the pressure under the curved surface; that is, the Young-Laplace correction $2\gamma/r$ has to be added (γ is a surface tension, r is a radius of a droplet). Then

$$dF = -\left(p_l - \left(p_v + \frac{2\gamma}{r} \right) \right) dV_l + \sum_i (\mu_{li} - \mu_{vi}) dN_{li}. \tag{6}$$

In the state of equilibrium we have $dF = 0$ which gives

$$p_l = p_v + \frac{2\gamma}{r}. \tag{7}$$

This is the Young-Laplace equation and

$$\mu_{li} \left[p_v + \frac{2\gamma}{r} \right] = \mu_{vi} [p_v]. \tag{8}$$

Here and later the square brackets show the functional dependence to avoid misreading as multiplication. If the index of variable is absent it means that the dependence takes place over the whole set of variables.

Now it is necessary to go in chemical potentials from p to $p + 2\gamma/r$ explicitly. To do this it is necessary to calculate $\partial \mu_{li}/\partial p$. To fulfil this transformation we take the Maxwell relations for the Gibbs free energy $G_l = U_l - TS_l + p_l V_l$ with a differential

$$dG_l = -S_l dT + V_l dp_l + \sum_i \mu_{li} dN_{li}. \tag{9}$$

Then

$$\frac{\partial \mu_{il}}{\partial p_l} = v_{li}, \tag{10}$$

where v_{li} is the volume per one molecule of component i in a liquid phase. We suppose the liquid to be incompressible. So, the rhs of the previous equation is constant and can be easily integrated. Equation (10) is of great importance since it will lead to the Gibbs-Thomson equation. Then

$$\mu_{li} \left[p + \frac{2\gamma}{r} \right] = \mu_{li} [p] + \frac{v_{li} 2\gamma}{r} \tag{11}$$

and (8) looks like

$$\Delta \mu_i = \frac{v_{li} 2\gamma}{r}, \tag{12}$$

where $\Delta \mu_i$ is the difference of chemical potentials at the external pressure in the system. The last relation is the so-called Gibbs-Thomson equation well known in thermodynamics.

Equation (12) leads to invariant

$$\frac{\Delta \mu_{li}}{v_{li}} = \frac{\Delta \mu_{lj}}{v_{lj}} \tag{13}$$

and allows a clear physical interpretation. Namely, (12) is the basis for RW-model.

Here it is necessary to make one very essential comment. Having written equation (9) for the differential of $G_l = U_l - TS_l + p_l V_l$ we miss the term γA, that is, the surface tension γ multiplied on the surface area A. We can include this term and write

$$dG_l = -S_l dT + V_l dp_l + \sum_i \mu_{li} dN_{li} + \gamma dA. \tag{14}$$

This does not change the derivation. It is another moment which is important here. Beside this we have to note that ordinary it is implied that γA is independent of other characteristics presented in (14). But in the droplet there is a connection between A and N_{li}. This puts a question on the validity of this derivation. It will be discussed below.

Equation (6) for dF can be integrated from $N_{li} = 0$ up to the current size which gives $F[N_i]$. To fulfil this procedure it is convenient to present the dependence on N_{li} as the dependence on concentrations defined[3] as

$$\xi_i = \frac{N_{li}}{N_0}, \tag{15}$$

where

$$N_0 = \sum_i N_{li} \tag{16}$$

is the total number of molecules in a drop.

As an extensive variable[4] we can take N_0, but some other variants of choice are possible and will be presented below.

Instead of integration one can suggest to present the model for F and then to check whether it leads to (7), (12) by differentiation. We are interested here, namely, in the last relations.

One can easily suggest the following expression for F:

$$F[N_{li}] = F[0] - \sum_i \Delta \mu_i N_{li} + \gamma A. \tag{17}$$

Here and below A is the surface area of the embryo. The term $V_l(p_l - p)$ is missed here since it is very small. It corresponds to

the difference between the situation when the volume of the system is fixed or the pressure in the system is fixed. Concrete conditions ordinary are not well posed.

The condition for the equilibrium is

$$\frac{\partial F}{\partial N_{li}} = 0. \tag{18}$$

The explicit differentiation has to be done with account of the Gibbs-Duhem equation for the bulk liquid

$$\sum N_{li} d\mu_{li} + S_l dT - V_l dp = 0 \tag{19}$$

which is actually

$$\sum N_{li} d\mu_{li} = 0. \tag{20}$$

The last relation will be satisfied automatically and inevitably when we use some concrete dependencies for chemical potentials in liquid.

The result of differentiation (we take for simplicity a two-component case) on account of

$$A = C \left(\sum_i v_{li} N_{li} \right)^{2/3} \qquad C = (36\pi)^{1/3} \tag{21}$$

is

$$\frac{\partial F[N_{li}]}{\partial N_{li}} = -\Delta\mu_i + \frac{2\gamma}{r} + \left(\frac{3v_m (1 - \xi_i)}{r} \right) \left(\frac{d\gamma}{d\xi_i} \right), \tag{22}$$

where

$$v_m = \sum \xi_i v_{li}. \tag{23}$$

We see that the equilibrium condition

$$\Delta\mu_i = \frac{2\gamma}{r} + \left(\frac{3v_m (1 - \xi_i)}{r} \right) \left(\frac{d\gamma}{d\xi_i} \right) \tag{24}$$

differs from the Gibbs-Thomson equation by the last term. This equation is the basis in D-model.

In RW-model one can also explain how to come to (12) starting from (17). In the differentiation of F instead of (19) it is necessary to take the surface variant of the Gibbs-Duhem equation

$$\sum N_{li} d\mu_{li} + S_l dT - V_l dp + A d\gamma = 0 \tag{25}$$

which can be approximately reduced to

$$\sum N_{li} d\mu_{li} + A d\gamma = 0. \tag{26}$$

The last term in the previous equation cancels the derivative of the surface tension on concentration and we come to Gibbs-Thomson equations (12).

For a long time it seemed that (12) is preferable because there exists a differential method to see (12). But Reiss and Reguera showed that it is possible to get (24) in modification of the way we came here to (12). In integration $d\mu_{li}/dp$ it is necessary to take into account not only the direct dependence

$\partial\mu_{li}/\partial p = v_{li}$ but also the dependence on size of the embryo through the dependence

$$\frac{\partial\mu_{li}}{\partial A} = \frac{\partial\gamma}{\partial N_{li}}. \tag{27}$$

The last relation can be found if we start with the Gibbs potential taking into account that in U_l there already exits the surface term γA. Then

$$dG_l = -S_l dT + V_l dp_l + \sum_i \mu_{li} dN_{li} + \gamma dA. \tag{28}$$

Then the Maxwell relation on variables N_{li}, A gives (27). Then the integration will lead precisely to (24). This derivation revitalizes D-model.

To complete the overview it is necessary to add the approach of Mirabel and Katz [13] who follow the differential way of consideration which led to (12). In order to get (24) Mirabel and Katz modified Young-Laplace equation (7) as

$$p_l - p_v - \frac{2\gamma}{r} \sim \left(\frac{d\gamma}{d\xi_i} \right). \tag{29}$$

In [10] this approach was classified as an inappropriate one. We see that this approach is one of explanations how to reconcile the requirement to get the Gibbs-Kelvin equation and the requirement to have the free energy in the capillary model as described above. So, under the mentioned form of the free energy the true alternative is to modify the Gibbs-Kelvin equation or to modify the Young-Laplace equation.

3. Physical Model

Ideas to find a tool outside the nucleation theory to solve the problem formulated above seem to be very attractive. But unfortunately there is no such tool. Speaking about the possibility of the direct measurement of the free energy of embryos one has to confess that except for some specific cases (see [27]) there is no direct mechanism to realize this possibility.

Certainly, practically every reliable model can be expressed in terms of statistic-mechanical approach (see [28]), but this can not be a tool to decide whether one can cancel the derivative of the surface tension. Here also both approaches can be justified on statistic-mechanical basis, the matter is which reference state of equilibrium is chosen.

One has to stress that the density functional theory cannot be the instrument to decide to cancel the derivatives [29, 30] because here the model form of the free energy is simply postulated at the level of the elementary hydrodynamic subsystems.

Unfortunately, the comparison with the 2D Ising model as it is proposed in [31] to solve the question of the necessity of cancelation cannot be fulfilled because one cannot generalize this model to the multicomponent case.

So, we have to formulate some physical model and discuss it.

3.1. Different Meanings of the Surface Tension. One cannot argue that some excesses initiated by the interface have to be put into the theory. The most common one is the excess of the free energy, that is, the surface tension.

The answer to the question what approach is the most appropriate one lies in the method of construction of the capillary approximation and the expression for a free energy in this approximation. We have to reformulate a question: what is the surface tension which we will put in the surface term for the free energy of the embryo? Several answers are possible.

  (i) This is the surface tension of an embryo.

   Then the nucleation theory is the absolutely self-closed theory and it cannot be checked. At the modern level of experimental devices there is no way to measure the surface tension of droplets otherwise than in the nucleation rate experiments. Everything which is measured in experiments is attributed to the value of surface tension according to theoretical dependencies derived in frames of an approach to calculate the nucleation rate.

  (ii) This is the surface tension γ_t observed in a capillary tube (index t) of the radius equal to the radius of the embryo (with corresponding wetting).

   Here one can perform direct experiments to measure the surface tension. This is the way to construct a theory with the predicting force contrast to the previous case.

  (iii) The surface tension is the plane surface tension γ_p.

   Certainly, this is a rather rough approximation, but ordinary, namely, the flat surface tension is known. By application of the methods of thermodynamics of small objects it is possible to construct some approximation for the surface tension in a tube and to reduce this case to the previous one. Also one has to mention that in some sense this case can be preferable because the surface excesses are mainly known in the case of the flat surface.

  (iv) One can propose the conventional variant: γ is the surface tension of a flat surface but at the surplus pressure (plus the Laplace-Young addition); this value can be found by interpolation from P, T coexistence curve to surplus temperature or pressure.

   There are no principal differences between this variant and the previous one. So, no special attention will be paid to this variant.

To go further one has to note that the capillary tube and the flat liquid are not a closed object as the droplet is. This is the inevitable difference and this difference will be important. The question is now the following:

  (i) *is it enough to account the compactness of the embryo only at the level of expression for A as a function of the number of molecules inside the embryo or is it necessary to rewrite the analog of the Gibbs-Duhem equation which will be different from (25)?*

Our conclusion is that there is no direct answer on this question in frames of macroscopic thermodynamics, but the principle of correspondence formulated below is rather reliable and solves this question.

3.2. Mean Chemical Potentials in Different Models. The object of further investigation will be the cluster of a liquid phase which is dense and compact contrast to a vapor phase. So, we will omit the index l, use ν_i instead of N_{li}, and speak about chemical potentials instead of differences in chemical potentials[5].

We will formulate the principle of correspondence.

  (i) *It is necessary to use the Gibbs-Duhem equation from the system which provides the surface tension used in the model.* If we use the surface tension from a flat surface, we write the Gibbs-Duhem equation for a flat surface. If we use the surface tension from a capillary tube, we write the Gibbs-Duhem equation for a capillary tube.

Certainly, the most similar system with the explicitly measured surface tension for the situation of the embryo is the capillary tube. We take the surface tension from the capillary tube and have to write the Gibbs-Duhem equation for the capillary tube. This leads (as it will be shown later) to the Renninger-Wilemski recipe. But one has to stress that the principle of correspondence is no more than a supposition. Also it is necessary to add that one can act in a manner of the explicit attribution of the surface excesses which is typical for the Gibbs dividing surface approach.

In capillary models one has to use the surface tension from the situation with a capillary tube. It leads to the following consequence discussed below.

  (i) In the droplet there is a strong connection between the radius r and the number of molecules ν_i; this connection is absent in the capillary tube.

The last connection can be written in a most simple version of the theory (without surface excesses taken into account) as

$$\frac{4\pi r^3}{3} = \sum_i \nu_i \nu_{li}. \qquad (30)$$

If we use the Gibbs formalism there are surface excesses Ψ_i of the substance (index s marks the surface) and then

$$\frac{4\pi r^3}{3} = \sum_i \left(\nu_i - \Psi_i \right) \nu_{li}. \qquad (31)$$

We attribute in frames of conception of a phase in the Gibbs method all other molecules to the bulk phase

$$\nu_{bi} = \nu_i - \Psi_i \qquad (32)$$

(index b marks the bulk region).

Approximately Ψ_i are proportional to the surface area $4\pi r^2$:

$$\Psi_i = 4\pi r^2 \rho_i, \qquad (33)$$

where ρ_i is the density of excess[6].

As the main dividing surface it is preferable to take the surface of tension where the Young-Laplace equation is precise.

Then

$$\frac{4\pi r^3}{3} = \sum_i \left(\nu_i - 4\pi r^2 \rho_i \right) \nu_{li} \tag{34}$$

is an equation on r as a function of ν_i.

The concentrations are defined as

$$\xi_i = \frac{\nu_{bi}}{\sum_j \nu_{bj}}. \tag{35}$$

It is a principal requirement that in the definition of concentration there stand the bulk numbers of molecules.

Now we will present constructions on the base of a capillary tube as a corresponding system for the free energy in capillary approximation. Until the place where the Gibbs model is formulated *we forget about the excesses at the dividing surface.* In the capillary tube there is no such balance relation as $\nu_{bi} = \nu_i - \Psi_i$. If one constructs the free energy of a capillary tube one gets

$$F_t = \sum_i N_i \mu_i + \gamma_t A \tag{36}$$

(index t marks that we deal with a tube; N_i are the numbers of molecules in a tube). Since the numbers N_i are not fixed in principle (the tube is connected with a bath) one has to express the last relation through concentrations. This gives

$$F_t = \sum N_i B_b [\xi] + \gamma A, \tag{37}$$

where B_b is

$$B_b = \sum \xi_i \mu_i [\xi]. \tag{38}$$

The value of B_b has the sense of the averaged chemical potential. Consider

$$B_b = \langle \mu \rangle. \tag{39}$$

The condition for the equilibrium will be

$$\frac{dB_b}{d\xi} = 0. \tag{40}$$

Since Gibbs-Duhem equation (19) takes place the last condition means

$$\mu_i = \mu_j \tag{41}$$

with a clear physical sense.

The same picture will be in a situation with a plane surface. The difference is that the surplus chemical potentials are counted here from the coexistence line, while in the case of a tube they are counted from the potentials in vapor phase under the Laplace pressure.

The term γA does not influence the concentration equilibrium when we suppose that the contact angle in a capillary tube is constant (namely, this situation is considered). Certainly, there exists a dependence on concentration through the increase of pressure, but we suppose that the dependence of activity coefficients, that is, the functions f_i staying in standard expressions

$$\mu_i = \ln \left(\frac{p}{p_{eq}} \right) - \ln \xi_i - \ln f_i [\xi_i] \tag{42}$$

on pressure, is small. Here p_{eq} is the pressure over a pure plane liquid phase and $\ln(p/p_{eq})$ is a logarithm of the supersaturation plus one.

The situation in a droplet is another one. The surface area A depends on N_i and we have to take this dependence into account. There are several ways how to do it.

To see the preferable way we will analyze the structure of the free energy in the embryo. We present F from (17) in the form like that in the one-dimensional case:

$$F = -B_d \Omega + \Omega^{2/3}. \tag{43}$$

Here Ω is defined in order that $\Omega^{2/3}$ is the surface surplus input into the droplet free energy

$$\Omega^{2/3} = A\gamma. \tag{44}$$

For B_d one can get on the base of (17):

$$B_d = C^{-3/2} \gamma^{-3/2} \left(\frac{B_b}{\nu_m} \right), \tag{45}$$

where ν_m is the mean volume of a molecule in a droplet.

The value of B_d allows the following interpretation:

$$B_d \sim \frac{\langle \mu \rangle}{\gamma^{3/2} \langle \nu \rangle} \tag{46}$$

and one can consider the denominator in the last expression as the mean surface tension for one molecule in a power $3/2$ (certainly, one molecule has no surface tension).

Condition for an equilibrium concentration ξ_c will be

$$\frac{dB_d}{d\xi_i} = 0. \tag{47}$$

Condition for an equilibrium when the derivative of γ is put to zero will be

$$\frac{d (B_b/\nu_m)}{d\xi_i} = 0. \tag{48}$$

Here one can also get the interpretation for B_b/ν_m as the ratio of two mean values $\langle \mu \rangle = \mu_m$ and $\langle \nu \rangle = \nu_m$.

Both conditions are independent of the value of Ω and it is important. When we choose as a variable which is supplementary to ξ any other variable we can come to the dependence of ξ_c on Ω but at the saddle point the result will be the same.

We will call B_d the mean chemical potential in the droplet in D-model and $B_{RW} \sim B_b/\nu_m$ the mean chemical potential in the droplet in RW-model.

The property of independence on γ of the minimum of B_b/ν_m is the serious argument for RW-model and against D-model.

(A1) In the capillary tube which gives the tension used in the capillary approximation for F there exists the same independence; the concentration is the argument which provides the minimum of B_b. The position of this minimum is independent of γ.

Immediately there arise two arguments for D-model against RW-model.

(A2) The number of molecules and the surface term γA (γ is the surface tension, A is the surface area) are not independent in droplet.

In the tube the situation is opposite. They are independent.

When the molecule comes to the droplet it enlarges the volume and, thus, the surface term γA. In the tube such effect is absent.

So, here appears a question why we will use the model of a tube[7].

Even when the molecule does not change the volume of an embryo (e.g., this molecule is changed by the molecule of another type but with the same volume) the surface tension will be changed. We come to the following conclusion.

(A3) The composition of the surface layer has to be chosen not only to minimize the surface tension as it is in the tube but to minimize the whole surface term γA; that is, the composition of the bulk region also acts on A and, thus, on the surface term in a way different from the case of a tube.

This argument strengthens the conviction not to use the tube as the source of approximation for F but to use directly D-model.

But the most important argument comes from the analysis of the Gibbs-Duhem relation. It is formulated below. The problem staying there is that the Gibbs-Duhem relation has to be used inevitably in any model, but to write it one has to adopt also some model. This model has the direct influence on the result.

3.3. Interpretation of the Gibbs-Duhem Relation. The principle of correspondence states that since we use the surface tension from the measurements with a capillary tube we have to use the Gibbs-Duhem relation for the surface of a tube. The Gibbs-Duhem relation for the surface in a tube has the following form[8]:

$$d\gamma + \sum \rho_i d\mu_i \left[\xi_{bi} \right] = 0. \tag{49}$$

One can easily note that if

$$\frac{\rho_i}{\sum_j \rho_j} = \xi_{bi} \tag{50}$$

then

$$\sum_i \rho_i d\mu_i \left[\xi_{bi} \right] \equiv 0 \tag{51}$$

and the derivative of the surface tension cannot be compensated[9].

So, the physical reason of the compensation of the derivative of the surface tension on the concentration is the difference of the concentration in the surface layer from the bulk concentration. Surface enrichment as a complication for consideration was noticed in [32], but there the different possibilities to formulate the reference system were not even mentioned.

Really, in any surface layer (let it be the layer of an imaginary thickness l) we see that the volume of the layer is approximately lA and there are

$$\frac{\xi_{bi} lA}{v_m} + \rho_i A \tag{52}$$

molecules of a sort i. So the concentration ξ_{si} in a surface layer will be

$$\xi_{si} = \frac{\xi_{bi} l/v_m + \rho_i}{\sum_j \xi_{bj} l/v_m + \rho_j} \tag{53}$$

and it does not coincide with ξ_{bi}. The difference between ξ_{bi} and ξ_{si} explains why segregation is size dependent in diluted solutions, as in droplets of small size there is no sufficient number of atoms. Certainly, l is a parameter and ξ_{si} cannot be calculated explicitly. But under any l the value ξ_{si} does not coincide with ξ_{bi}.

We see that D-model is the model with uniform liquid and RW-model is the model with nonuniform liquid. The account of nonuniformity of liquid in frames of RW-model is the simplest one but we see that this account is very important and makes the model more complete. It is rather difficult to realize that RW-model is the model with nonuniform liquid because the region of enrichment is not described explicitly. Also there are no explicit values of excesses which also can show the nonuniformity. The Gibbs-Duhem equation is the only trace of such nonuniformity. It is simply a necessary condition of enrichment in the model.

We come to the following argument.

(A4) Having used γ from the situation with capillary tube of flat surface where the surface tension region is enriched with the surface-active component it is reasonable to take the model where the surface region is enriched according to the same rule, that is, according to Gibbs-Duhem equation (49).

This argument is the decisive argument in a choice favorable for RW-model.

Despite the choice of RW-model as a more adequate model we see that both models are not free from objections. For the RW-model the arguments A2 and A3 are the features ignored by this model. For the D-model the arguments A1 and A4 are the unresolved problems. Below the Gibbs dividing surface method (G-model) will be presented and this method is more sophisticated than RW- and D-models. But still the Gibbs dividing surface method (at least at the level of the several first terms of decomposition) is no more than a model because the arguments A2 and A3 are not fully resolved. But

it is the best model one can propose at the relatively simple level.

The terminology "Gibbs model" or "Gibbs dividing surface method" means nothing without any concrete recipe of approximations. Certainly, if we can get the characteristics of the curved surface of the closed confined droplet then the description becomes precise. The problem is that we do not know these characteristics; the optimal thing we can do is to use the characteristics of the curved surface over the unbounded system like the capillary tube is. The transmission of these characteristics to the situation of a droplet means the usage of the model. Evidently the capillary model is rather accurate and natural. But it is still a model. Here lies the source of discrepancy between theory and experiments on nucleation which tortures this field more than half a century. Certainly, this difficulty takes place in one-component case also.

4. Gibbs Method

The more adequate model than D- and RW-models can be constructed on the base of surface excesses and it will be done in this section.

First of all it is necessary to stress that we speak about the simplest vulgar version of the Gibbs dividing surfaces method. Namely, such a version is necessary to be installed instead of D-model or RW-model because the information about excesses even in a flat case is rather poor.

The structure of the Gibbs dividing surface method in the simplest (zero) approximation requires to consider the surface (it is more convenient to consider the surface of tension, i.e., the surface where the Young-Laplace formula takes place precisely) and the surface excesses of all components $\widetilde{N}_{si}$ which will be marked by Ψ_i. Then the surface area A will be calculated on the base of

$$A = C \left(\sum_i \nu_{li} \left(\nu_i - \Psi_i \right) \right)^{2/3} \tag{54}$$

which forms an equation on A:

$$A = C \left(\sum_i \nu_{li} \left(\nu_i - A\rho_i \right) \right)^{2/3}. \tag{55}$$

The first iteration is sufficient:

$$A = C \left(\sum_i \nu_{li} \left(\nu_i - C \left(\sum_i \nu_{li}\nu_i \right)^{2/3} \rho_i \right) \right)^{2/3}. \tag{56}$$

We again recall that here and later we suppose the liquid to be incompressible and the volumes ν_{li} to be independent of concentration.

From the first glance it seems that the free energy F has to be approximately transformed from $F = \sum_i \mu_i \nu_i + \gamma A$ to

$$F = \sum_i \mu_i \nu_i$$
$$+ \gamma \left(C \left(\sum_i \nu_{li} \left(\nu_i - C \left(\sum_i \nu_{li}\nu_i \right)^{2/3} \rho_i \right) \right)^{2/3} \right). \tag{57}$$

But actually this transformation can be avoided by use of special variables as it will be clear below.

One can fulfil the same analysis as above but instead of Ω one has to choose

$$\Omega \longrightarrow \gamma^{3/2} \left(C \left(\sum_i \nu_{li} \left(\nu_i - C \left(\sum_i \nu_{li}\nu_i \right)^{2/3} \rho_i \right) \right)^{2/3} \right)^{3/2}. \tag{58}$$

Then

$$F = -\sum_j \lambda_j \mu_j - \sum_j \varrho_j \mu_j \frac{\Omega^{2/3}}{\gamma\left(\xi\right)} + \Omega^{2/3} \tag{59}$$

with

$$\lambda_i = \nu_i - \Psi_i. \tag{60}$$

Certainly,

$$\frac{\lambda_i}{\lambda_j} = \frac{\xi_i}{\xi_j}. \tag{61}$$

One can choose instead of Ω the variable κ by the following formula:

$$\kappa = A^{3/2} \left(\gamma - \sum_i \varrho_i \mu_i \right)^{3/2}. \tag{62}$$

In these variables the free energy F has the form

$$F = -\kappa b_g\left(\xi\right) + \kappa^{2/3} \tag{63}$$

with the generalized chemical potential

$$b_g = \frac{\sum_i \lambda_i \mu_i}{\kappa} \tag{64}$$

or

$$b_g = \sum_i \xi_i \mu_i \frac{\sum_j \lambda_j}{\kappa}. \tag{65}$$

One has to show that b_g does not depend on κ. To fulfill this derivation one can come to

$$b_g = \sum_i \xi_i \mu_i \frac{\sum_j \lambda_j}{A^{3/2}\left(\gamma - \sum_k \varrho_k \mu_k\right)^{3/2}} \tag{66}$$

or[10]

$$b_g = \sum_i \xi_i \mu_i \frac{\sum_j \lambda_j}{\left(\gamma - \sum_k \varrho_k \mu_k\right)^{3/2} \sum_l \nu_l \lambda_l}. \tag{67}$$

It can be also presented as

$$b_g = \sum_i \xi_i \mu_i \frac{1}{\left(\gamma - \sum_k \varrho_k \mu_k\right)^{3/2} \sum_l \nu_l \xi_l}. \tag{68}$$

The last relation evidently shows that b_g is really a function of ξ. The dependence on κ is absent.

Formula (63) is valid for the arbitrary Gibbs model. This form will be called the canonic representation. Now we see that it takes place for the arbitrary model in frames of the Gibbs dividing surface method. This result is of great importance. Directly from this result follows the Gibbs rule. It means that the free energy of the critical embryo is one-third of the surface energy. Now this rule is shown for the arbitrary model from the Gibbs dividing surface method.

One can use expression (68) to clarify the Renninger-Wilemski problem. According to the Gibbs absorption relation[11]

$$d\gamma = \sum_j \varrho_i d\mu_i \tag{69}$$

the derivative of the surface tension on concentration is canceled by the corresponding derivatives of ϱ_i on ξ. So, if we write b_g without surface excesses as

$$b_g = \sum_i \xi_i \frac{1}{\gamma^{3/2} \sum_j \nu_j \xi_j} \tag{70}$$

we have to forbid the differentiation of γ on concentration. We see that in frames of the Gibbs approach (G-model) the Renninger-Wilemski problem is explained. Here there are no artificial requirements not to differentiate the surface tension on concentration. It is necessary to stress that the reason is not the formal Gibbs absorption equation, but the difference of concentrations in the bulk solution from the integral values.

One has also to recall that in frames of G-model there is one undefined parameter because in the L component case there are only $L - 1$ independent equations:

$$\frac{d\gamma}{d\xi_{bi}} = \frac{\sum_j \rho_j d\mu_j}{d\xi_{bi}}. \tag{71}$$

One additional parameter in G-model is inevitable. Ordinary it is the sum of excesses with some weights.

5. The Reduced Gibbs Model

The G-model is wider than the D-model and the RW-model. It is important that G-model is the self-consistent one. But there exists one additional parameter which cannot be calculated. Namely, for two excesses ρ_1 and ρ_2 there exists only one equation:

$$\frac{\rho_1 d\mu_1}{d\xi_b} + \frac{\rho_2 d\mu_2}{d\xi_b} = \frac{d\gamma}{d\xi_b}. \tag{72}$$

For L-component case there exist $L - 1$ equations:

$$\frac{\sum_j \rho_j d\mu_j [\xi_b]}{d\xi_{bi}} = \frac{d\gamma}{d\xi_{bi}} \tag{73}$$

and the last Lth equation

$$\frac{\sum_j \rho_j d\mu_j [\xi_b]}{d\xi_{bL}} = \frac{d\gamma}{d\xi_{bL}} \tag{74}$$

is the superposition of the previous $L - 1$ equations. So, it is necessary to add one equation. When one knows the distance l between the surface of tension and the total equimolecular surface determined as

$$\sum_j \nu_j \nu_{lj} = \left(\frac{4\pi}{3}\right) r^3 \tag{75}$$

(certainly, it is possible to account the density in a vapor phase) then $(l \ll r)$

$$\sum A \rho_i \nu_{li} = Al. \tag{76}$$

The most simple variant is to say that the total equimolecular surface coincides with the surface of tension. This corresponds to initial relation (30). It gives

$$\sum \rho_i \nu_{li} = 0. \tag{77}$$

Certainly, this is artificial requirement and generally speaking it is wrong. The only justification is that this requirement is the simplest one and that it corresponds to the recipe (30) of the simplest and the oldest capillary approximation which is used since [9]. In [23, 24] this connection was announced to be the only true one. One has to stress that according to the Gibbs dividing surface method this connection has no preferences.

The main conclusion for the SG-model (simplified Gibbs model) is that the results for the free energy of the critical embryo, for concentration ξ_b and for the variable Ω (here κ), coincide with results of RW-model.

The last statement can be easily checked by comparison of corresponding formulas.

The coincidence of the free energy of the critical embryo, the concentration and the surface of the critical embryo in both (RW and SG) models, does not mean that all characteristics coincide. In RW-model one can get

$$\nu_i = \frac{\xi_{bi}\Omega}{\nu_m \gamma^{3/2} C^{3/2}} = N_{bi}. \tag{78}$$

Certainly, to see the critical numbers ν_{ci} of the molecules of ith component in SG-model one has to solve the system of equations and add $\rho_i 4\pi r^2$ to

$$\nu_{bi} = \frac{\xi_{bi}\Omega}{\nu_m \gamma^{3/2} C^{3/2}}. \tag{79}$$

Then

$$\nu_i = \frac{\xi_{bi}\Omega}{\nu_m \gamma^{3/2} C^{3/2}} + \rho_i 4\pi r^2 \tag{80}$$

or

$$\nu_i = \frac{\xi_{bi}\Omega}{(\nu_m \gamma^{3/2} C^{3/2})} + \rho_i \Omega^{2/3} \gamma^{-1} \qquad (81)$$

and the result slightly differs from RW-model.

But this difference means absolutely nothing for the height of activation barrier. For the rate of nucleation since the change of the Zeldovich factor is negligible the error is negligible also.

We come to the same functional dependencies but with slightly changed values of coefficients. Such simple dependencies are probably the source for the simple scaling factors like it is observed in [33]. One can also mention that the applicability of the scaling approach to the free energy like the Fisher droplet model and analogous ideas by Stauffer [34] and later by Bauchspiess and Stauffer [35] can be also interpreted as the result of the simple scaling observed here. They can be also included in this picture by some moderate transformations.

6. Self-Consistency of Thermodynamic Approaches

From the first glance the situation with the Renninger-Wilemski problem is strange; there are no evident errors in both D- and RW-models, but at least one result is wrong. Does it mean that in construction of thermodynamic theories it is possible to make an "invisible error"? Fortunately it will be shown below that the difference in results for the free energy of the critical embryo obtained in different models has the order of correction.

To see this smallness one can redefine κ as $A^{3/2}$ and forget about excesses. The value of κ is the big parameter of the theory. Really, the thermodynamic description is valid only at great number of molecules in the embryo which requires a big value of κ.

Then $F = -B_A\kappa - \gamma\kappa^{2/3}$ and it is important that $B_A \sim B_b/\nu_m$ does not contain γ. Really, from equation

$$\left.\frac{\partial F}{\partial \xi}\right|_{\kappa=\text{fixed}} = \frac{\partial \gamma}{\partial \xi}\kappa^{2/3} - \frac{\partial B_A}{\partial \xi}\kappa \qquad (82)$$

it is seen that the first term $(\partial\gamma/\partial\xi)\kappa^{2/3}$ with the derivative $\partial\gamma/\partial\xi$ has the correction order $\kappa^{2/3}$:

$$\frac{\partial\gamma}{\partial\xi}\kappa^{2/3} \sim \kappa^{2/3} \qquad (83)$$

in comparison with the second term $(\partial B_A/\partial\xi)\kappa$ having the order κ:

$$\frac{\partial B_A}{\partial \xi}\kappa \sim \kappa. \qquad (84)$$

It means that the correction will be small.

We extract this result because of its importance for the reconstruction of the logical self-consistency of thermodynamics. Only the correcting order of the term with the derivative of the surface tension allows to ignore it in the main order and to return the leading role of the ordinary capillary approximation.

Certainly, in situations of practical realization in experiments the difference between the order κ and $\kappa^{2/3}$ can be hardly seen.

Since the formal recipe to resolve the Renninger-Wilemski problem is to forbid the differentiation of γ on concentration then the equation on concentration will be different. It would cause the impression that there is a shift in a leading term. The true answer is that this result causes the shift in F_c which has a correction order as it follows from the last equation.

One can treat the surface tension as a coefficient in the first correction term proportional to the surface of the embryo. The coefficients at $\kappa^{1/3}$, $\ln\kappa$, $\kappa^{-1/3}$, and so forth depend on intensive variables (concentration is one example). Their derivatives will be canceled by derivatives of corresponding excesses. The structure will resemble the Renninger-Wilemski problem. But here the dimension of "surface" will be $\kappa^{1/3}$, $\ln\kappa$, $\kappa^{-1/3}$, and so forth. This effect will be called the "generalized cancelation of derivatives on intensive variables." The considerations to justify the cancelation are practically the same as those presented here for the leading correction.

The necessity to develop the theory with surface excesses is evident because the surface excesses will essentially shift the position of the near-critical region in comparison with the size of the near-critical region. In RW-model the form of the near-critical region can not be explicitly described. But this region is extremely important for solution of kinetic equation to get the rate of nucleation.

The Gibbs method allows to get the form of the near-critical region. Rigorously speaking to determine the form of the near-critical region one has to take the expression for F with correction terms up to the order which causes the shift of position of the near-critical region. Now it is clear that the effect results mainly in the shift of the near-critical region while the form of the near-critical region remains approximately the same.

7. Results and Conclusions

The main new results of the current analysis are the following:

  (i) It is shown that both D-model and RW-model are not complete ones.

 (ii) The principle of correspondence is formulated. It is shown that this postulate leads to the RW-model.

(iii) It is shown that canonic representation takes place in the arbitrary Gibbs model.

(iv) The Gibbs rule is shown for the arbitrary model in the class of the Gibbs dividing surface method.

 (v) The driving physical reason of RW problem is shown. It is the difference of concentration in a surface layer from the concentration in a bulk liquid phase.

(vi) The self-consistency of thermodynamic models is shown.

Does the performance of this analysis mean that the free energy of the critical embryo in nucleation has been found? To comment on this question one has to note that the conditions of applicability of thermodynamic approach to solve the RW problem are very strong. Namely, ordinary it is required that

$$\nu_i \gg 1. \tag{85}$$

But also the surface layer has to be the uniform media which requires

$$\Psi_i = A\rho_i \gg 1. \tag{86}$$

The last inequality is very hard to satisfy. The difficulty occurs not only because the surface layer has the small volume (we mean the real surface layer which has the finite thickness and it is only reflected in Ψ_i in Gibbs model) but also because there exists an effect of enrichment of the surface layer by the so-called surface active substances. Then there are only few molecules of the surface passive substance. This breaks the last inequality for the surface-passive components for rather big critical embryos. Otherwise we have to construct the theory with a nonuniform surface layer, which is extremely difficult to do, even approximately.

The theoretical constructions presented above can be generalized. In fact there exist several model methods to improve the construction of the free energy, for example, the Debenedetti Reiss method, discussed in [36]. These refinements can be inserted into the theory presented here without radical rearrangements.

One can refine the theory by inserting the dependence of the surface tension on radius (see, e.g., [37, 38]). The special effects which appeared in the constrained systems (see [39]) are not taken into account here but they can be easily introduced into this theory. One can add that the possibility of deformation of the center of the embryo can be also taken into account. This effect is quite analogous to the deformation of heterogeneous centers and it was considered in [40].

We keep aside the possibility of fluctuations widely investigated theoretically and observed experimentally [41]. They can be also included into consideration without essential transformation of the theory. One can insert here the Tolman-like corrections as well as the scaled expansions introduced in [42]. One has to note that any refinements like [43, 44] of the classical nucleation theory can be included here directly without any interference with results of this consideration. Refinements have to be put instead of the classical expression.

However, in this analysis we do not analyze the possibility that the bulk structure of the embryo can differ from the bulk structure of the reference bulk system in a capillary tube (for the principal possibility of such an effect see [45]). We consider the bulk of the embryos as the homogeneous media; for nonuniform density one can see [46]. The theory can be transformed to grasp this case also.

We do not pretend to go close to the critical point although the difference between concentrations in bulk and in surface layers can be interpreted in analogous manner. It seems that any extensions of the classical approach like [47] should be replaced by theoretical constructions based on the renormalized group approach.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

Endnotes

1. One can also suppose that the fixed variables are the temperature T and the pressure p and use the Gibbs free energy

$$G = F + pV. \tag{$*$}$$

The difference in the work of the droplet formation will be in a value of the volume of the appeared droplet multiplied on differences in pressure. Ordinary this term is very small and it is neglected. In the closed systems during the process of nucleation from diluted solution the concentration decreases. This effect is rather small for critical embryos and begins to be essential at big supercritical formations of a new phase. The corresponding effect in the global kinetics of nucleation is described in [48].

2. Already here we have to adopt some model: to divide U and S into two parts. Also we suppose that the temperature is one and the same for both parts; that is, we consider the isothermal nucleation. At this level of narration we do not need the surface excesses; these excesses will appear later.

3. Here this statement used in [18, 19] is not absolutely precise and will be corrected.

4. This variable used in [18, 19] as an extensive variable is only asymptotically extensive one which will be discussed.

5. Here we are not interested any more in the density of environment and denote the number of molecules inside the droplet by ν_i. This notation marks that we are not interested in the number of molecules in a vapor phase.

6. Later it may be useful to write another coefficient of proportionality as $\Psi_i = A\rho_i$.

7. Namely, the Gibbs dividing surface for a tube leads to the cancelation of $d\gamma/d\xi_i$.

8. For the embryo we cannot extract the surface explicitly as an independent object since there is the connection (30). So, the base for such type of the Gibbs-Duhem relation is absent. Instead of this one has to express A via the numbers of molecules taking into account relation (27).

9. Since in reality it is compensated it means that this possibility cannot be realized.

10. We miss C for simplicity.

11. The sign is changed because of specific choice of differences of chemical potentials.

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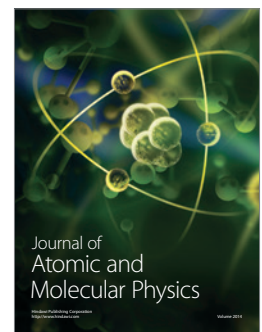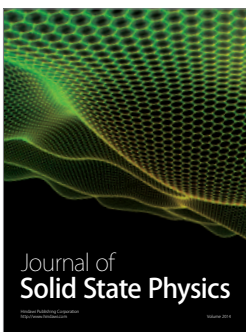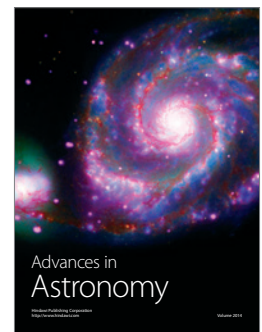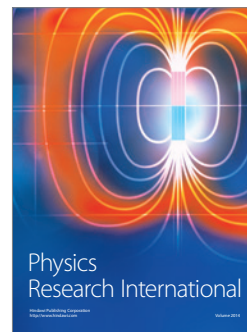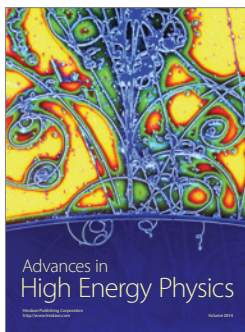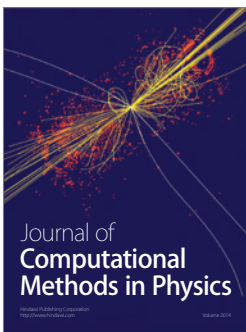
Research Article

Theoretical Description of the Glass Preparation with the Necessary Optical Properties

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The method to get the glass media with necessary optical characteristics is proposed. This method is based on inserting a necessary number of heterogeneous centers of given activity into the system. The theoretical description of the nucleation process in such situation is given and the resulting formulas allow choosing the characteristics of heterogeneous centers necessary to get the required optical characteristics of the media.

1. Introduction

The theory of a vitreous state inevitably includes the nucleation phenomena [1]. Every vistreous medium contains the embryos of a crystal phase which are growing extremely slowly. So one can say that they are practically stable objects. Such embryos are the centers of scattering and they affect the optical properties of glass. The start of systematic scattering theory was given by Lord Rayleigh [2]; the scattering on fluctuations was considered by Smoluchowsky and Einstein [3, 4]. Essential contribution in the consideration of the scattering with account of magnetic properties was made by Cabannes [5, 6]. A bright example of the theory of scattering on particles of essential sizes is given by the famous Mie scattering theory [7]. This approach was essentially generalized by Jobst [8] and Debye [9].

In every scattering theory the distribution of the embryos sizes is reflected in the optical coefficients of material. Ordinary it is necessary to know only several first momentums of the distribution of the embryos over sizes. Sometimes it is sufficient to know only the mean size of the embryos.

Impurities are inevitably presented in the media and they are like some heterogeneous centers. The nucleation theory on heterogeneous centers was investigated already by Frenkel in [10] and this paper completes the classical theory of nucleation created by Becker and Doering [11], Volmer [12], Kramers [13], and Zeldovich [14]. The full analysis of

the stationary nucleation rate in the case of heterogeneous condensation was given by Kuni [15]. Even without the solution of kinetic equation one can evidently see that the main factor in the rate of nucleation is the Boltzmann distribution $\exp(-F)$, where F is the free energy of the critical embryo counted in the thermal units. This value is the central object of the theory and the main efforts were paid to find a correct expression for F. Unfortunately it is rather difficult to do and even in the simplest case of the charged nuclei it is necessary to build a rather complex theory with decompositions [16–18]. These decompositions were constructed in frames of the general Gibbs dividing surfaces theory [19]. In the formalism of these decompositions there appear several coefficients with very specific physical meaning.

During the process of the glass preparation it is necessary to have the glass with the necessary optical properties. So it is necessary to have impurities in the necessary quantity and of the given size.

Around the embryos there appear specific profiles of density of the substance. The role of the density profiles in the light propagation has been studied in [20]. The analogous property in frames of the embryos in nucleation theory was investigated in [21].

The classical theory of nucleation [22, 23] is like an elegant necklace which has to be around the free energy of critical embryo. The problem here is not only in the necessity to know what the surface tension has to be put in these

constructions [24] and to describe the surface layer [25], but also to know the influence of the heterogeneous center on these objects. Even in the case without the heterogeneous center the question of the free energy profile is one of the most actual questions [26]. Considering the possibility of the direct measurement of the free energy of embryos one has to state that except special situations (see [27]) there is no clear way to do it. The direct application of the statistical mechanical approach [28] also causes certain difficulties. The same can be said about the comparison with the 2D Ising model as it is proposed in [29]. The density functional approach [30–33] also can not give the absolutely precise result. But the accuracy of the last approach is rather satisfactory. One has to mention also the possibility of using the approximate scaling formulas [34–36] based on some characteristic basic points for decompositions as parameters. One can also insert here the generalizations associated with the dependence of the surface tension on the size [37, 38], the effects in constrained systems [39], and the deformation of heterogeneous centers [40]. Here the possibility of fluctuations [41] and the Tolman-like corrections [42] is not considered. The refinements of [43, 44] can be introduced here directly.

The most evident way to get the necessary properties is to govern the law of creation of the ideal metastability Φ, that is, the imaginary metastability which would be in the system when the process of the new phase formation is forbidden. The value of the ideal metastability is fully governed externally and it seems that this function can be regulated to have the necessary properties. Unfortunately, the preparation of the glass requires the absolutely prescribed conditions to have the glass with optimal properties and it is impossible to change the conditions of the glass preparation. So Φ as a function of time t is supposed to be fixed.

But one can propose another rather simple and effective method. The main idea is to inject a given number of heterogeneous centers of the given activity to change the effective conditions of the nucleation of the main quantity of impurities which occurs pseudo-homogeneously (i.e., without exhaustion of the potential sites). The theoretical description of this method will be the matter of the current paper. This paper is organized as follows:

(i) At first the *properties of the nucleation rate* will be recalled. The exponential approximation for the nucleation rate as a function of a supersaturation will be introduced.

(ii) To construct the description of the multistage process which is the nucleation with the presence of the active heterogeneous impurities at first the *nucleation without heterogeneous impurities* will be studied. This process is more simple but the extraction of the characteristic features will help in construction of the more complex process.

(iii) Having started the description of the nucleation process with the presence of the active heterogeneous impurities one can consider the separate process of exhaustion of these impurities or the *formation of the embryos on the active heterogeneous impurities*. This part of consideration will give the parameters

of the influence of the embryos on heterogeneous centers on the process of formation of the pseudo-homogeneous embryos of a crystal phase.

(iv) Under the influence of heterogeneously formed embryos the *formation of the pseudo-homogeneous embryos* will be studied. Namely, this part of consideration will give the necessary optical characteristics of the media.

(v) To get the necessary optical characteristics it is necessary to formulate the *conditions on parameters of the active heterogeneous centers*. This is the matter of the next section. Here the ways to solve the system of algebraic equations of parameters are also discussed.

(vi) The final section of the paper is Conclusions where the results are summarized and the limitations and restrictions of the theory are described.

2. Properties of the Nucleation Rate

The rate of nucleation J is proportional to exponent of the free energy of the critical embryo. This factor is the main factor and that is why the free energy F of the critical embryo is the main object of interest in the investigations devoted to the nucleation.

The general formula for the rate of nucleation is the following:

$$J = n_1 \exp\left(-F\right) Z. \tag{1}$$

In (1) n_1 is the number of sites (or the molecules) which can be the starting point for the nucleation (crystallization) formation of the embryo and the factor Z is the Zeldovich factor. The value of Z is given by the numerous considerations but the approach appearing in the classical theory of nucleation is not yet radically reconsidered. Although there are some attempts to refine the Zeldovich factor these refinements do not lead to the change of this value in the order of the magnitude. Some interesting ideas for Z appear in the multidimensional consideration [45, 46] but this is not the subject of the current paper.

It is reasonable to extract in Z the kinetic factor W_c^+ (the number of adsorbed molecules in the time unit) and to write

$$Z = Z^+ W_c^+ \tag{2}$$

speaking about the truncated Zeldovich factor Z^+ because contrary to the liquid-vapor nucleation or the solid-liquid nucleation in the situation considered here (i.e., in the process of vitrification) the kinetic factor has specific behavior: at some moment of time it becomes so small that even the supercritical embryos practically stop growing. Otherwise it is impossible to explain why the crystal embryos do not gradually transform the whole volume of the glass into the set of crystals.

In the traditional approach mentioned above it is supposed that the intensity of absorption of new molecules by the embryo W^+ is

$$W^+ = \frac{A}{4} n_{\text{near}} \nu_t K, \tag{3}$$

where n_{near} is the density of the molecules in the vicinity of the embryo, v_t is the mean thermal velocity of the molecule, K is the condensation coefficient, and A is the surface area of the embryo.

The last formula (3) is supposed to be valid both for the critical and for the supercritical embryos. The evolution of undercritical embryos is not too interesting because in the region of undercritical embryos there is the quasi-equilibrium state.

Really, formula (3) has a rather general range of application. Then it follows that the peculiarities of W^+ are caused by the peculiarities of K. This explains the factorization (2). The condensation coefficient K contains the main dependence specific for the vitrification process. Ordinary it is presented as

$$K = \exp(-\Pi) \qquad (4)$$

implying that in the process of adsorption there is a necessity to overcome some barrier. The height of barrier is denoted by Π. This barrier can have a very specific origin including the barriers for displacement of the molecules in the environment of the embryo in order to give enough space for the appropriate installation of the new molecule in the embryo (this seems to be the main reason for annulation of K). So only some general remarks can be made concerning (4).

Instead of the previous formula (4) it is better to write

$$K = K_0 \exp(-\Pi) \qquad (5)$$

implying that even when the thermodynamic conditions correspond to the absence of imaginary barrier there remain other factors (like thermal relaxation, noncorrespondence of the position of the molecule and the profile of the adsorbing region of the embryo, etc.) which affects the probability of adsorption. Note that barrier in (5) is an abstract effective barrier.

In the liquid-vapor nucleation it is reasonable to suppose that the explicit dependence of K on the time t is rather smooth. In the vitrification process K has to go to zero when t grows. It is rather easy to explain why it is so. It is supposed that ordinary there are no thermal effects of nucleation and the creation of Φ is attained by the cooling of the system. Then the vapor consumption leads to the decrease of the number n of the molecules but the temperature T is not affected by embryos. The decrease of T ordinary leads to increase of the activation barriers. If it is supposed that $K \sim \exp(-\Pi)$, where Π is the activation barrier of accommodation, then we need the increase of Π with decrease of temperature. Really, it is quite natural because the activation barrier is measured in thermal units. Then it can be seen that K goes to zero.

If Π is linearized as a function of t then it is possible to come to

$$K \sim \exp(-k_\pi t) \qquad (6)$$

with the linearization coefficient k_π. The linearization (6) invokes a question of the dependence of Φ on time. Here it is also supposed that the linearization can be made and one can come to

$$\Phi \approx \phi t + \Phi_0 \qquad (7)$$

with parameters ϕ and Φ_0. Parameter Φ_0 can be put to zero by the appropriate shift of the time scale.

Certainly, it is necessary to have some concrete dependence in order to present some concrete formulas. Analogous theory can be constructed for some other concrete dependence of Φ on t.

Certainly K can not be greater than 1. The exponential approximation does not correspond to this property. A more simple and effective approximation is the following: $K = K_0$ for $t < t_0$ and $K = 0$ for $t > t_0$. Namely, this approximation will be used. Fortunately it is possible to determine t_0, at least to estimate t_0 in order to ensure the correct final size of embryos.

One has to stress that K appears both in expression for J and in expression for the rate of growth. So after t_0 there will be no appearance of the supercritical droplets nor growth of the already existing droplets. The process is therefore stopped.

Since it is required that the system is metastable it means that it is supposed that without active heterogeneous centers there will be some embryos of the new phase. This means that

$$t_0 > t_+, \qquad (8)$$

where t_+ is the moment of intensive formation of the pseudo-homogeneous embryos. Certainly the moment t_* in (8) of characteristic time of appearance of embryos on the active heterogeneous centers has to be smaller than t_+. Then

$$t_* < t_+ < t_0. \qquad (9)$$

One can prove that the moment t_{**} of the pseudo-homogeneous formation in the presence of active heterogeneous centers satisfies inequality

$$t_{**} < t_+. \qquad (10)$$

Then

$$t_{**} < t_0. \qquad (11)$$

Inequalities (8), (9), (10), and (11) presented above are rather important because they allow stating that the process of nucleation can be considered at the practically constant value of K.

A special question which has to be analyzed here is whether the rate of nucleation is really the stationary one. Justifications of the stationarity are quite similar to the liquid-vapor case.

The mechanism of the embryos growth can be chosen as the free molecular one which corresponds to the case of crystallization. This leads to $n_{near} = n$, where n is the mean concentration of the molecules in the noncrystalline phase.

The rate of nucleation J is the function of the power of metastability ζ which is called the supersaturation. Ordinary ζ is presented as

$$\zeta = \frac{n}{n_\infty} - 1, \qquad (12)$$

where n_∞ is the concentration of molecules in the noncrystalline phase at the state of the phase coexistence. Certainly then

$$\zeta = \Phi - G, \qquad (13)$$

where G is the number of the molecules in the crystalline phase calculated in units of n_∞. Because of the growth of the crystals the value G grows also. At t_0 the value G stops to grow but the process of the new droplets formation stops also.

One can see that according to (12), (13) the supersaturation ζ is not governed purely externally but depends on the process of nucleation and on the process of the substance consumption and the media heating by the regular growth of supercritical embryos. So there appears the self-consistent problem which is the subject of investigation in the theories of the global nucleation.

To see how J depends on ζ it is reasonable to notice that the main dependence occurs through the factor $\exp(-F)$. The free energy F is the smooth regular function of thermodynamic parameters and of ζ and it is reasonable to linearize it on the deviation in ζ. It leads to

$$J(\zeta) = J(\zeta_0) \exp\left(\Gamma \frac{\zeta - \zeta_0}{\zeta_0}\right), \qquad (14)$$

where ζ_0 is some base for decomposition and Γ is a parameter of linearization. For Γ in (14) one can get

$$\Gamma = \zeta_0 \left.\frac{dF}{d\zeta}\right|_{\zeta=\zeta_0} = \zeta_0 \nu_c \left.\frac{d\mu}{d\zeta}\right|_{\zeta=\zeta_0}, \qquad (15)$$

where μ is the chemical potential and ν_c is the number of the molecules in the critical embryo. The function $\zeta_0 d\mu/d\zeta$ is rather smooth and takes moderate values. For μ of the mother phase system like the ideal gas (i.e., for every mother phase where the mean field approximation works) one can easily come to

$$\zeta_0 \left.\frac{d\mu}{d\zeta}\right|_{\zeta=\zeta_0} = \frac{\zeta_0}{\zeta_0 + 1}. \qquad (16)$$

So according to (15), (16) one can estimate Γ as ν_c and it is possible to see that Γ gets the big values ($\nu_c \gg 1$ to ensure the thermodynamic description of the critical embryo). It means that the dependence of J on ζ is rather sharp.

Later the mentioned estimate leads to the estimate

$$\frac{|\zeta - \zeta_!|}{\zeta_!} \sim \nu_c^{-1} \qquad (17)$$

during the period of intensive nucleation. Here $\zeta_!$ is the value of ζ at some characteristic moment which belongs to the nucleation period.

Also one can get the estimate analogous to (17) for Φ

$$\frac{|\Phi - \Phi_!|}{\Phi_!} \sim \nu_c^{-1} \qquad (18)$$

and on the base of (18) one can see that also

$$\frac{|t - t_!|}{t_!} \sim \nu_c^{-1}. \qquad (19)$$

The last estimate shows that the nucleation period is relatively short in time. Namely, estimate (19) allows speaking above about $t_+, t_*,$ and t_{**} as some moments of time for nucleation.
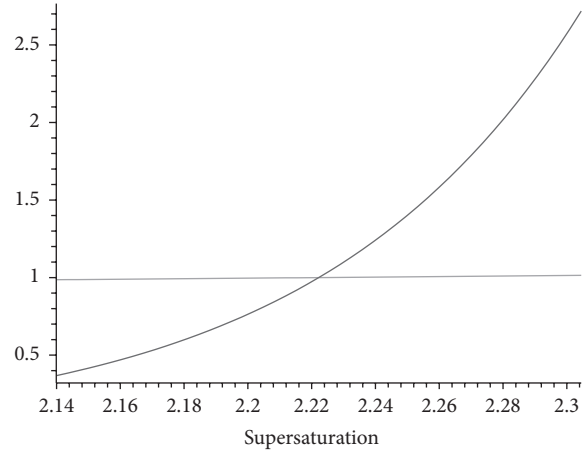

Figure 1: Behavior of the exponential and preexponential factors for the nucleation rate.

To see that the exponential approximation really works one can present the characteristic behavior of the Zeldovich factor Z^+ for the pseudo-homogeneous case. It is shown in Figure 1. One can see here two lines: the practically constant line which is the reduced Zeldovich factor and the exponent which is the main Boltzmann factor. So one can see that the preexponential factor (Zeldovich factor) does not really change. Here the worst value for the parameter Γ is $\Gamma = 27$ and the worst value for the renormalized surface tension σ is $\sigma = 10$ (the biggest possible value in the normal conditions). Namely, these values are taken for this example. Certainly, one can not include here the explicit time dependence of the kinetic coefficient of adsorption.

Really, the relative change of the preexponential factor here has the order $1/27 = \Gamma^{-1}$. It can be hardly seen in Figure 1 because the variation is very small.

3. Nucleation without Heterogeneous Impurities

To calculate G one has to know not only the rate of nucleation J but also the rate of the embryos growth. Fortunately the free molecular regime leads to the following rather simple rate of growth of the number ν of the molecules inside the supercritical embryo:

$$\frac{d\nu^{1/3}}{dt} = \frac{\zeta}{\tau} \qquad (20)$$

with characteristic parameter τ. Certainly,

$$\tau \sim K_0^{-1}. \qquad (21)$$

Namely, (21) shows that the time t_0 of freezing stops the growth.

One can prove that in calculation of G only the input from the supercritical embryos has to be taken into account.

Fortunately $d\nu^{1/3}/dt$ according to (20) is rather unsensitive to the supersaturation and there is no need to observe

the influence of the nucleation on the rate of the embryos growth. Then for the embryo appeared at t' the number of molecules will be approximately

$$\nu = \left(\frac{\zeta}{\tau}\right)^3 (t - t')^3 \tag{22}$$

and with account of (17) one can transform (22) into

$$\nu = \left(\frac{\zeta_!}{\tau}\right)^3 (t - t')^3. \tag{23}$$

On the base of (23) the expression for G will be

$$G(t) = \int_{-\infty}^{t} dt' (t - t')^3 \frac{J(t')}{n_\infty} \left(\frac{\zeta_!}{\tau}\right)^3. \tag{24}$$

Then balance equation (13) on the base of (24) can be written as

$$\zeta = \Phi - \int_{-\infty}^{t} dt' (t - t')^3 \frac{J(t')}{n_\infty} \left(\frac{\zeta_!}{\tau}\right)^3. \tag{25}$$

Having inserted the mentioned linearizations and exponential approximation (14), (15) for J it is possible to come in (25) to

$$\zeta(t) = \phi t - \frac{J(\zeta(t_+))}{n_\infty}$$
$$\cdot \int_{-\infty}^{t} dt' (t - t')^3 \exp\left(\Gamma \frac{(\zeta(t') - \zeta_+)}{\zeta_+}\right) \left(\frac{\zeta_+}{\tau}\right)^3. \tag{26}$$

Expression (26) has enough high accuracy.

One can prove that

$$\frac{|\Phi_+ - \zeta_+|}{\Phi_+} \sim \nu_c^{-1}. \tag{27}$$

Estimate (27) allows taking Φ_+ instead of ζ_+ and writing (26) as

$$\zeta(t) = \phi t - \frac{J(\Phi(t_+))}{n_\infty}$$
$$\cdot \int_{-\infty}^{t} dt' (t - t')^3 \exp\left(\Gamma \frac{(\zeta(t') - \Phi_+)}{\Phi_+}\right) \left(\frac{\Phi_+}{\tau}\right)^3. \tag{28}$$

Having shifted the time to have the zero point at t_+ one can come instead of (28) to

$$\zeta(t) = \phi t + \Phi_+ - \frac{J(\Phi(t_+))}{n_\infty}$$
$$\cdot \int_{-\infty}^{t} dt' (t - t')^3 \exp\left(\Gamma \frac{(\zeta(t') - \Phi_+)}{\Phi_+}\right) \left(\frac{\Phi_+}{\tau}\right)^3. \tag{29}$$

The last equation (29) is typical for nucleation and is formulated, for example, in [47] as one of the limit cases. It can be solved by iterations

$$\zeta_{(i+1)}(t) = \phi t + \Phi_+ - \frac{J(\Phi(t_+))}{n_\infty} \int_{-\infty}^{t} dt' (t - t')^3$$
$$\cdot \exp\left(\Gamma \frac{(\zeta_{(i)}(t') - \Phi_+)}{\Phi_+}\right) \left(\frac{\Phi_+}{\tau}\right)^3. \tag{30}$$

The lower index in brackets indicates the number of iteration. The initial approximation in the iteration procedure (30) is

$$\zeta_{(0)} = \Phi_+ + \phi t. \tag{31}$$

The first approximation calculated on the base of (31) is

$$\zeta_{(1)}(t) = \phi t + \Phi_+ - \frac{J(\Phi(t_+))}{n_\infty} \left(\frac{\Phi_+}{\tau}\right)^3$$
$$\cdot \int_{-\infty}^{t} dt' (t - t')^3 \exp\left(\Gamma \frac{\phi t'}{\Phi_+}\right). \tag{32}$$

Since

$$\int_{-\infty}^{t} dt' (t - t')^3 \exp\left(\Gamma \frac{\phi t'}{\Phi_+}\right)$$
$$= \exp\left(\Gamma \frac{\phi t}{\Phi_+}\right) \left(\Gamma \frac{\phi}{\Phi_+}\right)^{-4} 6 \tag{33}$$

it is easy to come in (32) on the base of (33) to

$$\zeta_{(1)}(t)$$
$$= \phi t + \Phi_+$$
$$- \frac{J(\Phi(t_+))}{n_\infty} \left(\frac{\Phi_+}{\tau}\right)^3 \exp\left(\Gamma \frac{\phi t}{\Phi_+}\right) \left(\Gamma \frac{\phi}{\Phi_+}\right)^{-4} 6. \tag{34}$$

Equation (34) has enough high accuracy.

One can prove that already the first approximation is rather good and the size spectrum

$$J(t) = J(\Phi_+) \exp\left(\Gamma \frac{\left(\phi t - (J(\Phi(t_+))/n_\infty)(\Phi_+/\tau)^3 \exp(\Gamma(\phi t/\Phi_+))(\Gamma(\phi/\Phi_+))^{-4} 6\right)}{\Phi_+}\right) \tag{35}$$
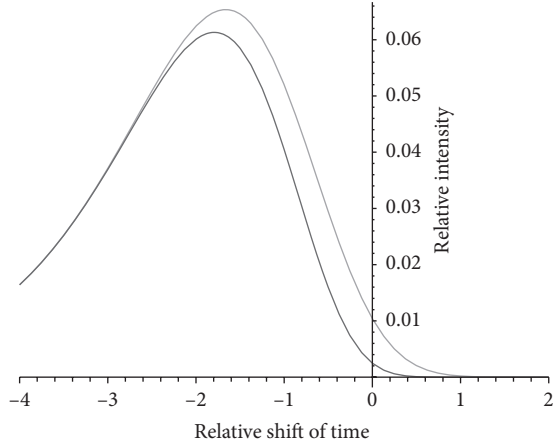
is rather accurate.

FIGURE 2: The fist and the second iterations for the nucleation rate as a function of the time shift. Here the nucleation rate is drawn in special renormalized units.

The rate of nucleation in the first (see (35)) and the second approximations of the iteration procedure is drawn in Figure 2. One can see here two lines: the lower line is the first iteration and the upper line is the second iteration for the nucleation rate as a function of the special shifted and scaled time.

One can see that the first iteration is rather close to the second one. One can see the similarity of the forms of the first and the second iteration. If it is necessary to increase the accuracy one can make a simple shift.

One can choose t_+ as the moment of the maximal supersaturation. Then

$$\phi = \frac{J(\Phi(t_+))}{n_\infty} \left(\frac{\Phi_+}{\tau}\right)^3 \left(\Gamma \frac{\phi}{\Phi_+}\right)^{-3} 6 \qquad (36)$$

is the algebraic equation on parameters (actually on Φ_+) and the good approximation to solve (36) is

$$\phi = \frac{J(\Phi(t_+))}{n_\infty} \tau^{-3} \left(\frac{\Gamma}{\phi}\right)^{-3} 6. \qquad (37)$$

Approximation (37) is rather accurate.

All what has been done is necessary to show that G at t_+, that is, G_+, can be estimated as

$$G_+ = \Gamma_+^{-1} \Phi_+ = \nu_c(t_+)^{-1} \Phi_+. \qquad (38)$$

Although (38) is rather simple it will be absolutely sufficient for further constructions.

Now the further evolution will be considered. One can see there two periods. The first period is the rapid consumption of the surplus substance

$$G_{\text{surplus}} = \Phi_+ \left(1 - \Gamma_+^{-1}\right). \qquad (39)$$

It is finished at some moment of time $t_{|+}$ when the whole (or practically all) surplus substance G_{surplus} is in the embryos. Now one has to estimate $t_{|+}$. It is possible to see on the base of (39) that

$$t_{|+} - t_+ \sim \Gamma^{-2/3} t_+. \qquad (40)$$

So according to (40) this period is rather rapid. It allows supposing that the condition $t_0 > t_+$ also ensures

$$t_0 > t_{|+}. \qquad (41)$$

The probability that (41) is not observed is lower than $\Gamma^{-2/3} \ll 1$.

Later the supersaturation is fallen and there will be an asymptotic period where $G \approx \Phi$. Here the mean effective linear coordinate L of the spectrum grows very slow like $L \sim t^{1/3}$. At t_0 it stops to grow. It is reasonable to put

$$L(t_0) \approx L(t_{|+}) \qquad (42)$$

and (42) gives the natural condition for the mean linear size of the embryos.

Here one has to make one important notation. In the liquid-vapor transition the volume ν_v per molecule in a vapor phase is a thousand times greater than the volume per particle ν_l in a liquid phase. This ensures that the relative volume of the new phase in vapor-liquid transition is small.

In the opposite liquid-vapor transition it seems that the situation will be opposite and the whole volume begins to be the vapor phase. But here the main effect of the bubble formation is to take away the surplus stretching. It is necessary to keep in mind.

In the situation of the liquid-crystal transition the volume ν_k per the molecule in a crystal phase is comparable with ν_l and it is possible to see the crystallization of the whole volume (ordinary this does not take place because of the heat release effects). But in the process of vitrification the mother phase is so viscous that the main effect of the appearance of the crystal embryo is to take away the stretching and the tension in the mother media. Then the relative volume of the new crystal phase will be small at $t_{|+}$.

Later without t_0 the crystal phase would cover practically the whole volume. But the cut-off of the nucleation and condensation process at t_0 will stop the consumption of the volume by the crystal phase. Unfortunately one can not radically change $\Phi(t)$ and t_0. That is why the method of heterogeneous centers insertion is suggested.

4. Formation of the Embryos on the Active Heterogeneous Impurities

Now the process of the heterogeneous condensation will be studied. It is supposed that the centers are relatively active. This means that all of them are exhausted in the process of nucleation. This property simplifies the theoretical description of kinetics of the phase formation.

One can note that the attribution of the centers (sites) to the group of the active ones depends on the intensity of the change of the external conditions. So this property is not absolute.

It is supposed also that the embryos on the heterogeneous centers can be described thermodynamically. It means that the number of molecules ν_c in the critical embryo is big enough. As for the number ν_e of the molecules inside the equilibrium center one can avoid the restriction $\nu_e \gg 1$ necessary for the thermodynamic description of the equilibrium
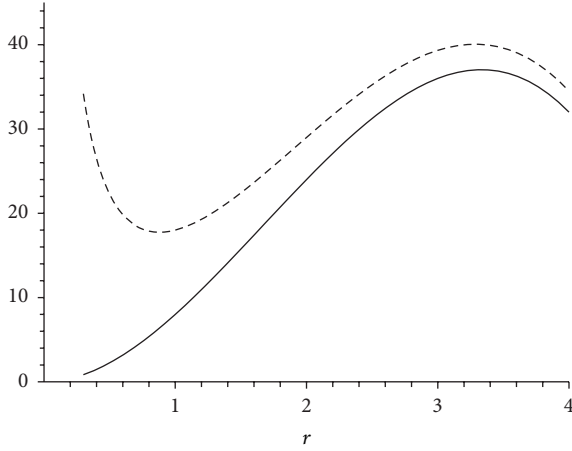
FIGURE 3: Heterogeneous and homogeneous free energies.

embryo. It can be done since only the behavior of the height of the activation barrier

$$\Delta F = F\left(\nu_c\right) - F\left(\nu_e\right) \tag{43}$$

is interesting and it determines the results of nucleation. Here the variation of $F(\nu_e)$ because of uncertainty of deviation of the embryos description from the thermodynamic one will be small in comparison with ΔF.

The behavior of the heterogeneous embryo free energy together with the behavior of the homogeneous free energy is drawn in Figure 3. The solid line is the homogeneous free energy and the dashed line is the heterogeneous free energy. Here the capillary model

$$F = \sigma r^2 - \ln\left(\zeta + 1\right) r^3 \tag{44}$$

for $r = \nu^{1/3}$ is used for the homogeneous case. As in Figure 1 the values $\sigma = 10$ and $\zeta \approx 2$ are used. In the heterogeneous case

$$F = \sigma r^2 - \ln\left(\zeta + 1\right) r^3 + \frac{\tilde{c}}{r}. \tag{45}$$

Here $\tilde{c} = 10$ is used as a value comparable with σ. Certainly, this example (namely, (44), and (45)) is no more than a model.

Since one can prove that

$$\begin{aligned} \frac{dF_c}{d\mu} &= \nu_c, \\ \frac{dF_e}{d\mu} &= \nu_e, \end{aligned} \tag{46}$$

where μ is a chemical potential, one can see that according to (43), (46) only when $\nu_e \gg 1$ is the value $dF_e/d\mu$ essential in $d\Delta F/d\mu$. So when ν_e is small one can not describe the equilibrium embryo adequately but the dependence of F_e on ζ (which means the dependence on μ) is not important.

For heterogeneous nucleation the nucleation rate is given by

$$\widehat{J} = n_{\text{het}} W_c^+ \exp\left(-\Delta F\right) \frac{Z^+}{\Delta_e \nu}, \tag{47}$$

where n_{het} is the number of the free heterogeneous centers (unoccupied by the supercritical embryos) and $\Delta_e \nu$ comes from the equilibrium distribution

$$n^e = n_{\text{het}} \frac{\exp\left(-\left(F - F_e\right)\right)}{\Delta_e \nu}. \tag{48}$$

So the structure of the rate of nucleation (47), (48) remains the same; it is the equilibrium distribution formally prolonged until the critical embryo and multiplied by the kinetic factor and by the truncated Zeldovich factor Z^+.

Instead of the general theory (see [47]) one can simply note that all centers will be exhausted when the ideal number of the formed droplets $N_{\text{id het}}$ which is calculated as

$$N_{\text{id het}} = \int_{-\infty}^{t} \widehat{J}\left(\Phi\left(t'\right), n_{\text{het}} = n_{\text{tot}}\right) dt', \tag{49}$$

where n_{tot} is the total number of heterogeneous centers, is equal to n_{tot}. The requirement of essential exhaustion of heterogeneous centers together with (49) gives an equation

$$\int_{-\infty}^{t} \widehat{J}\left(\Phi\left(t'\right), n_{\text{het}} = n_{\text{tot}}\right) dt' = n_{\text{tot}} \tag{50}$$

on t.

To solve (50) more effectively it is reasonable to introduce an approximation

$$\begin{aligned} &\widehat{J}\left(\Phi\left(t\right), n_{\text{het}} = n_{\text{tot}}\right) \\ &= \widehat{J}\left(\Phi\left(t_*\right), n_{\text{tot}}\right) \exp\left(\Gamma_{\text{het}} \frac{\Phi\left(t\right) - \Phi_*}{\Phi_*}\right), \end{aligned} \tag{51}$$

where

$$\Gamma_{\text{het}} = \Phi_* \left(\frac{dF_c}{d\zeta} - \frac{dF_e}{d\zeta}\right)\Bigg|_{\zeta = \Phi_*}. \tag{52}$$

The accuracy of (51), (52) is rather high.

One can easily estimate Γ_{het} as

$$\Gamma_{\text{het}} = \Phi_* \left(\nu_c - \nu_e\right) \frac{d\mu}{d\zeta}\Bigg|_{\zeta = \zeta_0}. \tag{53}$$

Then (50) can be rewritten with the help of (53) as

$$\widehat{J}\left(\Phi\left(t_*\right), n_{\text{tot}}\right) \int_{-\infty}^{t} \exp\left(\phi t'\right) dt' = n_{\text{tot}} \tag{54}$$

and gives

$$\widehat{J}\left(\Phi\left(t_*\right), n_{\text{tot}}\right) = n_{\text{tot}} \phi \tag{55}$$

or

$$W_c^+ \exp\left(-\Delta F\left(\Phi_*\right)\right) \frac{Z^+}{\Delta_e \nu} = \phi. \tag{56}$$

Equation (56) does not contain n_{tot}. Certainly (54) and (54) do not contain it also. So the power of exhaustion and the level of exhaustion are purely determined by the nature of centers

and do not depend on their quantity. This allows speaking about the active centers. It is possible to see that having changed the number of centers one can change the numbers of the embryos which begin to consume metastability rather actively after t_*.

The detailed justification of the presented method is rather long but it exists at the level of precise analytical derivation.

5. Formation of the Pseudo-Homogeneous Embryos

Now the formation of the pseudo-homogeneous embryos will be studied. The difference from the consideration of the homogeneous nucleation presented above will be the change of conditions for the new process because there are the heterogeneous consumers of metastability.

Certainly, the new forming embryos consume metastability and this leads to the perturbation of the rate of growth of the supercritical embryos formed on heterogeneous centers. But one can prove that this influence is very small and can be neglected. So one can see two separate problems here.

The first problem is to determine the supersaturation which appears after the heterogeneous embryos have been formed. The second problem is to determine the characteristics of the embryos size spectrum when the homogeneous process takes place.

The balance equation with account of only heterogeneous centers is written as

$$\phi t + \Phi_+ = \zeta + n_{\text{tot}} \frac{z(t)^3}{n_\infty}, \tag{57}$$

where $z(t)$ is the coordinate of the linear size of embryos and it can be found as

$$z(t) = \tau^{-1} \int_{t_*}^{t} dt' \zeta(t'). \tag{58}$$

So (57), (58) lead to the first-order differential equation which can be solved. One can reduce (57) with the help of (58) to

$$\frac{dz}{dt} + cz^3 t - at = 0 \tag{59}$$

with parameters a and c and get the solution of (59):

$$t = \sqrt{\left| \frac{2}{3} \frac{\ln\left|\left(z - (a/c)^{1/3}\right)\right|}{c(a/c)^{2/3}} - \frac{1}{3} \frac{\ln\left|\left(z^2 + z(a/c)^{1/3} + (a/c)^{2/3}\right)\right|}{c(a/c)^{2/3}} - \frac{2}{3} \frac{\sqrt{3}\arctan\left(\left((2/3)\left(z/(a/c)^{1/3}\right) + 1/3\right)\sqrt{3}\right)}{c(a/c)^{2/3}} + C_1 \right|} \tag{60}$$

with the arbitrary constant C_1 which has to be chosen to satisfy the initial condition

$$z|_{t=t_+} = 0. \tag{61}$$

So then (61) leads to the concrete value of the constant in (60) which will be the following:

$$C_1 = \sqrt{\left| \frac{2}{3} \frac{\ln\left|(a/c)^{1/3}\right|}{c(a/c)^{2/3}} - \frac{1}{3} \frac{\ln\left|(a/c)^{2/3}\right|}{c(a/c)^{2/3}} - \frac{2}{3} \frac{\sqrt{3}\arctan\left(((2/3)(1/3))\sqrt{3}\right)}{c(a/c)^{2/3}} \right|}. \tag{62}$$

Expression (62) has to be inserted into (60).

Unfortunately it is impossible to inverse the dependence $t(z)$ given by (60) and get the explicit solution. The dependence $t(z)$ for $a = 1, c = 1$ is drawn as an example in Figure 4.

One has to note that here it is impossible to use an approximation

$$z(t) = \frac{\Phi_+ (t - t')}{\tau} \tag{63}$$

analogous to (7) but it is necessary instead of (63) to integrate dz/dt explicitly.

Now the behavior of ζ will be analyzed qualitatively. The difference $\Phi - \zeta$ at first increases in time t very rapidly (faster than t^4) and this leads to the maximum of ζ even without homogeneous appearance of embryos. After attaining the maximum of the supersaturation it decreases and the conditions for the intensive homogeneous formation of new embryos disappear. So there exist two possibilities for the further homogeneous nucleation.

The first possibility is to see the nucleation in conditions of the growing Ψ which is

$$\Psi = \Phi - n_{\text{tot}} z^3(t) t. \tag{64}$$

Here in (64) the homogeneously formed embryos take part in the metastability consumption rather actively.

Alternative possibility is the following: the supersaturation ζ fully coincides with Ψ and homogeneously formed embryos do not play any essential role in evolution. Here the number of embryos is

$$N_{\text{hom}} = \int_{-\infty}^{\infty} dt' J\left(\Psi(t')\right) \tag{65}$$
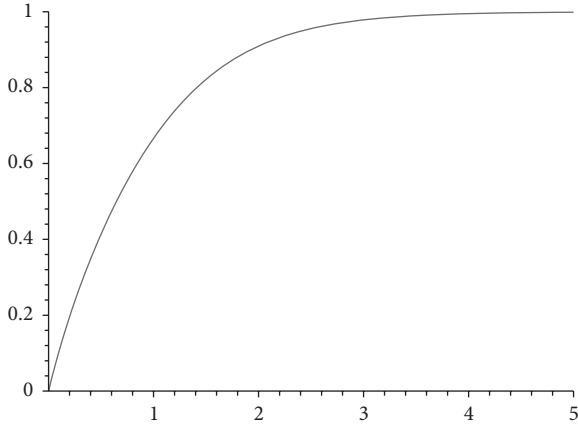
FIGURE 4: Solution $z(t)$ for $a = 1$, $c = 1$.

and the embryos linear size spectrum is

$$f\left(\rho\left(t''\right)\right) = \frac{J\left(t''\right)}{\left(\zeta\left(t''\right)/\tau\right)}, \qquad (66)$$

where

$$\rho\left(t''\right) = \int_{t''}^{t} dt' \frac{\Psi\left(t'\right)}{\tau} \qquad (67)$$

for $t < t_0$ and

$$\rho\left(t''\right) = \int_{t''}^{t_0} dt' \frac{\Psi\left(t'\right)}{\tau} \qquad (68)$$

for $t > t_0$. The accuracy of expressions (65), (66), (67), and (68) is sufficient.

One can use the exponential approximation based on max Ψ to calculate the number of droplets and the size spectrum. Also one can use the power decomposition of Ψ at the point of maximum.

The second possibility is not interesting also from the practical point of view because it requires essential number of heterogeneous centers (sites).

The only necessary fact which remains to be clarified is the existence of the time of the end of the rapid growth $t_|$ of the embryos sizes. Really, the rapid increase of $z^3 t$ can be stopped only when Φ comes to zero. But it has to be stopped because $z^3 t$ can not be greater than Φ. So $t_|$ exists.

How can one calculate $t_|$ and the linear size at the end of intensive growth $L_|$ (here these values are marked as $t_{|*}$ and $L_{|*}$)? There is no sharp sensitivity of these values to the supersaturation and one can get these values by the simple iteration procedure

$$z\left(t\right) = \frac{\phi}{2\tau}\left(t^2 - t_+^2\right),$$

$$\Psi = \phi t - \left(\frac{n_{\text{tot}}}{n_\infty\left(t_*\right)}\right)\left(\frac{\phi}{2\tau}\left(t^2 - t_+^2\right)\right)^3 t. \qquad (69)$$

Expressions (69) present the first step of this procedure.

The time $t_{|*}$ is determined as to satisfy the following equation:

$$\phi = \left(\frac{n_{\text{tot}}}{n_\infty\left(t_*\right)}\right)\left(\frac{\phi}{2\tau}\left(t_1^2 - t_+^2\right)\right)^3. \qquad (70)$$

The value $L_{|*}$ is

$$L_1$$
$$= \int_{t_*}^{t_1} dt \left(\phi t - \left(\frac{n_{\text{tot}}}{n_\infty\left(t_*\right)}\right)\left(\frac{\phi}{2\tau}\left(t^2 - t_+^2\right)\right)^3 t\right)\tau^{-1}. \qquad (71)$$

Expressions (70) and (71) have the necessary accuracy.

It is also necessary to determine the mean size $\widetilde{L}$ for the homogeneously formed embryos. It is

$$\widetilde{L}_{|*}$$
$$= \int_{t_m}^{t_1} dt \left(\phi t - \left(\frac{n_{\text{tot}}}{n_\infty\left(t_*\right)}\right)\left(\frac{\phi}{2\tau}\left(t^2 - t_+^2\right)\right)^3 t\right)\tau^{-1}, \qquad (72)$$

where t_m is the point of the maximum of Ψ. The last integral can be easily taken analytically since the integrand is the power function. Then (72) becomes a simple algebraic formula.

6. Conditions on Parameters of the Active Heterogeneous Centers

Now the first possibility will be considered. Here consideration is similar to the case of the pure homogeneous nucleation but it is necessary to consider Ψ instead of Φ.

The function Ψ is determined and it is possible to approximately linearize it at the point t_{**} and to get

$$\Psi\left(t\right) = \Psi_{**} + \psi\left(t - t_{**}\right), \qquad (73)$$

where

$$\psi = \left.\frac{d\Psi}{dt}\right|_{t=t_{**}}. \qquad (74)$$

Formula (73) (with account of (74)) is quite analogous to (7).

The balance equation is

$$\zeta\left(t\right) = \psi t + \Psi_{**} - \frac{J\left(\Psi\left(t_{**}\right)\right)}{n_\infty}$$
$$\cdot \int_{-\infty}^{t}\left(t - t'\right)^3 \exp\left(\Gamma\frac{\left(\zeta\left(t'\right) - \Psi_{**}\right)}{\Psi_{**}}\right)\left(\frac{\Psi_{**}}{\tau}\right)^3 \qquad (75)$$

and t is counted from t_{**}.

The last equation (75) can be solved by iterations

$$
\zeta_{(i+1)}(t) = \psi t + \Psi_{**} - \frac{J(\Psi(t_{**}))}{n_\infty}
$$
$$
\cdot \int_{-\infty}^{t} (t - t')^3 \exp\left(\Gamma \frac{(\zeta_{(i)}(t') - \Psi_{**})}{\Psi_{**}}\right) \left(\frac{\Psi_{**}}{\tau}\right)^3. \tag{76}
$$

The lower index in brackets which appeared in (76) indicates the number of iteration. The initial approximation will be

$$
\zeta_{(0)} = \Psi_{**} + \psi t. \tag{77}
$$

The first approximation on the base of (77) is

$$
\begin{aligned}
\zeta_{(1)}(t) &= \psi t + \Psi_{**} \\
&- \frac{J(\Psi(t_{**}))}{n_\infty} \left(\frac{\Psi_{**}}{\tau}\right)^3 \exp\left(\Gamma \frac{\psi t}{\Psi_{**}}\right) \left(\Gamma \frac{\psi}{\Psi_{**}}\right)^{-4} 6.
\end{aligned} \tag{78}
$$

One can prove that already the first approximation (78) is rather good and gives the size spectrum

$$
J(t) = J(\Psi_{**}) \exp\left(\Gamma \frac{\left(\psi t - J(\Psi(t_{**}))(\Psi_{**}/\tau)^3 \exp(\Gamma(\psi t/\Psi_{**}))(\Gamma(\psi/\Psi_{**}))^{-4}(6/n_\infty)\right)}{\Psi_{**}}\right). \tag{79}
$$

The form of the size spectrum given by (79) is rather accurate.

One can choose t_{**} as the moment of the maximal supersaturation. Then

$$
\psi = \frac{J(\Psi(t_{**}))}{n_\infty} \left(\frac{\Psi_{**}}{\tau}\right)^3 \left(\Gamma \frac{\psi}{\Psi_{**}}\right)^{-3} 6 \tag{80}
$$

is the algebraic equation on Ψ_{**}. The solution of (80) is approximately

$$
\psi = \frac{J(\Psi(t_{**}))}{n_\infty} \tau^{-3} \left(\frac{\Gamma}{\psi}\right)^{-3} 6. \tag{81}
$$

Formula (81) solves the problem to find parameters of the spectrum.

Now the further evolution will be considered. Since Ψ already ensured $t_|$, here one can also see $t_|$ which will be marked as $t_{|**}$. One can show that

$$
\frac{|t_{|**} - t_{**}|}{t_{**}} < \frac{|t_* - t_{|*}|}{t_*} \tag{82}
$$

if it is supposed that Γ_* is equal to Γ_{**}. So here also

$$
\frac{|t_{|**} - t_{**}|}{t_{**}} < \Gamma_{**}^{-1} \tag{83}
$$

and one can see on the base of (82), (83) that $t_0 > t_+$ practically ensures $t_0 > t_{|**}$.

The final values will be

$$
\begin{aligned}
L(t_0) &\approx L(t_{|**}), \\
\tilde{L}(t_0) &\approx \tilde{L}(t_{|**}).
\end{aligned} \tag{84}
$$

Equations (84) demonstrate the necessary accuracy.

The value $L(t_{|**})$ is calculated as

$$
L(t_{|**}) \approx L(t_m), \tag{85}
$$

where

$$
L(t_m) = \int_{t_*}^{t_m} \frac{\Psi(t')}{\tau} dt'. \tag{86}
$$

Approximation of (85), (86) has enough high accuracy.

The value $\tilde{L}(t_{|**})$ is calculated as

$$
N_{\text{tot hom}} \left(\tilde{L}(t_{|**})\right)^3 = \Psi(t_{**}), \tag{87}
$$

where $N_{\text{tot hom}}$ is the total number of embryos formed homogeneously in units of $n_\infty(t_{**})$. The value $N_{\text{tot hom}}$ appearing in (87) is already determined. If one takes an approximation

$$
\tilde{L}(t_{|**}) = \left(\frac{\Psi_{**}}{\tau}\right)(t_{|**} - t_{**}) \tag{88}
$$

one can get the following expression for $t_{|**}$:

$$
t_{|**} = t_{**} + \frac{(\Psi(t_{**})/N_{\text{tot hom}})^{1/3}}{(\Psi_{**}/\tau)}. \tag{89}
$$

Expressions (88), (89) complete the recipe of calculations.

7. Conclusions

The known value of Φ_{**} allows getting the total number of the homogeneously formed embryos as

$$
N_{\text{tot hom}} = \frac{J(\Psi_{**})}{n_\infty(t_{**})} \int_{-\infty}^{\infty} dt' \exp\left(\Gamma_{**} \frac{\left(\psi t' - J(\Psi(t_{**}))(\Psi_{**}/\tau)^3 \exp(\Gamma(\psi t'/\Psi_{**}))(\Gamma\psi/\Psi_{**})^{-4}(6/n_\infty)\right)}{\Psi_{**}}\right). \tag{90}
$$

The integration can be performed analytically which brings (90) to

$$N_{\text{tot hom}} = \frac{J(\Psi_{**})}{n_\infty(t_{**})} \frac{\Psi_{**}}{\Gamma_{**}\psi} \left(\Gamma_{**} J(\Psi(t_{**})) \right) \left(\frac{\Psi_{**}}{\tau} \right)^3$$
$$\cdot \left(\Gamma \frac{\psi}{\Psi_{**}} \right)^{-4} \frac{6}{n_\infty \Psi_{**}} \right)^{-1} . \tag{91}$$

Simple formula (91) allows calculating $N_{\text{tot hom}}$.

Changing ΔF one can choose t_*. Changing n_{tot} one can choose the force of the action of heterogeneous centers and then choose t_{**}. Then one can get necessary $\widetilde{L}(t_0)$ and $N_{\text{tot hom}}$.

The second possibility when the supersaturation is determined by the heterogeneously formed embryos is not too attractive because here the number of heterogeneous centers is greater than in the first variant and can be even greater than the number of homogeneously formed embryos. The only positive property is that in the majority of situations

$$t_{|*} < t_{|+} \tag{92}$$

and one can hope that

$$t_{|*} < t_0. \tag{93}$$

So the process of nucleation is frozen only after the end of essential stages of nucleation. The probability of violation of (92), (93) is practically negligible.

In the first variant the number $n_{\text{tot}}/n_\infty(t_*)$ is many times smaller than $N_{\text{tot hom}}$:

$$\frac{n_{\text{tot}}}{n_\infty(t_*)} \ll N_{\text{tot hom}}. \tag{94}$$

Then one can simply say that the optical properties are determined according to (94) by $\widetilde{L}(t_0)$ and $N_{\text{tot hom}}$. Now the method of how to regulate these values is presented.

The most serious limitation of the theory is the free molecular regime of growth. It leads to the collective consumption of metastability. But when the quantity of the heterogeneous centers is small the region of influence of every heterogeneous center is large enough and it is impossible to keep the free molecular regime here. Fortunately there is a certain analogy between the situation of the collective consumption and the situation with the zones of depletion. This analogy was established in [48]. The mentioned fact was seen for the period of nucleation. Here the situation is more complex because there is no appearance of new embryos after t_*. So here there is a nucleation in the system with some very curved boundaries (the boundaries of exhausted regions) and these boundaries move rather slowly. But although the situation is another it is possible to see that the maximum of Ψ can be taken in the first iteration, that is, on the base of the metastability consumption which occurs by the ideal law, that is, in approximation $\zeta = \Phi$. This approximation is good for all Φ with $d^2\Phi/dt^2 \leq 0$, that is, for convex functions. But for $d^2\Phi/dt^2 > 0$ there appears another stabilizing factor: the rate of the supersaturation growth rapidly increases and the consumption of metastability increases. It means that the boundaries begin to move rather rapidly and the error in the position of these boundaries is not too important. So the form of the free volume can be smoothed and it is possible to come to the absence of the effects of the noncollective consumption. In any case this question forms a matter of a separate publication.

List of Variables

A: Surface area of the embryo

a: Parameter in the equation for the evolution after the heterogeneous nucleation stops

b: Surplus chemical potential

c: Parameter in the equation for the evolution after the heterogeneous nucleation stops

$\widetilde{c}$: Parameter in the model for the free energy of the embryo on heterogeneous center

c: Index to mark the critical embryo

e: Index to mark to equilibrium embryo

F: Free energy of the embryo measured in the thermal units $k_B T$ (K_B is the Boltzmann constant and T is the absolute temperature)

f: Size spectrum of the embryos

G: Number of the molecules in the crystalline phase calculated in units of n_∞

J: Rate of nucleation

K: Condensation coefficient

K_0: Basis for the approximation for K

k_π: Coefficient in linearization of Π

$L_|$: Number of molecules in a new phase at the end of intensive growth

$\widetilde{L}$: Mean size for the homogeneously formed embryos

$N_{\text{id het}}$: Number of heterogeneously formed droplets calculated in approximation of the total number of the free heterogeneous centers

n: Mean concentration of the molecules in the noncrystalline phase

n_1: Number of sites (or the molecules) which can be the starting point for the nucleation (crystallization) formation of the embryo

n^e: Equilibrium distribution

n_{het}: Number of the free heterogeneous centers (unoccupied by the supercritical embryos)

n_{near}: Density of the molecules in the vicinity of the embryo

n_{tot}: Total number of heterogeneous centers

n_∞: Concentration of molecules in the noncrystalline phase at the state of the phase coexistence

r: Linear size of the embryo

T: Absolute temperature

t: Time

t_0: Time of the "freezing" of the system, which is a parameter in approximation for kinetic coefficient

t_+: Moment of intensive formation of the pseudo-homogeneous embryos

t_*: Time of appearance of embryos on the active heterogeneous centers

t_{**}: Moment of the pseudo-homogeneous formation in the presence of active heterogeneous centers

$t_|$: Time of the end of the rapid growth of the embryos sizes

v_t: Mean thermal velocity of the molecule

W_c^+: Kinetic factor (intensity of adsorption of the molecules by the embryo)

Z: Zeldovich factor

Z^+: Truncated Zeldovich factor

z: Coordinate of the spectrum of the heterogeneously formed embryos

ΔF: Height of the activation barrier of nucleation

$\Delta_e \nu$: Width of the equilibrium zone

Γ: Parameter of decompositions for the free energy, which ordinary equals the total number of the molecules inside the homogeneous critical embryo or the difference between the number of molecules in the critical embryo and the number of molecules in the equilibrium embryo

Γ_{het}: Parameter Γ for heterogeneous nucleation

μ: Chemical potential

ν: Number of molecules in the embryo

ν_c: Number of molecules in the critical embryo

ν_e: Number of molecules in the equilibrium embryo

Π: Activation barrier of accommodation

Φ: Imaginary metastability which would be in the system when the process of the new phase formation is forbidden

Φ_0: Basis for linearization of Φ

ϕ: Coefficient in linearization of Φ

Ψ: Supersaturation that would be in a system when the heterogeneous formation is allowed and the homogeneous mechanism is forbidden

ψ: Parameter of linearization of Ψ

ρ: A cubic root of ν

σ: Renormalized surface tension

τ: Characteristic time, parameter in the law of growth, which ordinary equals the mean time between collisions of some given molecule of the saturated disordered phase with other molecules in this phase

ζ: Power of metastability or the supersaturation

ζ_0: Basis for decompositions for ζ

!: Index denoting the values at the period of nucleation.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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Research Article

Decay of Metastable State with Account of Agglomeration and Relaxation Processes

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Theoretical description of the metastable phase decay kinetics in the presence of specific connections between the embryos of small sizes has been given. The theory of the decay kinetics in the presence of relaxation processes is constructed in analytical manner. The *m*-mers nucleation is investigated and the global kinetics of decay is also constructed in this case analytically.

1. Introduction

The first-order phase transition kinetics is actively investigated since the publication of the pioneer papers by Wilson [1–3] concerning the famous chamber which became the main tool in investigations of the microworld. The range of applications of the first-order phase transition kinetics inevitably grows since the phenomena concerning the self-organization [4, 5] and aggregation [6] become the field of application of ideas lying in the base of the mentioned kinetics. The word "nucleation" has nothing in common with nuclear phenomena but comes from the evident fact that the embryos of a new phase are rather compact objects and can be treated as some nucleus of a new phase. The main content of the theory which predicts the rate of appearance of the embryos of a new phase was published in several papers in the 1930s and 1940s which forms the classical theory of nucleation. The classical theory of nucleation [7, 8] gives a complete theoretical description but the problem is that there exists no correspondence between the theoretical predictions and experimental results.

The first theoretical investigation on the problem of the embryos (droplet) formation belong to W. Thomson (1870), who got the work of formation of the critical embryo and the size of the critical embryo. However, Laplace and Young were able to do this after their invention of the additional pressure under the curved surface. Certainly, the true meaning of the formulas arises only with the theoretical investigations by Gibbs (1877).

Historically the classical nucleation theory is associated with the following four papers [9–12] although many other contributions (see, e.g., [13], where for the first time was stressed that the preexponential kinetic factor has to account collisions of a vapor molecule with cluster) are rather important in creation of the nucleation theory.

After the creation of the classical nucleation theory the most radical reconsideration was proposed by Lothe and Pound [14] who suggested including into the free energy of a cluster the translational and rotational degrees of freedom. This point of view leads to the reconsideration of the rate of nucleation in dozen of orders of magnitudes. In some cases it brings the theory to the coincidence with experiment; in some cases the situation is the opposite one. The point of view of Lothe and Pound was reconsidered in [15, 16] and the effect in comparison with the classical nucleation theory became radically smaller. Here it is necessary to stress that the arguments of additional consideration of rotational and translational degrees of freedom for an embryo are rather doubtful.

Other approaches to improve the classical nucleation theory do not suggest such radical improvements. One can mention here the attempts to account the partial pressure of the cluster which is treated as a molecule [17, 18]. The effect of this idea is not too big in comparison with the effect of Lothe-Pounds' reconsideration.

The next approach is the so-called kinetic theory of nucleation suggested in [19, 20]. The long derivations in order

to solve the chain of kinetic equations finally led to the practically known results except the requirement to take into account the term corresponding to the surface tension of a cluster with one molecule which can not be treated formally in this sense but is certainly rather small correction factor.

The Dillmann-Meier theory of nucleation is a rather model version which can be treated as some postulate on the surface tension of a curved surface together with requirements of thermodynamic consistency and some other minor improvements [21, 22]. Certainly the theoretical ground of this approach is rather doubtful although the ideas are physically attractive.

The famous paper of Cahn and Hillard [23] is very beautiful theoretically but the jumps of the density between phases can be hardly described only by the first nontrivial term in the gradient decomposition. This makes the range of application of this approach rather narrow, namely, in the vicinity of a critical point. But in this vicinity one can hardly consider the embryo as a closed object. So, the use of the mentioned approach is rather restricted.

One can not find any mathematical gaps in the classical theory of nucleation. It means that some physical assumptions of the model are not too appropriate since the mathematical frames of theoretical construction are certainly correct.

One of the possible sources of the deviation of the theoretical predictions from the experimental results is the existence of the clusters (nonmonomers) with a relatively small free energy which actively changes the picture of the nucleation process. Nowadays effect is known under the name of prenucleation [24], although some of such clusters can belong to the blind channels which can not lead to the big supercritical clusters [25]; they are not nucleation centers. Nevertheless such terminology exists.

The last example belongs to biological systems. The complex behavior of the nucleation kinetics in biological systems is not a surprising fact since the complex structure of biological molecules is well known. More intriguing is the prenucleation importance in calcium containing systems [26]. The further analysis of the prenucleation phenomena [27] shows the possibility of many paths through a nucleation barrier to a supercritical zone. The nucleation processes through the different channels can even compete [28]. Unfortunately the experimental observations are rarely accompanied by the weighted theoretical constructions.

An evident intention to solve the appearing problems is to use computer calculations. Unfortunately it is impossible to check all suppositions of the theory by computer simulation since the nucleation process is the principally collective phenomenon and the true simulation has to consider billions of particles with precise numerical integration because the effect of nucleation is hidden in excesses from the phase coexistence line.

Ordinarily the attempts to improve the theory are aimed at getting the more reliable expression for the free energy of the critical embryo. There is no doubt that the critical embryo is the central object of the nucleation theory consideration but the constructions of the classical nucleation theory approach are valid only under the "good" behavior of the free

energies of embryos of other sizes and kinetic coefficients of ejection and absorption of the molecules for the embryos far from the critical one.

The "good" behavior means that there are no peculiarities in behavior of kinetic coefficients and no local extremal points of the free energy of classically noncritical embryos. Meanwhile there is absolutely no insurance that the mentioned "good" behavior really takes place. The experimental information is rather poor, kinetic coefficients are mainly measured on the basis of the growth rate [29], and this characteristic is measured with such an accuracy that one can put a question about the excesses in the growth rate [30]. The measurements of the growth rates can give only the difference between the adsorption and ejection coefficients but not exactly the values of these coefficients.

One can note that in the presence of the prenucleation centers the reconsideration of the rate of the stationary nucleation can be a nontrivial problem only in situations when the embryos have rather complex structure coming from various structural components (see, e.g., [25]). The methods to construct the stationary rate of nucleation are rather well known although one can find many interesting subjects in this question also.

Here we will focus on the kinetics of the global nucleation, that is, on the description of the global evolution of the system starting from the appearance of metastability up to the end of the active formation of the embryos of a new phase which grow irreversibly until the Ostwald ripening. The last stages of the phase transition including the coagulation [31] and Lifshic-Slezov asymptote [32, 33] are not the subject of this analysis because we are interested in the total number of supercritical embryos and formation of their sizes spectrum. The total number of embryos and their size spectrum are the main results of the phase transformation and later the coagulation and mutual consumption (it is better to use, namely, this terminology because the ordinary used word "coalescence" implies absolutely another physical process) will only deform the size spectrum and the total number of supercritical embryos.

To describe the global nucleation kinetics it is necessary to put the initial conditions. This requirement seems to be quite natural. We suppose that at the initial moment of time there exists in the system a metastable phase without a new phase and the process of nucleation begins. Otherwise we can define the initial moment as the last moment before appearance of the first traces of a new phase. No further external action on the system is implied. This type of the initial and boundary conditions is quite natural and has the name of the decay of the metastable state.

The situation of decay without peculiarities in behavior of the free energy of a small cluster was considered in [34] where the complete theory was constructed. It is shown that the evolution of the system can be described by the substance balance equation in some special form. For our purposes to describe the kinetics in the situation where one size of clusters is extracted by a very small free energy the analogy with heterogeneous nucleation will be very useful. In heterogeneous nucleation the kinetics of the process is governed not only by the fall of the supersaturation but also by

the exhaustion of heterogeneous centers which become the centers of the droplets. Here the theory was given in 1989 [35] but the gap in the theory was filled only in 1993 [36].

The peculiarities in connections between the small clusters in a mother phase can cause very specific behavior of the global nucleation kinetics. Although already many important cases were considered there exist enough important situations necessary to be described theoretically. Below we will give the theoretical description of some of them.

2. Weak Relaxation of Seeds in Monomer Nucleation

The first important case is the situation when in the monomer nucleation there exists a weak connection between the region (in the scale of sizes) of monomers and the region of m-mers and it is necessary to take into account not only the consumption of m-mers by the supercritical embryos (every embryo has to consume one m-mer to start the life) but also the weak source of monomers being transformed into m-mers. This source changes the kinetics of the process.

Here it is very useful to use the analogy with heterogeneous nucleation. Really, the m-mers can be considered as some objects analogous to heterogeneous centers. But the situation with the relaxation of heterogeneous centers has not been considered. So, there exists a nontrivial mathematical content of the constructions presented below.

We introduce the value of θ as

$$\theta = \frac{n\,[m, t]}{n\,[m, t = 0]}. \tag{1}$$

This value can be less or greater than 1. Here $n[m, t]$ is the number of embryos with m molecules at the time moment t.

One can formulate the system of equations for unknown functions g and θ and after some scaling get

$$\frac{d\theta}{dt} = -j\,(\theta - \theta_{\lim}) - T\theta\,[t]\exp\left(-g\,[t]\right) \tag{2}$$

$$g\,[t] = \int_0^t \left(t - t'\right)^3 \theta\,[t']\exp\left(-g\,[t']\right) dt'. \tag{3}$$

Here T is some positive parameter which can not be avoided. The positive parameter j shows the intensity of the relaxation process. The value $\theta_{\lim}$ is the equilibrium value. It is also a parameter.

Now we will clarify the meaning of two unknown functions g and θ of the time t. The function g is the relative number of the molecules in a new phase. The function θ is the relative number of the free (unoccupied by the supercritical embryos) heterogeneous centers.

Ordinarily the solution of the system of condensation equations (analogous to (2)-(3)) is given by iterations (see [37]). The behavior of the spectrum of sizes

$$f\,[t] = \theta\,[t]\exp\left(-g\,[t]\right) \tag{4}$$

is rather complex even already in the first iterations which are constructed in a way to simplify the form of the size

spectrum. This fact means that in our case one can not invent too "intelligent" iterations. Namely, the presentation of (3) in the already integrated form seems to produce too complex iteration procedure.

In investigation of the nucleation process with the absence of the relaxation process (see [37]) the following chains of inequalities,

$$\theta_{(1)} < \theta_{(3)} < \cdots < \theta < \cdots < \theta_{(2)}$$

$$g_{(0)} < g_{(2)} < \cdots < g < \cdots < g_{(3)} < g_{(1)}, \tag{5}$$

were formulated. This chain is very productive for the accuracy estimates which lead to the guaranteed accuracy of the obtained approximations.

To conserve these chains one can propose the following recurrent scheme:

$$\frac{d\theta_{(i+1)}}{dt} = -j\,(\theta_{(i)} - \theta_{\lim}) - T\theta_{(i)}\,[t]\exp\left(-g_{(i)}\,[t]\right)$$

$$g_{(i+1)}\,[t] = \int_0^t \left(t - t'\right)^3 \theta_{(i)}\,[t']\exp\left(-g_{(i)}\,[t']\right) dt' \tag{6}$$

with initial condition

$$\theta\,[t = 0] = 1 \tag{7}$$

and initial approximations

$$\theta_{(0)} = \theta_{\lim} \tag{8}$$

or

$$\theta_{(0)}\,[t] = \theta\,[t = 0]\,,$$

$$g_{(0)} = 0 \tag{9}$$

or the recurrent scheme

$$\frac{d\theta_{(i+1)}}{dt} = -j\,(\theta_{(i+1)} - \theta_{\lim})$$

$$- T\theta_{(i+1)}\,[t]\exp\left(-g_{(i)}\,[t]\right) \tag{10}$$

$$g_{(i+1)}\,[t] = \int_0^t \left(t - t'\right)^3 \theta_{(i)}\,[t']\exp\left(-g_{(i)}\,[t']\right) dt'$$

with the same initial condition and the same initial approximations. The third scheme is

$$\frac{d\theta_{(i+1)}}{dt} = -j\,(\theta_{(i)} - \theta_{\lim}) - T\theta_{(i+1)}\,[t]\exp\left(-g_{(i)}\,[t]\right)$$

$$g_{(i+1)}\,[t] = \int_0^t \left(t - t'\right)^3 \theta_{(i)}\,[t']\exp\left(-g_{(i)}\,[t']\right) dt' \tag{11}$$

with the same initial approximations and the same initial condition.

We have to choose what type of iterations is the best one.

The first procedure is absolutely correct and it can not lead to divergence at some step of iterations. The second and the third schemes require additional regularization. One has to put an additional restriction.

The Nucleation Process Stops When θ Attains Zero. This restriction is necessary to avoid the negative rate of nucleation and the divergence of iterations.

The account of the relaxation process in the nucleation kinetics is a hard problem. Already the first iteration from those where the effect of the relaxation term can be seen in the behavior of the supersaturation can not be calculated analytically.

To fulfil analytical calculations we have to fulfil an additional simplification based on the *property of the avalanche consumption.*

The mentioned property can be formulated as follows.

Under Any Behavior of $\theta > 0$ the Relative Growth of g Occurs Faster Than $(t - t_0)^3$. One can prove this property analytically. Actually, this property is evident since we take into account that $g = \int_0^t (t - t')^3 \theta[t'] \exp(-g[t']) dt'$ and $\theta > 0$.

On the basis of this property we see that the "pseudo-homogeneous spectrum of sizes" (the spectrum of sizes which would be formed if there would be no action of the number of free seeds on the nucleation process)

$$f_{\text{hom}} \sim \exp(-g) \tag{12}$$

will be truncated in a manner sharper than

$$\exp\left(-\left(\frac{t}{t_{\text{cut}}}\right)^3\right), \tag{13}$$

where t_{cut} is the characteristic time. Then one can speak about the cut-off type of the pseudo-homogeneous spectrum of sizes.

Now one can see the qualitative behavior of θ. At first θ relaxes to the value

$$\theta_n = \frac{j}{j + T} \theta_{\text{lim}} \tag{14}$$

with characteristic time

$$t_{\text{rel}\,n} = (j + T)^{-1}. \tag{15}$$

This relaxation can lead to the increase of θ when

$$\theta[t = 0] < \theta_n \tag{16}$$

or to the decrease of θ in the opposite situation.

At the moment t_{cut} this relaxation is changed by the relaxation of θ to θ_{lim} with the characteristic time $t_{\text{rel}} = j^{-1}$.

The question which we are interested in is whether the change of θ can destroy the cut-off type of the real spectrum of sizes $\theta \exp(-g)$ (earlier the cut-off type was shown for $\exp(-g)$).

The destruction of the cut-off type of $\theta \exp(-g)$ can take place only under the sharp relative increase of θ. So, we have to estimate $(d\theta/dt)/\theta$. Since

$$\frac{d\theta}{dt} < j\theta_{\text{lim}}$$
$$\theta > \frac{j}{j + T} \theta_{\text{lim}} \tag{17}$$

we see that

$$\frac{d\theta/dt}{\theta} < j + T. \tag{18}$$

When $T \gg j$ one simply can not see the relaxation. The picture in this case is the picture described earlier (see [37]) plus some small perturbation. Then having excluded this situation we can rewrite the last inequality as

$$\frac{d\theta/dt}{\theta} < (3 \div 4)\, j. \tag{19}$$

Now we see that the danger of destruction of the cut-off form of the size spectrum can appear only at big values of j. Actually it has to be

$$j \gg t_{\text{cut}}^{-1}. \tag{20}$$

If $t_{\text{cut}} \ll T^{-1}$ then there is no exhaustion of seeds. So, the actual situation is $t_{\text{cut}} \geq T^{-1}$ and then we see that

$$j \gg T. \tag{21}$$

Here θ_{lim} is close to θ_n and then t_{cut} based on θ_{lim} is close to θ based on θ_n. This means that the cut-off behavior is not broken here. So, the property of the cut-off takes place in all situations.

The property of the cut-off allows using the approximation $\exp(-g) = 1$ for $t < t_{\text{cut}}$ and $\exp(-g) = 0$ for $t > t_{\text{cut}}$. The moment t_{cut} can be determined as the root of equation

$$g(t_{\text{cut}}) = 1. \tag{22}$$

Then for $t < t_{\text{cut}}$

$$\frac{d\theta}{dt} = -j(\theta - \theta_{\text{lim}}) - T\theta[t]$$
$$g[t] = \int_0^t (t - t')^3 \theta[t'] dt' \tag{23}$$

and one can explicitly calculate

$$\theta[t] = \theta_n - (\theta_n - \theta[t = 0]) \exp(-(j + T)t). \tag{24}$$

The value of g can be presented as

$$g = \int_0^t (t - t')^3$$
$$\cdot (\theta_n - (\theta_n - \theta[t = 0]) \exp(-(j + T)t')) dt' \tag{25}$$

and can be easily found analytically which allows getting t_{cut} as the solution of an ordinary algebraic equation.

Equation (22) can be easily solved since we know the estimates $\theta_n z^4/4$ and $\theta[0]z^4/4$ for the behavior of g which leads to the estimates for the roots. What estimate is the above estimate and what the below estimate is are determined by the sign of $\theta_{\text{lim}} - \theta[0]$.

The total number of droplets in the renormalized units can be found as

$$N = A \int_0^{t_{\text{cut}}} 1\, dt = At_{\text{cut}}, \tag{26}$$

where A is the initial amplitude (in renormalized values it equals 1) or as

$$N = A \int_0^{t_{cut}} \exp\left(-g\left[t\right]\right) \theta\left[t\right] dt, \qquad (27)$$

where for g and for θ one can take the mentioned approximations. The linearization of appearing exponents is also approximately suitable and leads to the presence of the result in elementary functions. One has to note that the first recipe seems to be more rough than the second one but it gives better results. The reason is the effective compensation of decrease of the intensity of appearance of new embryos before t_{cut} by the existence of the tail after t_{cut}. The refinement of equation for t_{cut} (it is better to use $g[t_{cut}] = \ln 2$) can make the first recipe very accurate. Certainly the further refinement with the help of the perturbation technique can be fulfilled.

Even the linear approximation

$$\theta = \theta\left[0\right] + \left(j + T\right)\left(\theta_n - \theta\left[0\right]\right) t \qquad (28)$$

truncated at the crossing point with θ_n, that is, at $(j + T)^{-1}$, and prolonged further as θ_n gives a rather good approximation for the characteristics of the process. This approximation ensures the pure algebraic equation of the fifth power for t_{cut}. It is a really suitable approximation since this approximation has the maximal deviation as $(j+T)^{-1}$ which is relatively small ($\sim \exp(-1)$) in comparison with initial deviation of θ from θ_n. Then the difference in integrals staying in (22) is less than two times which gives the difference for the duration of the intensive nucleation period in $2^{1/4} \approx 1.2$ times (in reality the difference in duration is much more small). The last approximation brings equation on root to the explicit formulas.

This completes the analytical description of the situation of the decay in the system with the relaxation process for the centers of nucleation.

3. Accumulation of Several Seeds in the Monomer Nucleation

The second important task is to consider the situation when it is necessary to spend q m-mers to form the supercritical embryo and the rate of nucleation is proportional to the number of m-mers in power q:

$$J \sim n\left[m\right]^q. \qquad (29)$$

It is interesting to investigate this situation and to see the transition to the case when q is great enough. Certainly the probability

$$P \sim n\left[m\right]^q \qquad (30)$$

transfers into

$$P \sim \exp\left(-\mu q\right) \qquad (31)$$

with a chemical potential

$$\mu = -\ln\left(n\left[m\right]\right) \qquad (32)$$

corresponding to the chemical potential of ideal gas.

The equation

$$\frac{dn\left[m\right]}{dt} = n\left[m\right]^q f\left[t\right] \qquad (33)$$

with some known function $f[t]$ can be written in the following integral form:

$$n\left[m\right] = \frac{n\left[m, t = 0\right]}{\left(\left(q - 1\right) \int_0^t f\left[t'\right] dt' + 1\right)^{1/(q-1)}}. \qquad (34)$$

Now we write the expression for the rate of nucleation in the generalized Clausius-Clapeyron integrated form as

$$J = J_0 \theta^q \exp\left(-\frac{\Gamma\left(\zeta - \Phi_*\right)}{\Phi_*}\right), \qquad (35)$$

where

$$\Gamma = \left.\frac{\Phi_* dF_c}{d\zeta}\right|_{\zeta = \Phi_*} \qquad (36)$$

and Φ_* is the base of decomposition. Here J_0 is the initial value of the rate of nucleation and θ is the relative number of m-mers referred to initial value.

One can get

$$\Gamma = \left(\frac{\Phi_*}{\left(\Phi_* + 1\right)}\right) \nu_{1c}, \qquad (37)$$

where ν_{1c} is the number of monomers in critical embryo. This number is connected with the total number of molecules ν_c in the critical embryo as

$$\nu_c = \nu_{1c} + qm. \qquad (38)$$

After the scaling the system of evolution equations is the following one:

$$g\left[z\right] = \int_0^z \left(z - x\right)^3 \theta^q\left[x\right] \exp\left(-g\left[x\right]\right) dx$$

$$\theta\left[z\right] = \left(\left(q - 1\right) A \int_0^z \exp\left(-g\left[x\right]\right) dx + 1\right)^{-1/(q-1)}. \qquad (39)$$

Here A is the coefficient which remains after the scaling and can not be canceled.

We can formulate the iteration procedure as follows:

$$g_{(i+1)}\left(z\right) = \int_0^z \left(z - x\right)^3 \theta_{(i)}^q\left[x\right] \exp\left(-g_{(i)}\left[x\right]\right) dx$$

$$\theta_{(i+1)}\left[z\right]$$

$$= \left(\left(q - 1\right) A \int_0^z \exp\left(-g_{(i)}\left[x\right]\right) dx + 1\right)^{-1/(q-1)}. \qquad (40)$$

The separation of the spectrum in g and θ which seems to be natural from the physical point of view is quite unusual from the formal point of view when the unique equation

$$g[z] = \int_0^z (z-x)^3$$
$$\cdot \left((q-1)A\int_0^x \exp\left(-g[x']\right)dx' + 1\right)^{-q/(q-1)} \quad (41)$$
$$\cdot \exp\left(-g[x]\right)dx$$

is considered. Then it is more natural to construct iterations as

$$g_{(i+1)}[z] = \int_0^z (z-x)^3$$
$$\cdot \left((q-1)A\int_0^x \exp\left(-g_{(i)}[x']\right)dx' + 1\right)^{-q/(q-1)} \quad (42)$$
$$\cdot \exp\left(-g_{(i)}[x]\right)dx$$

but this way does not correspond to appearance of the above and below estimates although it is possible to prove that these iterations with the initial approximation

$$g_{(0)} = 0 \quad (43)$$

converge to solution.

The procedure for θ and g as the separate functions which was formulated above will lead under the initial approximations

$$\theta_{(0)} = 1,$$
$$g_{(0)} = 0 \quad (44)$$

to the chains of inequalities

$$g_{(0)} < g_{(2)} < \cdots < g < \cdots < g_{(3)} < g_{(1)}$$
$$\theta_{(1)} < \theta_{(3)} < \cdots < \theta < \cdots < \theta_{(2)} < \theta_{(0)}. \quad (45)$$

Parameter A is considered here as constant value for all iterations and the concrete value of A will be determined on the basis of the last (precise) iteration.

It is useful to calculate the total number of supercritical embryos as

$$N_{\text{tot}} \sim \int_0^\infty \theta^q[x]\exp\left(-g[x]\right)dx. \quad (46)$$

On the basis of iteration procedure one can calculate

$$N_{\text{tot}(i+1)} \sim \int_0^\infty \theta_{(i)}^q[x]\exp\left(-g_{(i)}[x]\right)dx. \quad (47)$$

The calculation of iterations gives

$$g_{(0)} = \frac{z^4}{4}$$
$$\theta_{(1)} = \left((q-1)Az+1\right)^{-1/(q-1)}. \quad (48)$$

Then

$$N_{\text{tot}(2)} = \int_0^\infty \left((q-1)Az+1\right)^{-q/(q-1)} \exp\left(-\frac{z^4}{4}\right)dz \quad (49)$$

and this can be expressed through the hypergeometric function

$$N_{\text{tot}(2)} = 2^{(-9/2+2(q/(q-1)))}(q+A)^{-q/(q-1)}\left(\frac{1}{3}\right.$$

$$\cdot 2^{-(5/2)(q/(q-1))+1/2}\pi^4(q+A)^3\left(\frac{1}{q+A}\right)^{-q/(q-1)} H\left(\left[\frac{3}{4}\right.\right.$$

$$+\frac{1}{4}\frac{q}{q-1}, 1+\frac{1}{4}\frac{q}{q-1}, \frac{5}{4}+\frac{1}{4}\frac{q}{q-1}\right], \left[\frac{3}{2}, \frac{7}{4}, \frac{5}{4}\right],$$

$$\left.-\frac{1}{4}(q+A)^4\right)$$

$$\cdot \frac{\sec\left((1/4)\pi(q/(q-1))\right)\Gamma\left(3+q/(q-1)\right)}{\Gamma\left(3/2+(1/4)(q/(q-1))\right)}$$

$$-2^{(1-(5/2)(q/(q-1)))}\pi^4(q+A)^2\left(\frac{1}{q+A}\right)^{-q/(q-1)} H\left(\left[\frac{3}{4}\right.\right.$$

$$+\frac{1}{4}\frac{q}{q-1}, 1+\frac{1}{4}\frac{q}{q-1}, \frac{1}{2}+\frac{1}{4}\frac{q}{q-1}\right], \left[\frac{3}{2}, \frac{3}{4}, \frac{5}{4}\right],$$

$$\left.-\frac{1}{4}(q+A)^4\right)$$

$$\cdot \frac{\csc\left((1/4)\pi+(1/4)\pi(q/(q-1))\right)\Gamma\left(2+q/(q-1)\right)}{\Gamma\left(5/4+(1/4)(q/(q-1))\right)}$$

$$+2^{(5/2-(5/2)(q/(q-1)))}\pi^4(q+A)\left(\frac{1}{q+A}\right)^{-q/(q-1)} H\left(\left[\frac{3}{4}\right.\right.$$

$$+\frac{1}{4}\frac{q}{q-1}, \frac{1}{4}+\frac{1}{4}\frac{q}{q-1}, \frac{1}{2}+\frac{1}{4}\frac{q}{q-1}\right], \left[\frac{3}{4}, \frac{5}{4}, \frac{1}{2}\right],$$

$$\left.-\frac{1}{4}(q+A)^4\right)$$

$$\cdot \frac{\csc\left((1/4)\pi(q/(q-1))\right)\Gamma\left(1+q/(q-1)\right)}{\Gamma\left(1+(1/4)(q/(q-1))\right)}$$

$$+2^{(3-(5/2)(q/(q-1)))}\pi^4\left(\frac{1}{q+A}\right)^{-q/(q-1)} H\left(\left[\frac{1}{4}\frac{q}{q-1}, \frac{1}{4}\right.\right.$$

$$+\frac{1}{4}\frac{q}{q-1}, \frac{1}{2}+\frac{1}{4}\frac{q}{q-1}\right], \left[\frac{3}{4}, \frac{1}{2}, \frac{1}{4}\right], \left.-\frac{1}{4}(q+A)^4\right)$$

$$\cdot \frac{\sec\left((1/4)\pi+(1/4)\pi(q/(q-1))\right)\Gamma\left(q/(q-1)\right)}{\Gamma\left(3/4+(1/4)(q/(q-1))\right)}$$

$$+2^{(13/2-2(q/(q-1)))}\pi^3\left(-\frac{1}{2}+\frac{1}{4}\frac{q}{q-1}\right)(q+A)$$

$$\cdot H\left(\left[1, \frac{3}{4}, \frac{1}{2}, \frac{1}{4}\right], \left[\frac{5}{4} - \frac{1}{4}\frac{q}{q-1}, -\frac{1}{4}\frac{q}{q-1} + \frac{1}{2},\right.\right.$$

$$\left. -\frac{1}{4}\frac{q}{q-1} + \frac{3}{4}, -\frac{1}{4}\frac{q}{q-1} + 1\right], -\frac{1}{4}(q+A)^4\right)\Gamma\left(-2\right.$$

$$\left.\left. + \frac{q}{q-1}\right)\right)\left(\pi^3\Gamma\left(\frac{q}{q-1}\right)\right)^{-1}, \tag{50}$$

where Γ is the gamma-function and H is the hypergeometric function.

It is possible to show analytically that this expression is rather accurate. The error is less than one percent. Despite the known form it is rather difficult to perform calculations according to this expression and it is necessary to simplify the calculations.

Again we use the property of the avalanche consumption. Here one can show that θ is the decreasing (or at least not rapidly increasing) function of time (or of the size of the initial embryo). Then one can see the cut-off type of the function $\exp(-g)$ and the possibility of truncation of the function $\theta^q \exp(-g(z))$ at t_{cut}. The value of t_{cut} can be chosen as the root of equation $g = 1$. Then the spectrum of sizes

$$f \sim \theta^q [x] \exp(-g[x]) \tag{51}$$

can be approximated as

$$f \sim ((q-1)Az + 1)^{-q/(q-1)} \tag{52}$$

for $z < z_{\text{cut}}$, where z_{cut} is the size corresponding to t_{cut}. For other z the spectrum is zero.

The number of embryos can be easily calculated:

$$N_{\text{tot}} = \int_0^z ((q-1)Ax + 1)^{-q/(q-1)}\, dx$$
$$= -\frac{(Azq - Az + 1)^{-1/(q-1)} - 1}{A}. \tag{53}$$

This solves the formal problem of our investigation.

To show the consistency of the presented approach we have to investigate the inclusion of the m-mers consumption kinetics into the general nucleation. Here one can find at least two aspects of the problem. The first aspect is the input of m-mers in the overcoming of activation barrier and the corresponding input in the stationary rate of nucleation. The second aspect is the consumption of the m-mers by the near-critical and precritical embryos (this is the first type) and by the supercritical embryos (the second type). The rate of consumption will be different and their manifestation in the global kinetics s will be described by different ways.

To clarify the first aspect we rewrite the stationary rate of nucleation as

$$J \sim \exp(-q \ln(n[m]))\exp(-F_c). \tag{54}$$

One has to stress that here F_c is the free energy of the critical embryo formation on q m-mers. This implies that the work

of collecting of m-mers is considered separately. This work in approximation of ideal gas of m-mers is

$$F_0 = -q \ln(n[m]). \tag{55}$$

At the same time we have to note that in the embryo containing ν_c molecules there are only $\nu_c - qm$ molecules coming from monomers. Then F_0 has to be written as

$$F_0 = -b(\nu_c - qm) + \gamma A, \tag{56}$$

where b is the excess of the chemical potential for monomers, γ is the renormalized surface tension, and A is the surface area of the embryo. It is clear that in the determination of the surface area it is necessary to account that the part of the volume inside the embryos surface is occupied by the molecules coming from m-mers. When the surface of the embryo simply surrounds the embryo one has to write

$$A = 4\pi\left(\frac{3\nu_l(\nu_{1c} + qm)}{4\pi}\right)^{2/3}, \tag{57}$$

where ν_l is the volume per one molecule in a liquid phase and ν_{1c} is the number of molecules coming from monomers.

In the state of equilibrium the chemical potential of m-mer has to be equal to m chemical potentials of monomers (here we neglect the surface term or consider the deformed chemical potential). So

$$\frac{n[m]}{n[m, s = 0]} = \exp(bm) \tag{58}$$

and we see that the total free energy $\widehat{F}$ is

$$\widehat{F}_c = F_c - qbm = -\nu_c b + \gamma A \tag{59}$$

and the total free energy coincides with the classical expression.

One has to stress that the parameter Γ in the previous simplification of the dependence of the free energy on supersaturation (or the dependence of the stationary rate of nucleation on the supersaturation) is the number of molecules coming from monomers multiplied on $\Phi_*/(\Phi_* + 1)$; that is,

$$\Gamma \longrightarrow \Gamma_1 = \frac{\Phi_* \nu_{1c}}{(\Phi_* + 1)}. \tag{60}$$

Γ_1 is $\Phi_* dF_c/d\zeta|_{\zeta=\Phi_*}$.

If we calculate the derivative of the total free energy $\widehat{F}_c$ we get

$$\Phi_*\left.\frac{d\widehat{F}_c}{d\zeta}\right|_{\zeta=\Phi_*} = \Gamma_1 + qm\frac{db}{d\zeta} \tag{61}$$

or

$$\Phi_*\left.\frac{d\widehat{F}_c}{d\zeta}\right|_{\zeta=\Phi_*} = \Gamma_1 + \Gamma_m, \tag{62}$$

where

$$\Gamma_m = \left.\frac{\zeta q m}{(\zeta + 1)}\right|_{\zeta = \Phi_*}. \tag{63}$$

As a result

$$\Phi_* \left.\frac{d\widehat{F}_c}{d\zeta}\right|_{\zeta = \Phi_*} = \Gamma.$$

$$\Gamma = \left.\frac{\zeta \nu_c}{(\zeta + 1)}\right|_{\zeta = \Phi_*} \tag{64}$$

We will call this property the separation of Γ. It takes place only in the first derivatives of the free energies and only because the surface term does not act on the derivative of the free energy. The surface term in the free energy only changes the number of molecules in the critical embryo and has no direct influence on derivative.

So, we see that in the free energy there is the direct correspondence between the m-mers picture and monomers picture.

One can propose another picture when the number of m-mers necessary to form the critical embryo is proportional to the number of molecules inside the critical embryo. In the enormously big critical embryos, namely, this mechanism has to be considered. Then the picture is equivalent to the binary nucleation with two vapors (the vapor of monomers and the vapor of m-mers).

The second aspect is connected with the mechanism of consumption. Here one has to confess that there are two principal mechanisms of the substance consumption. The first mechanism is "one embryo-fixed number of clusters (monomers or m-mers)." The second mechanism is "one embryo-growing number of clusters (monomers and m-mers) corresponding to the law of the regular growth."

Rigorously speaking we have to write for each type of active monomers two types of consumption and the balance equations. With the help of exponential approximations mentioned above one can unify these mechanisms in one law of growth. Ordinarily when the first mechanism is important the second is absent. When the second mechanism acts it means that there is enough clusters of such type to neglect the exhaustion of seeds. We will call this effect as the dominating preference of one mechanism.

Despite the mentioned dominating preference property the simultaneous existence of several mechanisms can not be excluded as a specific case. But it is clear that with the help of approaches developed here it is possible to construct the theoretical description of any process with different mechanisms of formation, different mechanisms of substance consumption, and different relaxation processes corresponding to bounds or connections between the resources of clusters of different sizes.

The different relations between the characteristic times of the mentioned processes make the processes of nucleation rather different. The size spectrums are very various also. To describe these situations one has to demonstrate the power of the approaches making the base of theoretical description.

In every situation the leading idea will be the avalanche consumption of metastability in different manifestations of this property.

4. Main Results

This paper contains at least two important derivations concerning the *kinetics of decay with account of the relaxation processes* and *the kinetics of decay when the m-mers nucleation is important*. Both cases are important and one can see that account of these processes radically changes the numerical values of parameters of the nucleations process. But one has to confess that the qualitative picture remains similar to the traditional case. The last does not mean that nothing in the form of the particles size distribution is changed. Contrarily, the form of the size spectrum will be absolutely another. But the property of the avalanche cut-off of the pseudo-homogeneous size spectrum remains. The last property was very productive in construction of the above presented procedure.

It would be interesting to analyze these situations in the case of the smooth external influence on the system which causes nucleation, that is, in the case of dynamic conditions. Also it would be interesting to see the influence of the relaxation processes in the overcoming of the near-critical region in the process of the binary nucleation. Certainly, these perspectives make the subjects of separate publications.

Beside the direct construction of the nucleation global kinetics description we managed to extract some important features of the effect of m-mers inclusion into the nucleation process. One can mention here *the property of separation of* Γ and *the correspondence between the monomers picture and m-mers picture*. These properties are important enough to be mentioned in the general theory of nucleation.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.
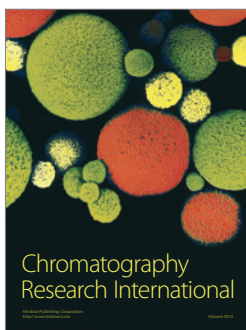
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Distribution of Supercritical Nuclei in Nucleation Kinetics

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Abstract—The system of equations of the condensation kinetics in a multicomponent system has been analyzed, which showed that many terms of the standard Zeldovich–Frenkel kinetic equation are insignificant. Using the apparatus of Green's functions, an almost exact solution of the kinetic equation in a supercritical region is constructed.

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In the course of a global first-order transition [1], an important role is played by substantially supercritical nuclei of the new phase [2, 3], since these nuclei exhibit regular growth and mostly account for the consumption of a metastable phase. Therefore, it is important to consider a fluctuation-induced spreading of the size distribution of particles of the new phase. The results of analysis [4] of this phenomenon have been used in many problems related to the kinetics of phase transformations [5–8]. It should be noted that, in a single-component isothermal case, fluctuation-induced spreading is important at the final stage of the process. At the same time, during multicomponent nucleation, the spreading of the particle size spectrum with respect to an intense variable—solution concentration in a nucleus—should be taken into consideration already during surmounting of the activation barrier for nucleation. In this context, it is effective to study the spectrum of nucleus sizes in the entire supercritical region in the multicomponent case. Previously, this problem has been solved in [9], where the solution was obtained by quite lengthy and rather approximate summation of series expansions. A nonisothermal nucleation was considered in [10].

In the present Letter, we consider the case of multicomponent nucleation, which is mathematically even more general than the nonisothermal case and the role of an intense variable instead of the "temperature" is played by the "concentration." A solution will be presented by an elegant formula that is constructed using a rapid and simple procedure.

The Zeldovich–Volmer–Frenkel evolution equation [1] can be written in the following form:

$$\frac{\partial n}{\partial t} = -\sum_a \frac{\partial n K_{\xi_a}}{\partial \xi_a} - \frac{\partial n K_\kappa}{\partial \kappa} + \sum_a \sum_b \frac{\partial^2 n K_{\xi_a \xi_b}}{\partial \xi_a \partial \xi_b}$$
$$+ \sum_a \frac{\partial^2 n K_{\kappa \xi_a}}{\partial \xi_a \partial \kappa} + \frac{\partial^2 n K_{\kappa \kappa}}{\partial \kappa^2}, \tag{1}$$

where

$$K_{\xi_a} = \sum_i \delta_i \xi_a (W_i^+ - W_i^-), \quad K_\kappa = \sum_i \delta_i \kappa (W_i^+ - W_i^-), \tag{2}$$

$$K_{\xi_a \xi_b} = \frac{1}{2} \sum_i \delta_i \xi_a \delta_i \xi_b (W_i^+ + W_i^-),$$

$$K_{\kappa \kappa} = \frac{1}{2} \sum_i \delta_i^2 \kappa (W_i^+ + W_i^-),$$

$$K_{\kappa \xi_a} = \sum_i \delta_i \xi_a \delta_i \kappa (W_i^+ + W_i^-). \tag{3}$$

Here, n is the distribution density of the number of droplets; δ_i are the changes in characteristics upon the attachment and detachment of molecules; ξ_i are the concentrations of molecules in droplets; κ is the droplet surface area in 3/2 power; W_i^+ is the coefficient of absorption of ith component molecules by the droplet; W_i^- is the coefficient of detachment of ith component molecules from the droplet; and the subscripts a, b, and i indicate component numbers in the droplet. Taking into account that $\delta_i \xi_a = \partial \xi_a / \partial v_i$ and $\delta_i \kappa = \partial \kappa / \partial v_i$, we arrive at the following expressions:

$$K_{\xi_a} = \sum_b \frac{\partial \xi_a}{\partial v_b} (W_b^+ - W_b^-) = \frac{\partial \xi_a}{\partial t},$$

$$K_\kappa = \sum_b \frac{\partial \kappa}{\partial v_b} (W_b^+ - W_b^-) = \frac{\partial \kappa}{\partial t}. \tag{4}$$

We can then obtain estimations of $\delta_a \kappa \sim v_{la}$ and $\delta_a \xi \sim \kappa^{-1}$, where v_{la} is the volume of a molecule in the liquid phase. Assuming that all W_a^+ values are on the same scale ($\sim \kappa^{2/3}$), we obtain the following estimations

for a region of substantially supercritical sizes of nuclei:[1]

$$K_{\xi_a} \sim W_i^+ \frac{\xi_a - \xi_{a+}}{\kappa}, \quad K_\kappa \sim W_i^+, \quad K_{\xi_a \xi_b} \sim \frac{W_i^+}{\kappa^2},$$

$$K_{\kappa\kappa} \sim W_i^+, \quad K_{\xi_a \kappa} \sim \frac{W_i^+}{\kappa}. \tag{5}$$

It is important to note that all coefficients except K_{ξ_a} retain power with respect to ξ_a.

The terms on the right-hand side of Eq. (1) obey the following estimations:

$$\left| \frac{\partial n K_{\xi_a}}{\partial \xi} \right| \sim \left| \frac{n W_i^+ (\xi_a - \xi_{a+})}{\kappa \Delta \xi_a} + \frac{n W_i^+}{\kappa} + \frac{n W_i^+}{\kappa} \right.$$
$$\left. + \frac{n W_i^+}{\kappa} \frac{\partial L}{\partial \xi_a} (\xi_a - \xi_{a+}) \right|, \tag{6}$$

$$\left| \frac{\partial n K_\kappa}{\partial \kappa} \right| \sim \left| \frac{n W_i^+}{\kappa} \right|,$$

$$\left| \frac{\partial^2 n K_{\xi_a \xi_b}}{\partial \xi_a \partial \xi_b} \right| \leq \left| \frac{W_i^+}{\kappa^2} \frac{n}{\Delta \xi_a \Delta \xi_b} + \frac{n W_i^+}{(\Delta \xi_a)\kappa^2} \right|,$$

$$\left| \frac{\partial^2 n K_{\kappa\kappa}}{\partial \kappa^2} \right| \leq \left| \frac{n W_i^+}{\kappa^2} \right|, \quad \left| \frac{\partial^2 n K_{\kappa \xi_a}}{\partial \kappa \partial \xi_a} \right| \leq \left| \frac{n W_i^+}{\kappa^2 \Delta \xi_a} \right|, \tag{7}$$

where $\Delta \xi_a$ is the full width at half height (FWHM) of the distribution with respect to the ξ_a axis and L is the operator of regular relaxation to steady-state values of concentration ξ^+. In order to derive the latter relations, it is necessary to consider the action of operator $\partial/\partial \kappa$ on n. Under steady-state conditions, the intensity of droplet formation can be assumed to be equal to a stationary value (J). For a regular growth of κ, this assumption implies that

$$\frac{\partial n}{\partial \kappa} \sim \frac{\partial}{\partial \kappa} \left(\frac{I}{d\kappa/dt} \right) \sim \frac{J}{\kappa d\kappa/dt} \sim \frac{n}{\kappa}. \tag{8}$$

Let us analyze the behavior of various terms in Eq. (1):

$$\frac{\left| \frac{\partial}{\partial \xi_a} n K_{\xi_a} \right|}{W_i^+ n} \equiv A \sim \frac{\xi_a - \xi_{a+}}{\kappa \Delta \xi_a} + \kappa^{-1} + \frac{\xi - \xi_{a+}}{\kappa} \frac{\partial L}{\partial \xi_a}, \tag{9}$$

$$\frac{\left| \frac{\partial}{\partial \kappa} n K_\kappa \right|}{W_i^+ n} \equiv B \sim \kappa^{-1},$$

[1] It is possible to produce renormalization such that $\delta_a \kappa \sim 1$.

$$\frac{\left| \frac{\partial^2}{\partial \xi_a \partial \xi_b} n K_{\xi_a \xi_b} \right|}{W_i^+ n} \equiv C \leq \kappa^{-2} (\Delta \xi_a)^{-1} (\Delta \xi_b)^{-1} + \kappa^{-2} (\Delta \xi_a)^{-1}, \tag{10}$$

$$\frac{\left| \frac{\partial^2}{\partial \kappa^2} n K_{\kappa\kappa} \right|}{W_i^+ n} \equiv D \sim \kappa^{-2}, \quad \frac{\left| \frac{\partial^2}{\partial \kappa \partial \xi_a} n K_{\kappa \xi_a} \right|}{W_i^+ n} \equiv E \sim \kappa^{-2} (\Delta \xi_a)^{-1}. \tag{11}$$

Here, $\Delta \xi$ is on the order of FWHM with respect to ξ. It is then necessary to consider ξ for which $\xi - \xi_+ \leq \Delta \xi$. Taking into account that $\partial L/\partial \xi_a \sim 1$ and $\Delta \xi_a \leq 1$, one can always omit the last part in the first term. When $\xi - \xi_+ \sim \Delta \xi$ (and the order of magnitude is independent of the component number), the first and second terms of the kinetic equation are on the same order of magnitude, while the fourth term is always negligibly small.

Let us assume that the fifth term and first part of the third term in Eq. (1) are on the same order of magnitude. Then, $\Delta \xi \sim 1$ (for any component) and

$$A \sim \kappa^{-1} (\xi - \xi_+) + \kappa^{-1}, \quad B \sim \kappa^{-1},$$
$$C \sim \kappa^{-2}, \quad E \sim \kappa^{-2}. \tag{12}$$

Consequently, the third and fifth terms are negligibly small compared to the second term. When $\Delta \xi$ decreases to reach a level of $\Delta \xi \sim \kappa^{-1/2}$, then $B \sim \kappa^{-1}$, $C \sim \kappa^{-1}$, and $E \sim \kappa^{-3/2}$.

Now let us assume that the fifth term in Eq. (1) is on the order of the second term. Then, $\Delta \xi \sim \kappa^{-1}$, which leads to

$$B \sim \kappa^{-1}, \quad C \sim 1, \quad E \sim \kappa^{-1}. \tag{13}$$

When $\Delta \xi$ decreases further, the latter estimation remains valid and, hence, the fifth terms is negligibly small everywhere because $\Delta \xi > 1/\kappa$ for $E < B$ and E is smaller than the first part of the third term for $\Delta \xi < 1$.

Analogous considerations can be used to establish insignificant magnitudes of higher derivatives and the possibility of using the Fokker–Planck approximation. It is important to note that going outside the framework of the Fokker–Planck approximation (i.e., allowance for derivatives above the second order in replacing finite differences by derivatives) is excessive both for multicomponent nucleation and in the nonisothermal case, where a significant role of higher derivatives can only be shown in situations in which the number of molecules in critical nuclei is small and, hence, their description in the capillary approximation of thermodynamics poses serious questions.

The first term in Eq. (1) determines the convergence of the spectrum with respect to the intense variable. If the third term is insignificant, then $\Delta \xi$ decreases until the third term is level with the first

term. If the distribution function is narrow and the influence of the first term is rather weak, the diffusion will lead to smearing of the distribution and increase in its FWHM increase, until a "contracting" effect of the first term starts to compensate this tendency. Thus, the first term has the same influence as the third term, which leads to the determination of $\Delta\xi \sim \kappa^{-1/2}$. From this, it follows that the droplet size spectrum along the ξ axis is rather narrow and, hence we can set $\xi = \xi_+$. Then, by integrating regular evolution equation

$$\frac{d\kappa}{dt} = \text{const}(\xi_+)\kappa^{2/3} \tag{14}$$

we obtain the following relation:

$$\kappa \approx \text{const} t^3. \tag{15}$$

Let us introduce the variables $\nu_=$ and $\nu_\perp$, which are defined from the numbers of molecules $\{\nu_a\}$ in the nucleus by rotating them so that the $\nu_=$ axis becomes parallel to κ. This rotation angle differs from 0 and $\pi/2$. In the new variables, elements of the matrix of kinetic coefficients are on the same orders of magnitude as W_i^+. The FWHM of the equilibrium distribution with respect to $\nu_\perp$ can be found as $\Delta\nu_\perp \sim \nu_=^{1/2}$. Equation (14) yields the following estimation for the FWHM of the equilibrium distribution moving along the κ axis:

$$\Delta\nu_\perp \sim t^{3/2}\text{const}. \tag{16}$$

The Green's function of the equations of diffusion in $x \sim \nu_\perp$ in the absence of regular growth is expressed as follows:

$$G(x_0, 0; x, t) \sim \frac{\exp\left(-\frac{(x-x_0)^2}{4Dt}\right)}{t^{(m-1)/2}D^{(m-1)/2}}, \tag{17}$$

where D is the diffusion coefficient ($D \sim W_a^+$) and m is the dimensionality of space. The distribution front propagates at a velocity below

$$\frac{d\Delta x}{dt} \sim D^{1/2}t^{1/2}. \tag{18}$$

In some time, this velocity becomes smaller than the rate of increase in $\Delta\nu_\perp$. The accuracy of the adopted approximation increases with time, so that the regular relaxation (which appears at $\nu_\perp - \nu_{\perp+} \sim \Delta\nu_\perp \sim t^{3/2}$) can be ignored. At the same time, $\nu_\perp$ approaches a stationary value of $\nu_{\perp+}$. The distribution function past some κ can be expressed as $n(\nu_=, \nu_\perp) = n_{\nu=}(\nu_=)n_{\nu\perp}(\nu_\perp)$, where the function $n_{\nu\perp}(\nu_\perp)$ is determined by the diffusion equation

$$\frac{\partial n_{\nu\perp}}{\partial t} = \sum_a D_a \frac{\partial^2 n_{\nu\perp}}{\partial \nu_{\perp a}^2}, \tag{19}$$

where D_a are the coefficients of diffusion with respect to the $\nu_{\perp a}$ basis set in $\nu_\perp$ hyperplane. A solution to this equation resembles after some time (or upon reaching some κ) the Green's function of the diffusion equation:

$$G \sim \Theta(t)\frac{\exp\left(-\frac{\sum\limits_a(\nu_{\perp a} - \nu_{\perp a+})^2}{4D_a t}\right)}{t^{(m-1)/2}}. \tag{20}$$

The function $n_{\nu=}$ is determined from the law of regular growth and, using relation (15), can be expressed as follows:

$$n_{\nu=}(\nu=) = \frac{J_s(t_{\nu=})}{d\nu_=/dt}, \tag{21}$$

where J_s is the intensity of formation of new supercritical nuclei and $t_{\nu=}$ is the time at which a supercritical nucleus of the given size appears in a substantially supercritical region.

Thus, the steady-state distribution is obtained by solving the following equation:

$$\frac{\partial n}{\partial t} \sim \frac{\partial n}{\partial \rho} \sim D\frac{\partial^2 n}{\partial \nu_\perp^2}, \tag{22}$$

where $\rho = \nu_=^{1/3}$. Taking into account that $D \sim \nu_=^{2/3} = \rho^2$, we arrive at the diffusion equation

$$\frac{\partial n}{\partial \nu_=} \sim \text{const}\frac{\partial^2 n}{\partial \nu_\perp^2} \tag{23}$$

with a δ-shaped source at $\kappa = 0$ and $\xi = \xi_+$, solution to which is given by the Green's function presented above.

The main result of this work consists in the justification of formulas (17) and (20). There would not be much sense in doing this if it were not an illusion brought by [10] that rather laborious procedures are necessary to seek for the solution. The accuracy of a solution obtained in [10] also posed some questions. The solution obtained in the present work is applicable to the general case of phase transformations in a multicomponent system and in the case of nonisothermal nucleation.

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Approximations of the Nucleus Size Spectrum in Nucleation Kinetics under Gradually Varied External Conditions

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Abstract—Several simple approximations have been presented for describing evolution of a condensing system at the stage of nucleation under dynamic conditions. All of them have been compared with the exact numerical solution, and their errors have been determined. All relative errors have been shown to be rather small.

1. INTRODUCTION

The stage of intense formation of supercritical nuclei (droplets) of a new phase plays a great role in the kinetics of a first-order phase transition, which is commonly studied by the example of supersaturated vapor condensation [1−9].

This time period is referred to as the nucleation stage. In spite of the wide variety of substances prone to the first-order phase transitions, the evolution of new phase nuclei at this stage has a number of common regularities. These regularities underlie the general theoretical description of this phenomenon. The most exact solution for the problem of nucleation kinetics has been reported in [1]; it was obtained using the ideas of the universality of the stage of homogeneous nucleation. However, this universality is lost as soon as we start to consider specific situations and more complex processes. Therefore, it would be useful to know some simple approximations of kinetic dependences, with these approximations being applicable to studying more complex situations. The goal of this work is to derive such approximations.

In addition to the search for simple functional regularities, we shall discuss the physical processes underlying these approximations. This will enable us to formulate simpler models describing the evolution of an ensemble of droplets during the nucleation stage, which will be subsequently applicable to the consideration of fine details of phase transition kinetics, e.g., corrections for the stochastic formation of supercritical nuclei of a new phase.

This article continues and generalizes work [2]. Dynamic external conditions are considered in it. It is proposed that external parameters vary gradually. This variation in the parameters is more natural than the instantaneous generation of an initial supersaturation or maintaining supersaturation at a constant level.

Since the method proposed in [2] is compared with the so-called "perturbation theory" [3], it would be reasonable to perform analogous comparison here as well. This is of importance for, in particular, substantiation of the appropriateness of the study undertaken in this work. It should be noted that, in the case of dynamic external conditions, models that would yield exact solutions analogous to those obtained for the regime of the instantaneous generation of initial supersaturation are unavailable. However, having formulated these models independently, we may obtain a number of specific results, which will be considered below.

Initially, the droplet size spectrum was normalized with respect to the total amount of droplets formed in a system. Thus, the $f(x)dx$ value is the number of droplets, with linear sizes between x and $x + dx$ in unit volume. After passage to universal coordinates [1], this value changes by several times. Therewith, the $f(x_1)/f(x_2)$ ratio for two sizes x_1 and x_2 remains unchanged and represents the ratio between the number densities of droplets with these sizes; i.e., the renormalization factor appears to be the same for different sizes. In the variables introduced in the aforementioned work, the size spectrum is the same for different rates of variation in external conditions. This fact allows us to confine ourselves to presenting one curve for different situations. We shall keep to this normalization for all constructions in this work. Therefore, all coordinates in the figures presented below are dimensionless.

Figure 1 shows the universal exact droplet size distribution and an approximate solution obtained within the framework of the perturbation theory. It can be seen that the exact solution and that obtained in terms
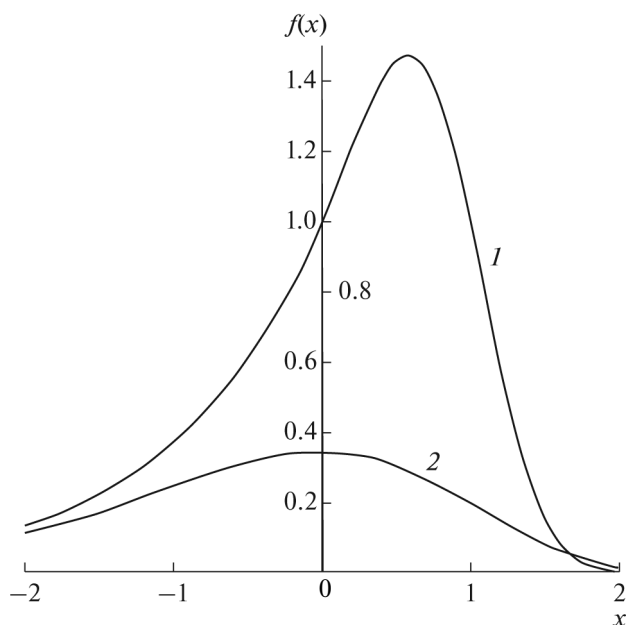
Fig. 1. (*1*) Universal exact droplet size distribution and (*2*) that determined in terms of perturbation theory.
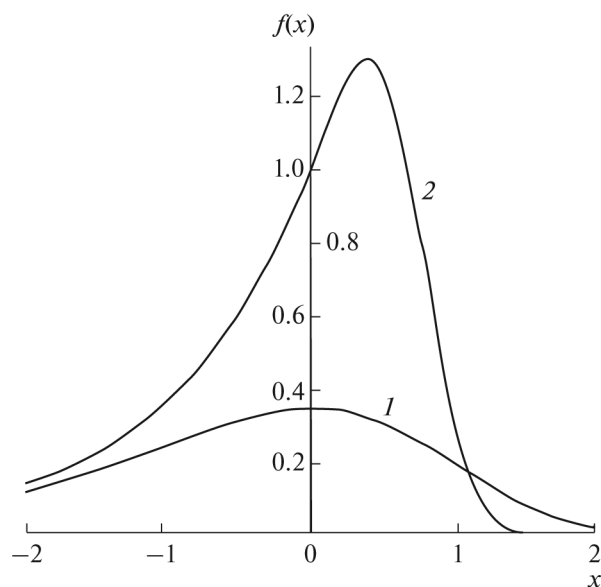

Fig. 2. (*1*) Universal exact droplet size distribution and (*2*) that determined in terms of perturbation theory with self-consistent determination of the total number of droplets.

of the perturbation theory are greatly different. The solution found within the framework of the perturbation theory may be somewhat improved by making it partly self-consistent. When searching for the exact solution under dynamic conditions, the parameter "maximum nucleation intensity" is introduced in the self-consistent manner rather than being imposed from outside. Accordingly, the perturbation theory requires writing an equation for self-consistent determination of this parameter as well. In accordance with the ideology of the perturbation theory, the total number of droplets will appear in this equation. When determining the distribution presented in Fig. 1 in terms of the perturbation theory, it was taken equal to the exact value obtained from the universal solution. It could also be found in a self-consistent way, i.e., in a manner such that the size spectrum would comprise the number of droplets determined by the perturbation theory. In this case, a simple transcendental equation arises, which can be solved by the iteration method. The distribution that results from the self-consistent determination of the total number of droplets in terms of the perturbation theory is presented in Fig. 2, which also shows the exact spectrum. It can be seen that the agreement between the exact solution and that found within the framework of the perturbation theory has become somewhat better; however, the difference still remains to be substantial.

The way out seems to be simple: the universal solution should be always used. However, there are many situations in which this is impossible, e.g., when the

growth of nuclei deviates from the power law, as it does upon the heterogeneous nucleation [4]. When the regularities of the growth of nuclei vary with an increase in their size, the interference of nuclei that arise at different moments of nucleation must be taken into account explicitly. Another factor is allowance for stochastic effects accompanying nucleation. In this case, it is necessary to study the influence of fluctuations in the initial region of the spectrum on the formation of droplets in the central and rear regions of the size spectrum [8]. This influence can, in principle, be taken into account based on the universal solution; however, doing so encounters technical difficulties. Moreover, analysis shows that the physical mechanisms of the stochastic effects accompanying nucleation cannot be revealed in the solution thus obtained. An explicit determination of the droplet size spectrum, even if it is approximate, is necessary in the case. However, the approach proposed in [8] for determining the droplet size distribution is too rough. The nucleus size spectrum obtained in [8] is shown in Fig. 3 in comparison with the exact spectrum. A great difference between the approximate and exact spectra can be seen. Furthermore, the approximate spectrum undergoes a discontinuity.

The aforementioned circumstances make it urgent to find an approximation that would be simple and, at the same time, sufficiently precise for nucleus size spectra in complex situations. This is the goal of this work.
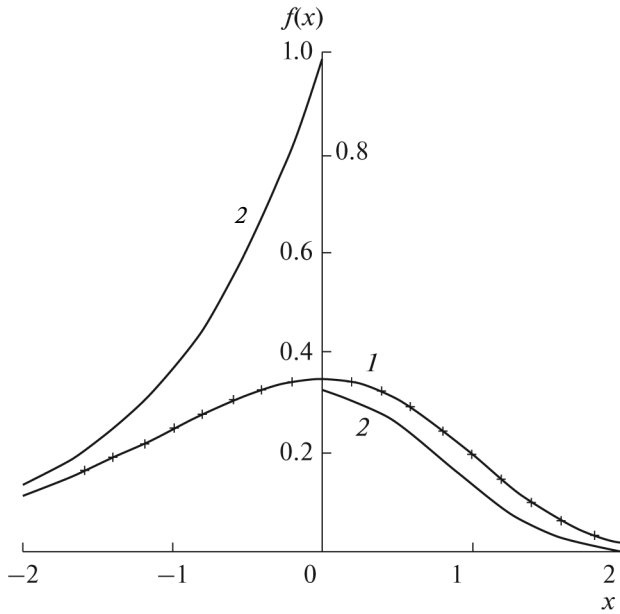
Fig. 3. (*1*) Universal exact droplet size distribution and (*2*) approximate solution obtained with allowance for stochastic effects.

2. THE BASIC EQUATIONS

As an example, we consider the free-molecular growth of nuclei in a three-dimensional space. In this case, the growth rate of a nucleus containing v molecules with time t is specified by the following standard relation:

$$\frac{d\rho_{dr}}{dt} = \frac{\zeta}{\tau}; \quad \rho_{dr} = v^{1/3}.$$

Here, τ is some characteristic time and we have isolated the dependence on the vapor density by means of supersaturation ζ, which is equal to

$$\zeta = \frac{n}{n_1} - 1,$$

where n is the molecule number density in a vapor and n_1 is the molecule number density in a saturated vapor.

The supersaturation value characterizes the degree of system metastability. An analogous value that would be reached in the system without nucleation is denoted as Φ and referred to as the ideal supersaturation. This value is completely governed by the external conditions and, therefore, assumed to be known.

Distribution $f(x)$ of droplets over linear sizes may be taken as quasi-stationary, and the following approximation may be written for it as a function of ζ:

$$f = f(\Phi_m) \exp[\Gamma(\zeta - \Phi_m)/\Phi_m].$$

Hereinafter, subscript "m" denotes parameter values at some characteristic time moment t_m, by which a half of the total number of droplets has been formed.

The value of Γ is the supersaturation derivative of critical nucleus free energy, with this derivative being multiplied by Φ_m.

After a scale has been properly selected, the following linear law may be used for variations in the supersaturation with time during the nucleation period:

$$\Phi = \Phi_m + z.$$

Here, z is the renormalized time (see [1]). Variable $x = z - a\rho_{dr}$ may also be introduced (a is some constant [1]), which determines the relation between z and x. In the collective regime of vapor absorption, the law of conservation of matter is written [1] as

$$g = c \int_{-\infty}^{z} (z - x)^3 \exp(x - g(x)) dx \qquad (1)$$

with suitable value of constant $c = 0.189$. In this case, the $\exp(x - g(x))$ curve has a maximum at $x = 0$ (this may be considered to be the condition for selecting constant c).

3. APPROXIMATION BY ITERATIONS

The exact solution of Eq. (1) has a universal form that was established in [1]. However, the explicit analytical expression for the nucleus size spectrum $f = \exp(x - g(x))$ cannot be obtained in this case. Therefore, subsequent constructions using the expression for f are impossible. It is necessary to find analytical approximations for f. The iteration method is the most widely known procedure for the construction of such approximations.

The iterative solution of Eq. (1) has been presented in [6]. The solution proposed in [5] requires the use of a new set of characteristic parameters at each step of the iteration procedure. The recurrent procedure has been specified in [6] as

$$g_{i+1} = c \int_{-\infty}^{z} (z - x)^3 \exp(x - g_i(x)) dx$$

with the zero approximation $g_0 = 0$.

The first iteration for

$$f = \exp(x - g(x))$$

has the following form:

$$f_1 = \exp(x - pc \exp(x)),$$

$$p = \int_{0}^{-\infty} x^3 \exp(-x) dx = 6,$$
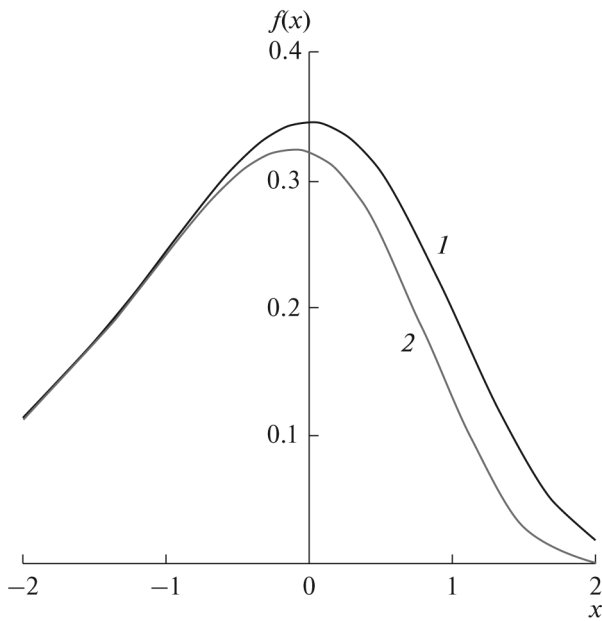
$$pc = 0.134.$$

Fig. 4. (*1*) Exact solution and (*2*) first iteration for droplet size spectrum.
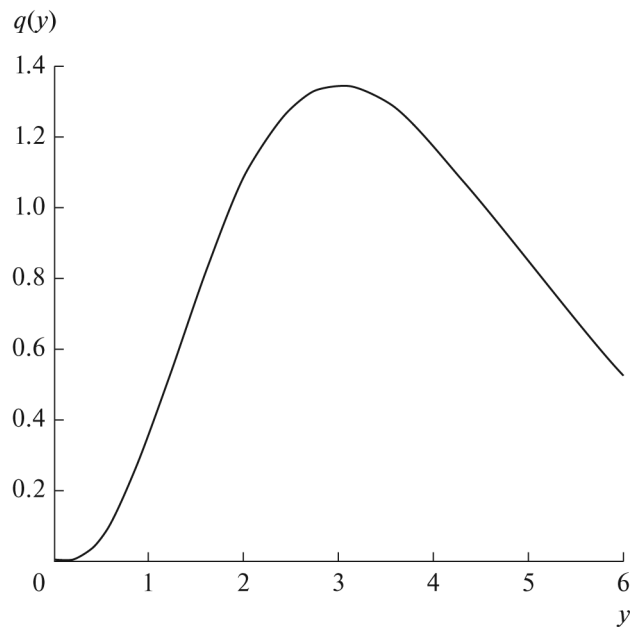

Fig. 5. Pattern of universal integrand in the first iteration for nucleus size spectrum.

As can be seen in Fig. 4, even the first iteration is very close to the exact solution. Now, we shall obtain new approximations that have a simpler physical meaning.

4. SIMILARITY OF CONDITIONS FOR NUCLEATION OF DROPLETS

A similarity of the conditions under which nuclei arise in a system takes place for metastable state decay [7]. This results from the scale invariance of external conditions with respect to time. Now, we have another situation. Time explicitly enters into the $\exp(x)$ factor for $f = \exp(x - g(x))$ and characterizes the effect of external conditions.

Let us analyze the integrand of the integral that arises when calculating the first iteration. Nucleus size ρ_{dr} may be calculated as follows:

$$\rho_{dr} = \frac{\Phi_m^2}{\Gamma\tau(d\Phi/dt)}(z - x).$$

To reveal the desired similarity, we have to pass to variable $y = z - x$. in the integrand. Integrand g_{s1} in the expression for g_1 is as follows:

$$g_{s1} = \exp(z)y^3\exp(-y).$$

Factor $\exp(z)$ is no more than a scale factor, and we arrive at the following universal expression for the integrand in the first iteration:

$$g_{s1} = \text{const}\, q; \quad q \equiv y^3 \exp(-y).$$

Since the first iteration resembles the exact solution, the last relation means that the conditions for the formation of droplets at different time moments are similar; only the scale factor changes. The pattern of the universal integrand is illustrated in Fig. 5. The figure shows that the maximum of the integrand is located at $y = 3$, while, at $y = 1.4 = \rho_b$, a half-amplitude value is reached. This value may be considered to be some characteristic boundary. Another boundary is $y = \rho_b = 5.8$.

5. FIRST ITERATION WITH SHIFTED MAXIMUM

The value of intensity $c = 0.189$, which corresponds to the maximum at $x = 0$, was established by the numerical solution of Eq. (1). A question arises as to the value of parameter c corresponding to the maximum at $x = 0$ in the case of the first iteration. It is natural that we, at once, obtain the answer $c = 1/6$ and arrive at a somewhat shifted function of the first iteration $f_{1sh} = \exp(x - g(x))$ at the effectively renormalized intensity of the source (or the absorption intensity, which is equivalent when determining the pattern of a droplet size spectrum).

The shifted function of the first iteration coincides with the exact solution even better than the previous variant of the first iteration does. This is clearly illustrated in Fig. 6. The curve with the steeper decrease represents the function of the first iteration.

The constructed approximations reproduce, to some extent (however, not completely), the idea of selecting parameters as applied to each iteration [5].

Let us explain the reason for the improvement of the approximation. Simplifying the situation, we may state that there are two reasons for the errors arising upon the first iteration. The first reason is the inexact determination of the effective intensity of the metastability source; here, both the external conditions and vapor consumption by already-nucleated droplets play their roles. The second reason is the appearance of a temporary nonlinearity of the effective source because of the vapor consumption (effect of previously nucleated droplets). Rescaling makes it possible to eliminate (of course, partly) the first reason. Evidently, it is this reason that is decisive for the difference between the exact solution and the first iteration. This is quite obvious, because the nonlinearity of the effective source at $z = -3$ cannot be too strong. It is easy to understand that the nonlinearity increases with time, so were it strong at these values of the argument, the attainment of the supersaturation maximum would be determined by the nonlinearity of the effective source and would take place sooner than the argument reaches its zero value. Hence, the rescaling is indeed an efficient instrument for improving the iterative solution.

6. APPROXIMATION BY MONODISPERSE ENSEMBLE

Let us calculate an expression for g by Eq. (1). In the calculation, we use the approximation corresponding to a monodisperse ensemble of droplets and obtain

$$g = c \int_{-\infty}^{z} (z - x)^3 \exp(x - g(x))dx \rightarrow cNz_{max}^3,$$

where z_{max} is the coordinate of the monodisperse distribution peak and N in the total number of droplets. The following expression may be proposed for N:

$$N = \int_{-\infty}^{z} \exp(x - g(x))dx.$$

Since the maximum is reached at $y = 3$, for z_{max}, we obtain $z_{max} = z + 3$.

The derived expressions represent the first variant of approximation by a monodisperse ensemble. It is not quite exact, because we have attributer the $z + 3$ coordinate to small droplets as well; their number is large in the vicinity of the maximum supersaturation. That is, this approximation should be improved. When calculating N, the range of integration may be cut off at ρ_b. Then, the renormalized number of droplets
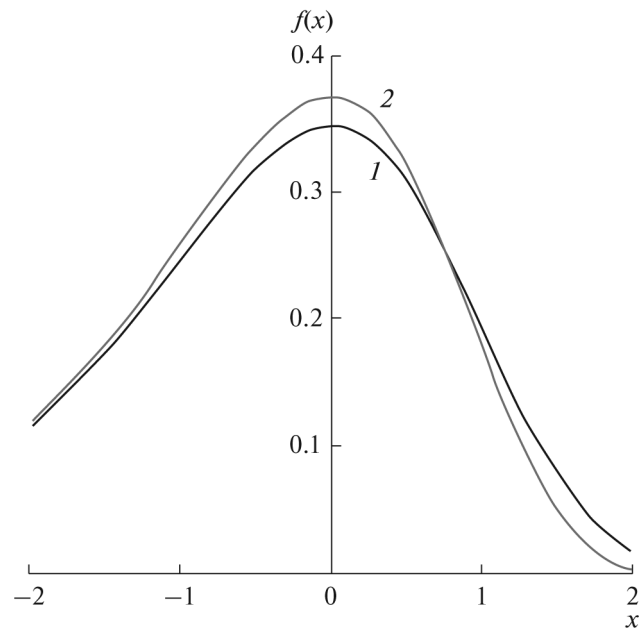

Fig. 6. (*1*) Exact solution and (*2*) distribution density corresponding to modified first iteration.

formed before the supersaturation maximum is reached is specified by the following formula:

$$N_m = N(z = 0) = \int_{-\infty}^{-\rho_b} \exp(x - g(x))dx.$$

For $\rho > \rho_b$, the contribution to g may be ignored. This allows us to use the ideal supersaturation instead of the real one that leads to the following equality:

$$N = \int_{\rho_b}^{\infty} \exp(-y)dy = \exp(-\rho_b) = \exp(-1.4).$$

At each time moment, the number of droplets is equal to

$$N = \exp(-1.4)\exp(z),$$

and the coordinate of the monodisperse peak is $x = 3$. Therewith, for $f = \exp(x - g(x))$ the following expression is obtained:

$$f = f_{mono1} = \exp[x - 3^3 c \exp(-1.4)\exp(z)].$$

Figure 7 illustrates the accuracy of this approximation. As can be seen from the figure, the accuracy of this approximation is quite satisfactory.

Above, we have considered only one variant of approximation by a monodisperse ensemble. Now, we present another variant. Note that, at each time moment, a droplet that corresponds to the maximum of the integrand (in the first iteration) has a size that is larger than the current size by three unities. This yields
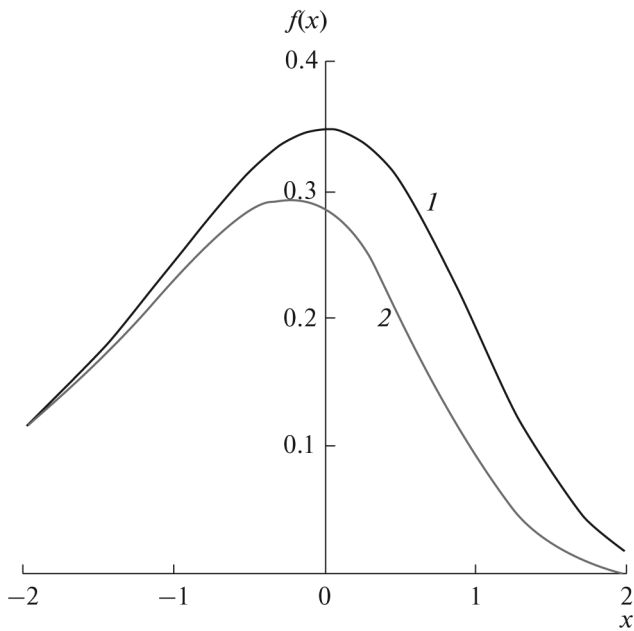
Fig. 7. Droplet size distributions resulting from (*1*) exact solution and (*2*) monodisperse ensemble approximation.
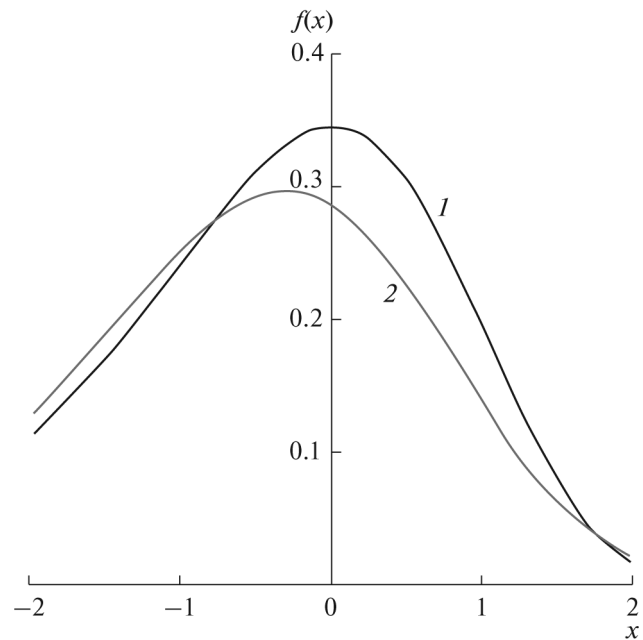

Fig. 8. Droplet size distributions resulting from (*1*) exact solution and (*2*) the second variant of monodisperse ensemble approximation.

$$f = f_{\mathrm{mono2}} = \exp[x - (x + 3)^3 c \exp(-1.4)].$$

The spectrum of sizes for the second variant is presented in Fig. 8. The accuracy of this approximation is also quite satisfactory.

7. APPROXIMATION BY A MONODISPERSE ENSEMBLE AT THE MAXIMUM SUPERSATURATION

Previously, we used the approximation by a monodisperse ensemble at each time moment. Now, we take into account the fact that the majority of droplets are formed in the vicinity of the maximum supersaturation, i.e., nearly at $z = 0$. In this case, we may take the coordinate of the monodisperse distribution peak to be equal to $z = -3$. Then, it may be stated that the model droplet size spectrum

$$f = \exp[x - A(x + 3)^3]$$

with parameter A has a maximum at $z = 0$. This leads to the value of $A = 1/27$. Moreover, we may replace $1/27$ by $6c/27$. Then, we arrive at

$$f = f_{\mathrm{mono3}} = \exp[x - (6c/27)(x + 3)^3].$$

This spectrum is depicted in Fig. 9 together with the exact solution. It can be seen that the exact and approximate solutions almost coincide with one another. The following approximate solution is obtained for $A = 1/27$:

$$f = f_{\mathrm{mono4}} = \exp[x - (1/27)(x + 3)^3].$$

This size spectrum is depicted in Fig. 10 together with the exact solution. It can be seen that the exact and approximate solutions coincide with one another in this case as well. Note that, when constructing the two latter approximations, we replaced $N = \exp(-1.4)\exp(x)$ by $N = 6c/27$ or $N = 1/27$ and retained fixed coordinate $x = 3$.
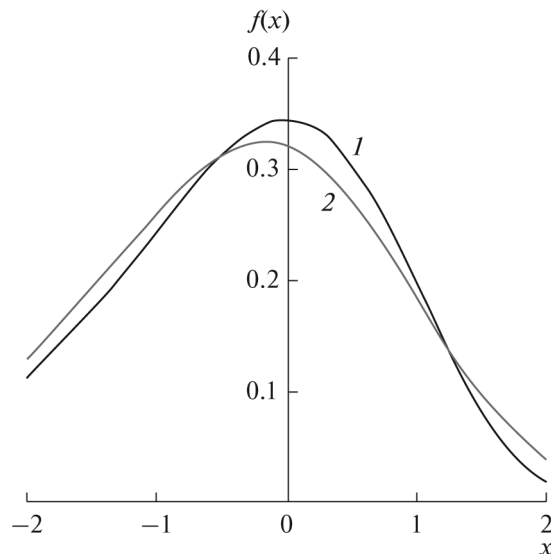

Fig. 9. Droplet size distributions resulting from (*1*) exact solution and (*2*) the third variant of monodisperse ensemble approximation.
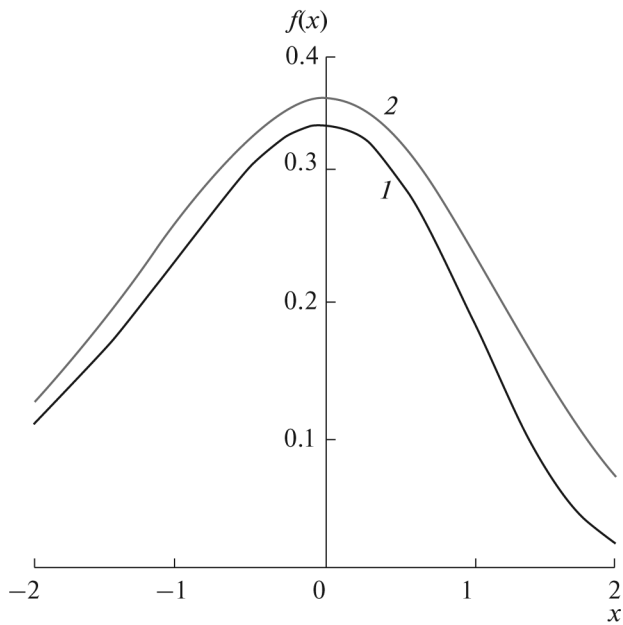
Fig. 10. Droplet size distributions resulting from (*1*) exact solution and (*2*) the fourth variant of monodisperse ensemble approximation.
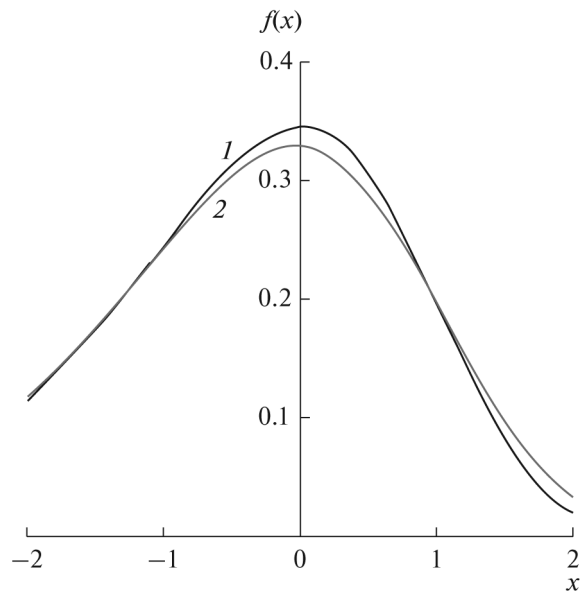

Fig. 11. Droplet size distributions resulting from (*1*) exact solution and (*2*) two-step approximation.

The same may be done for the first and second approximations by a monodisperse ensemble. In this case, we arrive at the following distributions:

$$f = f_{mono5} = \exp[x - (6c/27)\exp(x)3^3]$$

and

$$f = f_{mono5} = \exp[x - (1/27)\exp(x)3^3].$$

It is seen that f_{mono5} and f_{mono6} coincide with f_{mono3} and f_{mono4}.

Thus, we infer that the above-used substitution may be fulfilled at different steps of constructing an approximate solution.

8. TWO-STEP SCHEME

The next approximation for constructing the size spectrum is based on the property underlying the efficiency of the first iteration. What is the reason for the efficiency of the first iteration? The physical reason is that the nuclei that are the main vapor consumers at the nucleation stage were nucleated at its beginning, when the supersaturation was still very close to its ideal magnitude. This enables us to distinguish the primary step of the nucleation stage by condition $z < -1$ and its secondary step by condition $z > -1$. It is the secondary step at which the majority of new phase nuclei are formed. Indeed, the $g(-1) < c\exp(-1)$ value is small compared with the characteristic g value during the secondary step $g \sim c$. Then, at $z < -1$, the supersaturation is rather close to Φ.

The effect of nuclei formed at the primary step on the evolution of the spectrum at the secondary step is specified with the use of values

$$a_i = \int_{-\infty}^{-1} x^i \exp(x - cg(x))dx, \quad i = 0, 1, 2, 3.$$

Direct calculation based on the first iteration leads to

$$a_0 = \exp(-1),$$

$$a_1 = -2\exp(-1),$$

$$a_2 = 5\exp(-1),$$

$$a_3 = -16\exp(-1).$$

Then

$$g \to g_u = c(x^3 a_0 - 3x^2 a_1 + 3xa_2 - a_3),$$

and spectrum

$$f = \exp(x - g(x))$$
$$\to \exp[x - c(x^3 a_0 - 3x^2 a_1 + 3xa_2 - a_3)]$$

is depicted in Fig. 11 (curve *2*) together with the exact solution, with the peak of the latter being somewhat sharper (curve *1*). Here, the fact that this expression takes place only for $z > -1$ is as it were forgotten. We extend it to the region of $z < -1$, because, in this region, the height of the size spectrum is rather small as compared with the amplitude value. Of course, the asymptotic behavior at $z < -1$ will be qualitatively
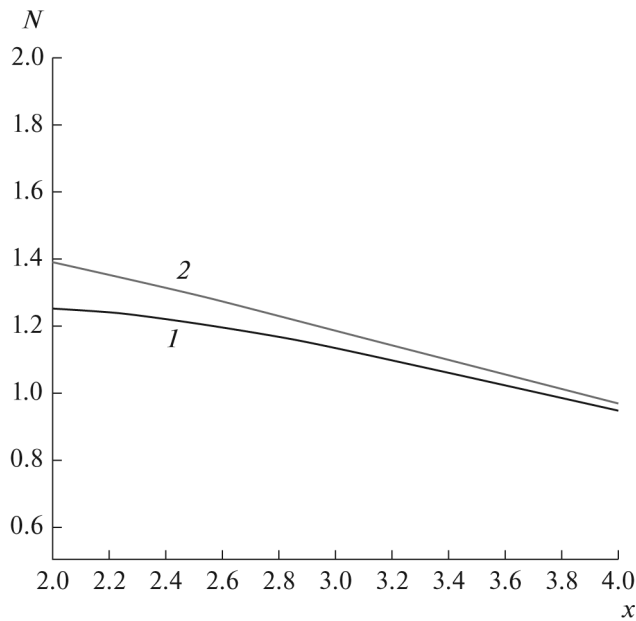
Fig. 12. Numbers (*1*) N_u and (*2*) N_{tot} of droplets as functions of *p*.
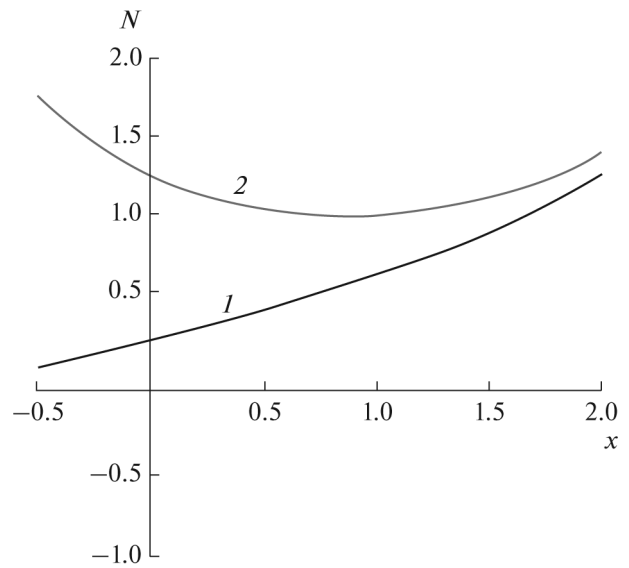

Fig. 13. Numbers (*1*) N_u and (*2*) N_{tot} of droplets as functions of *p* for two-step model.

incorrect. However, for the actually important region, the shapes of the two curves almost ideally coincide.

The constructed approximations may also be used when considering more complex kinetic problems, which are at present solved by numerical simulation [10−12].

9. BALANCE PROPERTY

The above-constructed model shapes of the size spectrum must be self-consistent. The self-consistency implies a weak dependence of the total number of particles on the number of particles contained in the region corresponding to a monodisperse ensemble, which results from the monodisperse approximation, with allowance for the varying coordinate of the peak. This effect is, to some extent, reflected in the moderate character of the dependence of the nucleation parameters on the magnitudes of stochastic effects [7]. In the two-step model, self-consistency implies a weak dependence of the total number of droplets on the position of the boundary between the primary and secondary steps of the nucleation stage.

We shall analyze both of the models, i.e., that based on a monodisperse ensemble and that resulting from the two-step scheme. Let us begin with the monodisperse ensemble. First, we generalize this model. Let the monodisperse peak be formed at $z = -p$. Then, instead of $A = 1/27$, we have $A = 1/(3p^2)$. For the size spectrum, we obtain

$$f = \exp[x - (1/3p^2)(x + p)^3].$$

For the total number of droplets, the following expression is derived:

$$N_{tot} = N_u + \exp(-p),$$

where N_u is the number of droplets that have appeared after $z = -p$. The latter value may be calculated as follows:

$$N_u = \int_{-\infty}^{-p} \exp[x - (1/3p^2)(x + p)^3]dx.$$

According to the renormalization used in this work, the number of droplets calculated in terms of the exact solution is equal to exactly 1.00. The numbers of droplets N_u and N_{tot} are shown in Fig. 12 as functions of *p*. It can be seen that the $N_{tot} - p$ dependence is very weak. This fact indicates a good self-consistency of the approach.

Let us perform the same operations for the two-step model. Before the boundary value $z = -p$, the droplet size spectrum is generated at the ideal supersaturation; i.e., the spectrum is described by the expression $f = \exp(x)$. For $z > -p$, the evolution of the spectrum is controlled by substance absorption on droplets formed before $z = -p$ alone. This leads to

$$f = \exp[x - c(x^3a_0 - 3x^2a_1 + 3xa_2 - a_3)],$$

where the universal moments are specified by the following formulas:
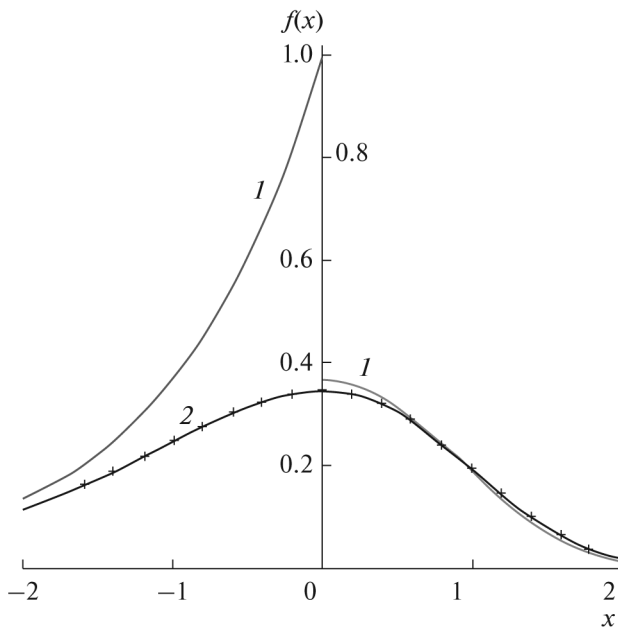
$$a_0 = \exp(-p),$$

$$a_1 = -p\exp(-p),$$

Fig. 14. (*1*) Model spectrum taken from [8] and (*2*) exact solution.

Fig. 15. Rear regions of (*1*) model spectrum taken from [8], (*2*) first iteration, and (*3*) exact solution.

$$a_2 = (p^2 + 2p + 2)\exp(-p),$$

$$a_3 = -(p^3 + 3p^2 + 6p + 6)\exp(-p).$$

Total number of droplets N_{tot} is equal to

$$N_{tot} = N_u + \exp(-p),$$

where N_u is the number of droplets formed after $z = -p$. This number is specified as

$$N_u = \int_{-p}^{\infty} \exp[x - c(x^3 a_0 - 3x^2 a_1 + 3x a_2 - a_3)]dx.$$

Numbers N_u and N_{tot} are presented in Fig. 13 as functions of p. The $N_{tot}-p$ dependence is seen to be weak. Moreover, the number of droplets, which is always larger than the exact value of 1.00 (this is attained by a corresponding scaling), has a minimum at a p value close to unity. This value is optimum. It can be seen that the value $p = 0$, which was used in [8], is very far from being optimum. It may be noted that this property (the weak dependence of the droplet number on the position of the boundary) is strongly related to the constructions in terms of the modified Gauss method for studying nucleation under the action of a strongly nonlinear effective source of metastability [9].

Let us continue the construction of model approximations. Almost complete coincidence of the rear edges of the spectra plotted within the frameworks of the two-step model [8] and the exact solution is a remarkable property. This coincidence is distinctly seen in Fig. 14. Note that scaled variables have been used in this case; Fig. 1 shows the absence of the coin-
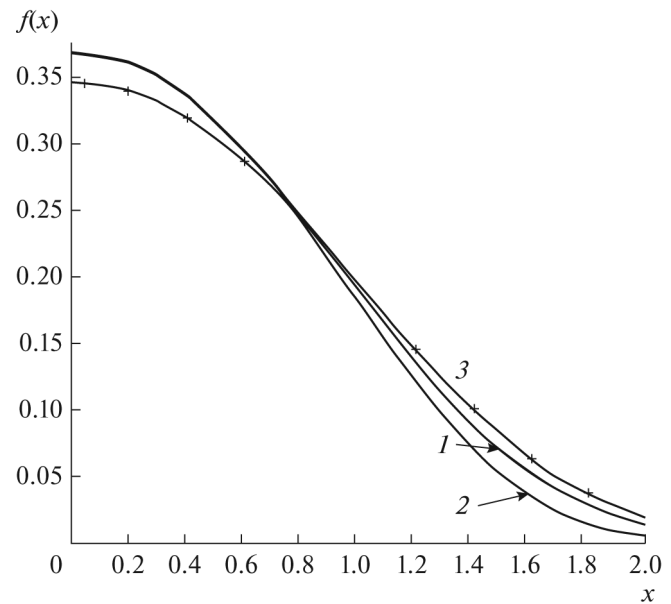
cidence at positive values of the argument in the initial coordinates.

The patterns of the model size spectrum and the size spectrum based on the exact solution seem to completely coincide with one another at positive argument values. Figure 15 shows the absence of the coincidence. Three curves, i.e., the exact solution, first iteration, and model solution taken from [8], are depicted in Fig. 15. These curves are seen to be different. The reason for the closeness of these curves is obvious: a decay in the nucleation intensity is always caused by droplets that have been nucleated under the action of an effective, although linear, source of a metastable phase. The scaling of the variables leads to equal intensities of this source for different cases, and we arrive at identical distributions. Thus, the property of identity has been established for all models of the pattern of size spectrum generated upon a reduction in the supersaturation after a proper scaling. The identity takes place under a linear law of variations in the supersaturation.

At negative argument values, a droplet size spectrum is generated under the action of an effective source, for which the time dependence of supersaturation can also be linearized. In this case, identical distribution curves can also be obtained in this spectral region after corresponding scaling. Thus, almost complete identity of the spectra takes place after appropriate scaling, however, separately for negative and positive values of the argument.

Note that the model [8] is rough to such an extent that particles generated in it have no effect on the pat-

tern of the spectrum at negative argument values. Therefore, it cannot be reduced to a universal form by scaling (although the universality takes place for two branches of the spectrum in separate).

10. COMPARISON OF MODELS

The aforementioned different approaches to the determination of nucleus size spectra have their advantages and drawbacks. Different approximations must be used depending on the type of a problem encountered when studying the nucleation kinetics.

The approximation of renormalized first iteration has an obvious advantage: it yields a universal pattern of the spectrum. Note that the general universality of the first-order phase transition kinetics is also reflected in the first iteration: it does not imply the dependence of a droplet size spectrum on the exponent in the droplet growth law. Accordingly, the first iteration does not comprise the dependence of the spectrum on the space dimensionality and specific features of the droplet growth law. Only its obvious property is assumed; i.e., the nucleus growth is considered to be avalanche-like.

A drawback of the first iteration renormalization is the fact that stochastic effects of nucleation are very difficult to incorporate into this scheme. It should also be recognized that this approach is, to a great extent, approximate. Its further refining by subsequent iterations appears to encounter technical difficulties and to be less efficient than other approaches. Furthermore, we have to admit that this approach does not enable one to clarify the sizes of droplets that are predominant in the nucleation kinetics at a given time moment.

The monodisperse ensemble approximation is an antipode of the first iteration method. According to this approach, some droplets are distinguished that "control" the nucleation kinetics at a given time moment. Accordingly, this method is convenient for studying stochastic effects. The variant of the monodisperse approximation in the vicinity of the maximum supersaturation is especially simple. It yields a simple and clear description of the process; however, it implies no further refinement. A possible refinement of the method consists in the use of a separate approximation by a monodisperse ensemble for each time moment. The main drawback of this method is the use of the model representation of a droplet size spectrum. Here, the pattern of a nucleus size spectrum cannot be spoken of, because it actually results from the approximation by a monodisperse ensemble. Moreover, the method becomes inapplicable upon a change in the nucleus growth regime.

Multistep schemes start playing a special role upon a change in the droplet growth regime. An adequate use of these schemes has been shown by the example of the two-step scheme. This scheme is advantageous in giving the possibility of explicitly seeing the roles of droplets with different sizes in the control over the nucleation kinetics. The main drawback of this scheme is the technical complexity of its realization. The integrals used during the implementation of this scheme change their forms upon changes in the regime of nucleus growth and complicate the simple interpretation of nucleation kinetics.

Thus, the renormalized first iteration should be recognized as the most efficient method for revealing the general analytical laws of nucleation kinetics. The stochastic effects can be most simply studied using approximation by a monodisperse ensemble. When changes take place in the regime and, accordingly, the law of droplet growth, one can hardly avoid the use of multistep schemes.

Nucleation is characterized by diverse kinetics. Therefore, one should use diverse approximations when studying real problems.

11. MAIN RESULTS

Let us list the main results of the work.

1. The method based on the perturbation theory has been shown to be unsatisfactory.

2. Rescaling has been proposed and analyzed to be used in the first iteration method. The reason for the efficiency of this procedure has been shown.

3. The similarity of the conditions for nucleation of droplets within the framework of the first iteration has been established.

4. Several variants of approximation by a monodisperse ensemble have been proposed. They have been shown to rather adequately describe the droplet evolution.

5. A generalized two-step model has been proposed. The optimum position has been determined for the boundary between the "primary" and "secondary" steps of nucleation.

6. Self-consistency has been established for approximations by a monodisperse ensemble and other models.

7. A scheme has been proposed for separate renormalization of the front and rear regions of the size spectrum. The high efficiency of the scheme has been substantiated.

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Different Methods for Describing the Nucleation Stage in Supersaturated State Decay

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Abstract—Different methods used for describing nucleation kinetics including a number of newly-proposed approximations have been analyzed. The causes have been revealed of the appearance of an error in the first approximation of the commonly used method based on the perturbation theory.

During the last decade, description of the nucleation kinetics for various systems under diverse external conditions has been an object of intense study [1−8].

At present, an approach that employs methods based on perturbation theory [4] is most commonly used. It was formulated for external conditions corresponding to the spontaneous decay of a metastable state, in which almost instantaneous appearance of initial supersaturation in a system at the first time moment is followed by the cessation of an external action on the system. In this situation, the system evolves only due to the internal processes of nucleation of droplets and their subsequent growth at the expense of vapor consumption. External conditions of this type are rather frequently realized in both experimental studies and theoretical descriptions. The reason for this prevalence is quite obvious—on the one hand, the value of the supersaturation is, in this case, known, and, on the other hand, the pattern of the rear edge of the droplet size spectrum and the characteristic time of the nucleation stage are controlled by the internal processes of the nucleation and subsequent growth of particles, thereby providing information on the nucleation kinetics.

In this communication, we shall analyze the perturbation theory, which was proposed in [4] for describing the decay of a metastable phase. The subject will be considered in the following order.

1. Initially, we shall demonstrate that the recommendations given in the perturbation theory [4] lead to nonuniform expansions.

2. It will be shown that the approach employing the perturbation theory may, as a first approximation (subsequent approximations are difficult to discuss, because even the first one has not yet been analytically solved to the end), be interpreted as some approximation of a monodisperse ensemble of droplets.

3. A more accurate solution will be presented for the evolution equations. It will be compared with that obtained in terms of the perturbation theory. The method based on the perturbation theory will be shown to lead to an essential error.

4. A new version of the monodisperse approximation will be proposed, with this approximation being much more accurate than that based on the perturbation theory.

TRANSFORMATIONS OF THE BALANCE EQUATION

Supersaturation value ζ is determined as follows:

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

where n is the molecule number density in a mother phase and n_∞ is the molecule number density in a saturated mother phase. Let us denote the initial supersaturation value, which is governed by external conditions, as ζ_0.

The balance equation that was formulated in [4] may be written in the following way:

$$\frac{\zeta_0}{\zeta} - 1 = A \int_0^\infty \rho^k g(\rho, t) d\rho,$$

where $g(\rho, t)$ is the droplet distribution function over linear size ρ at time moment t, this function satisfying continuity equation

$$\frac{\partial g(\rho, t)}{\partial t} = -v(t) \frac{\partial g(\rho, t)}{\partial \rho}$$

with boundary condition

$$g(0, t) = \frac{I(\zeta)}{v(t)}.$$

Here, ρ is the droplet size, which grows at rate

$$v(t) = \frac{\zeta(t)}{t_0},$$

which is independent of the value of ρ itself; $I(\zeta)$ is the nucleation rate; and A and t_0 are some parameters. The number of molecules in a droplet with size ρ will then be proportional to ρ^k, where k is a model parameter, and this proportionality explains the meaning of the first relation as the mass balance equation.

This rather simple law of growth describing the evolution of essentially supercritical droplets has formally been extended down to the zero size. This can be done for several reasons. First, it may be shown in an analytical way that, under the conditions of applicability of the thermodynamic approach to the description of a critical nucleus (when the number of molecules in the critical nucleus is much larger than unity), the characteristic size of supercritical nuclei at the stage of intense nucleation appears to be much larger than the critical size. Hence, the formal extrapolation of the growth law down to the zero size will lead to a small error. Second, the distribution of subcritical nuclei appears to be quasi-equilibrium. Therefore, its variations with variations in the amount of a substance in a vapor will be described by the known Gibbs distribution, and allowance for the contribution of subcritical droplets to the mass balance will only slightly change the process parameters. At the same time, the pattern of the condensation kinetics equations will remain unchanged, and only process parameters will alter. This property may be substantiated analytically; however, allowance for this effect is clearly a matter for a separate investigation.

The set of the aforementioned equations may be reduced to one formula,

$$\frac{\zeta_0}{\zeta(t)} - 1 = A \int_0^t (t - t')^k \frac{I(\zeta(t'))}{v(t')} dt' \tag{1}$$

with a somewhat altered value of parameter A.

The case of $k = 0$, which reflects a fixed number of molecules being absorbed by a formed nucleus, is distinguished by the possibility of the analytical solution of Eq. (1), which may be reduced to usual first-order differential equation

$$\zeta_0 \frac{d\zeta(t)}{dt} = -A\zeta^2(t) \frac{I(\zeta(t))}{v(t')} \tag{2}$$

which can obviously be integrated. We shall discuss this case below, as well as the case of $k \ll 1$, which may be rather precisely described based on the solution for $k = 0$.

The case of $k = 0$ corresponds to the formation of nuclei on active sites upon, e.g., cementation or micellization. In this case, the law of supercritical droplet growth cannot be extrapolated down to the zero size (the growth itself does not take place). How-

ever, the validity of the evolution equation may also be analytically shown in this case. The case of $k \ll 1$ is close to the aforementioned one and reflects a weak effect of the condensation sites on large nuclei. This effect slowly decreases with sizes and is especially inherent in cement—sand slurry thickening. In this case, the diffusion blurring of the mother phase density profiles is so strong that we may speak about a uniform medium.

SINGULAR TERMS OF EXPANSIONS

Having isolated the small parameter

$$\varepsilon = \left(\zeta_0 \frac{dH}{d\zeta} \right)^{-1},$$

where H is the height of the activation barrier of nucleation in thermal units $k_B T$ (k_B is Boltzmann's constant and T is temperature), one can clearly see that it is nearly equal to the reciprocal number of molecules in a critical cluster. This value will be the small parameter of the perturbation theory.

It may be that, after the calculation of all terms in the expansions of the perturbation theory and their summation we can obtain a rather accurate result. At the same time, the goal is to obtain specific results in terms of the approximations that could be solved analytically, at least, for main contributions. However, already in the first approximation of the perturbation theory, some auxiliary function φ_k arises, which is preset by the following relation:

$$\frac{d\varphi_k}{dx} = \exp(-x^k \varphi_k), \quad \varphi_0 = 0,$$

which already comprises the γ-function. Hence, already the first approximation (and then all the others) cannot be calculated with the use of simple formulas.

The last circumstance requires the search for a good first approximation for the true solution. Nevertheless, it will be shown that the first approximation is not quite accurate. Although it has been stated in [4] that the expansion is fulfilled in terms of the small parameter, which represents the reciprocal number of molecules in a critical nucleus, the first approximation is far from the true solution.

The aforementioned effect results from the non-uniform character of the expansions. Namely, balance equation (12) in [4] shows that ρ^k passes to the series

$$\left(1 - \frac{\varepsilon x}{\zeta_0 \tau} + \varepsilon w_1 + \dots \right)^k \tag{3}$$

with dimensionless variables

$$x = \frac{\zeta_0 t / t_0 - \rho}{\varepsilon},$$

which plays the role of a shifted size, and

$$\tau = \frac{t}{t_0} - \varepsilon w_1,$$

which plays the role of time. All other parameters have been presented in [4].

It can be seen that the right-hand side of the above equation becomes irregular, when τ tends to zero.

At first sight, the limiting case $\tau \to 0$ corresponds to a negligible contribution to the droplet formation. However, detailed analysis (see the next section) shows that the time of the nucleation period is characterized by a relative smallness, which is smaller than ε in comparison with the imaginary time of the absorption of all excess substance in the mother phase.

RELATIVE SMALLNESS OF NUCLEATION STAGE DURATION

For all k values, it may be established that

$$-\frac{\zeta_0}{\zeta^2(t)}\frac{d\zeta}{dt} = Ak\int_0^t (t-t')^{k-1}\frac{I(\zeta(t'))}{v(t')}dt' > 0$$

for $k > 0$ and

$$-\frac{\zeta_0}{\zeta^2(t)}\frac{d\zeta}{dt} = A\frac{I(\zeta(t))}{v(t)} > 0$$

for $k = 0$. Hence, supersaturation is a descending function of time.

The case of $k \ll 1$ is excluded from the consideration, because, for $k = 0$, the explicit solution has already been presented.

Let us consider all times shorter than some duration t_p, at which supersaturation ζ decreases to $\zeta_0(1-\varepsilon)$.

Then, in the leading term, Eq. (1) may be rewritten as follows:

$$1 - \frac{\zeta}{\zeta_0} = \frac{A}{v(\zeta_0)}\int_0^t (t-t')^k I(\zeta(t'))dt'. \tag{4}$$

For interval $[\zeta_0(1-\varepsilon), \zeta_0]$, the following approximation may obviously be used:

$$I(\zeta(t)) = I(\zeta_0)\exp\left(\varepsilon^{-1}\frac{\zeta(t)-\zeta_0}{\zeta_0}\right). \tag{5}$$

Hence,

$$1 - \frac{\zeta(t)}{\zeta_0} = \frac{AI(\zeta_0)}{v(\zeta_0)}\int_0^t (t-t')^k \exp\left(\varepsilon^{-1}\frac{\zeta(t)-\zeta_0}{\zeta_0}\right)dt' \tag{5a}$$

$$\text{or } \psi(t) = \frac{\varepsilon^{-1}AI(\zeta_0)}{v(\zeta_0)}\int_0^t (t-t')^k \exp(-\psi(t'))dt',$$

where the following function has been introduced:

$$\psi(t) = \varepsilon\left(1 - \frac{\zeta(t)}{\zeta_0}\right).$$

Obviously, Eq. (5a) can be solved, because renormalization

$$t \to \left(\frac{\varepsilon^{-1}AI(\zeta_0)}{v(\zeta_0)}\right)^{1/(k+1)}t$$

and

$$t' \to \left(\frac{\varepsilon^{-1}AI(\zeta_0)}{v(\zeta_0)}\right)^{1/(k+1)}t'$$

transforms it into the following parameter-free equation:

$$\psi(t) = \int_0^t (t-t')^k \exp(-\psi(t'))dt'. \tag{6}$$

In this case, ψ is a universal function. Condition $\psi(t_p) = 1$ makes time t_p a universal constant. It is natural that this solution coincides with the results of numerical simulation presented in [8] for some specific situation.

For $t \geq t_p$, the solutions of Eqs. (1) and (6) almost coincide with one another.

Let us consider the following relation:

$$\frac{\zeta_0}{\zeta(t)} - 1 = A\int_0^{\min(t,t_p)} (t-t')^k \frac{I(\zeta(t'))}{v(t')}dt', \tag{7}$$

which represents an abridged form of Eq. (1). Of course, solution $\zeta(t)$ of Eq. (1) actually coincides with solution $\zeta_{tr}(t)$ of Eq. (7) at $t \geq t_p$ and is smaller that $\zeta_{tr}(t)$ at $t > t_p$. Thus, we have obtained the upper estimate for $\zeta(t)$. Since $I(\zeta_1) > I(\zeta_2)$ for two arbitrary $\zeta_1 > \zeta_2$, we know the upper estimate of nucleation rate I.

It can be seen that, for $t > t_p$, Eq. (7) can be rather easily solved—for integral numbers k, the integral is transformed into a polynomial. In this case, it may be easily shown that, for all k values with the exception of $k \ll 1$, the solution of Eq. (7) ensures a rather rapid decrease in ζ_{tr} and $I(\zeta_{tr})$. Thus, the true solution of Eq. (1) shows a rapid decrease in $I(\zeta(t))$. This means the following.

(1) The period of nucleation, i.e., the period of relatively intense formation of new phase droplets, is rather well determined. There is a lower boundary of this period. There is no long tail of the droplet size spectrum in any noticeable form.

(2) The characteristic relative change in ζ over the nucleation period has an order of ε.

(3) The characteristic time of the nucleation period has an order of t_p, and, as compared with time t_{fin} of a substantial consumption of the metastable phase, it has smallness ε.

This last property indicates that the singularity in expression (3) is indeed of importance and cannot be ignored. The ignorance leads to incorrect results in the first approximation of the perturbation theory. Here, one can see another way to the calculation of nucleation characteristics. Indeed, in accordance with the aforementioned properties, we may extend Eq. (6) to the whole time interval after the end of nucleation, obtain a universal solution, and calculate universal constants as follows:

$$q_i = \int_0^\infty t^i \exp(\psi(t))dt.$$

Even q_i values alone provide the complete information important for the evolution of a system up to the onset of coalescence. For integral k numbers, the q_i values are finite. For arbitrary k values, the following expansion may be fulfilled:

$$(t - t')^k = t^k\left(1 - \frac{t'}{t}\right)^k = t^k\left[1 - k\frac{t'}{t} + \frac{k(k-1)}{2}\left(\frac{t'}{t}\right)^2 - \dots\right].$$

This set of the terms provides an almost ideal result, with only the first three q_i magnitudes being necessary.

MONODISPERSE ESSENCE OF THE FIRST APPROXIMATION

Now, let us analyze the first approximation in order to reveal its analytical structure. The key relation used to show the analytical structure is expression (15) from [4].

It can be seen that factor ρ^k disappears from the integrand, a fact that corresponds to a monodisperse approximation for the number of molecules in droplets. Indeed, only the g distribution function is integrated in Eq. (15) from [4], while factor ρ^k is absent under the integral.

The formal explanation is rather simple (but, however, incorrect): since the relative duration of the nucleation period is short, it may be believed that all droplets have been formed simultaneously. However, this argument does not work at the nucleation stage itself, during which the droplets are formed.

Since we have assumed the monodisperse approximation, in this approximation, it is necessary to determine number N of droplets or any equation for it. In the aforementioned renormalization, it has the following form:

$$\frac{dN}{dx} = \tau^2 \exp\left(-\frac{N}{\tau^{k+1}}x^k\right),$$

where

$$\tau = \left(\frac{1}{k+1}\right)^{1/(k+1)}.$$

It is of importance that, in the monodisperse approximation, all droplets that have already been formed make equal contributions. This leads to an error. The error may be eliminated using the monodisperse approximation proposed in [9].

This monodisperse approximation implies that only particles formed before a certain time moment are included into an ensemble. This approach yields the following equation for the nucleation rate, which is proportional to the derivative of N over x:

$$I(x) = I(\zeta_0)\exp\left[-N_{pr}\left(\frac{x}{l}\right)x^k\right],$$

$$N_{pr}(x) = \int_0^x I_{pr}(x')dx'. \tag{8}$$

Here, I_{pr} is the exact solution of Eq. (6).

Parameter l indicates that the droplets involved in the calculation are formed only during part of the total time interval (namely, at its fraction equal to $1/l$) preceding the current moment. The l value may be interpreted as the characteristic half-width of integrand $\rho^k g$. A more simple definition of this parameter will be given below.

The last relation may be substituted into exact solution I_{pr} as a value calculated in terms of the same monodisperse approximation. In this case, we arrive at the following self-consistent monodisperse approximation:

$$I_{sc}(x) = I(\zeta_0)\exp\left[-N_{sc}\left(\frac{x}{l}\right)x^k\right],$$

$$N_{sc}(x) = \int_0^x I_{sc}(x')dx'. \tag{9}$$

The monodisperse approximation may be further simplified. Note that, during the nucleation period, the argument of the exponent in the expression for the nucleation rate very rapidly increases. Thus, it may be assumed that, for the x values corresponding to the nucleation stage, argument x/l is conforms to an almost ideal case, in which the absorption of a substance by the droplets has actually no effect on the nucleation rate. This is valid at $l \gg 1$. In this way, we arrive at following relation:

$$N\left(\frac{x}{l}\right) \approx N'\frac{x}{l} = I(\zeta_0)\left(\frac{x}{l}\right).$$

Here, I is seen to have the following functional form:

$$I(x) = I(\zeta_0)\exp\left(-\frac{x^{k+1}}{l}\right). \qquad (10)$$

This form coincides with the functional form of the first iteration in the iterative solution of Eq. (6).

The iteration procedure, which has been determined in [3] as

$$\psi_{i+1}(t) = \int_0^t (t-t')^k \exp(-\psi_i(t'))dt', \quad \psi_0 = 0, \qquad (11)$$

leads to the following expression for the first approximation:

$$I_1(t) = I(\zeta_0)\exp\left(-\frac{t^{k+1}}{k+1}\right)$$

when $l = k + 1$ is selected. It is known that this is a rather good approximation for the nucleation rate, at least, at $k \gg 1$.

Complete coincidence with relation (10) will take place if we assume that $l = k + 1$. This is the most reasonable selection for the l value. It can be seen that inequality $l \gg 1$ is assumed to be met. Of course, l may also be selected in a more perfect manner. For this purpose, it is necessary to write an algebraic equation for l and solve it, which is not too difficult to perform. Here, we use the simplest variant by taking $l = k + 1$. In any case, it may be refined.

Now, it is worth returning to the problem of the analytical search for the solutions in terms of the aforementioned approximations. Only nucleation rate (10) can be calculated analytically. The procedure for finding other approximate solutions is as follows. Let us consider the solution of Eq. (10) as a basic approximation. Representing I as

$$I = I_1\frac{I}{I_1},$$

we expand the expression

$$\exp(\ln(I) - \ln(I_1))$$

into a series over argument $\ln(I) - \ln(I_1)$. This is rather efficient and simple, because both I and I_1 have an

exponential pattern. Thus, in relation (9), we arrive at expression

$$\int_0^x \exp(-x^{k+1})\,\mathrm{Polinomial}(x)dx,$$

which may be easily reduced to the sum of zeta functions or $\int_0^x \exp(-x^i)dx$. Thus, the problem has been solved.

The same method may be employed to calculate the higher iterations in procedure (11). In this case, it is clear that this method can be used.

A conviction arises that the new approximations will be much more adequate than are the already available ones. Let us test them.

RESULTS AND DISCUSSION

Now, we shall study in detail all cases described in [4]; namely, we shall consider parameter values $k = 0$, $1/2$, 1, and 2. Here, we add the case of $k = 3$, because it corresponds to nucleation under the free-molecular regime in a three-dimensional space, which is the most natural situation.

Examples of the situations with $k = 0$ have already been mentioned. The case of $k = 1/2$ is consistent with the condensation under the diffusion regime in a unidimensional system. Although the capillary approximation in the unidimensional system does not describe nucleation, allowance for the microscopic corrections, in this case, enables us to speak of nucleation. It may be shown that, in this case, the set of kinetic equations for nucleation will also lead to the balance equation under consideration. The case of $k = 1$ conforms to condensation in a unidimensional system under the free-molecular regime and the condensation in a two-dimensional system under the diffusion regime. The case of $k = 2$ corresponds to the condensation in a two-dimensional system (on a substrate) and the free-molecular growth of nuclei. The case of $k = 3/2$ is consistent with the condensation in a three-dimensional system and the diffusion growth of nuclei. The case of $k = 3$ conforms to the condensation in a three-dimensional system and the free-molecular growth.

In the case of $k = 0$, an analytical solution can be obtained. The corresponding $I(x)$ functions are shown in Fig. 1. It can be seen that, here, nucleation rate as a function of time (or the x coordinate) has a characteristic descending pattern. The nucleation rate as a function of x actually forms the spectrum of droplet sizes. It may be noted that it is rather wide and has a relatively smoothly decreasing tail. The tail plays the key role, the number of particles is infinite, at least,
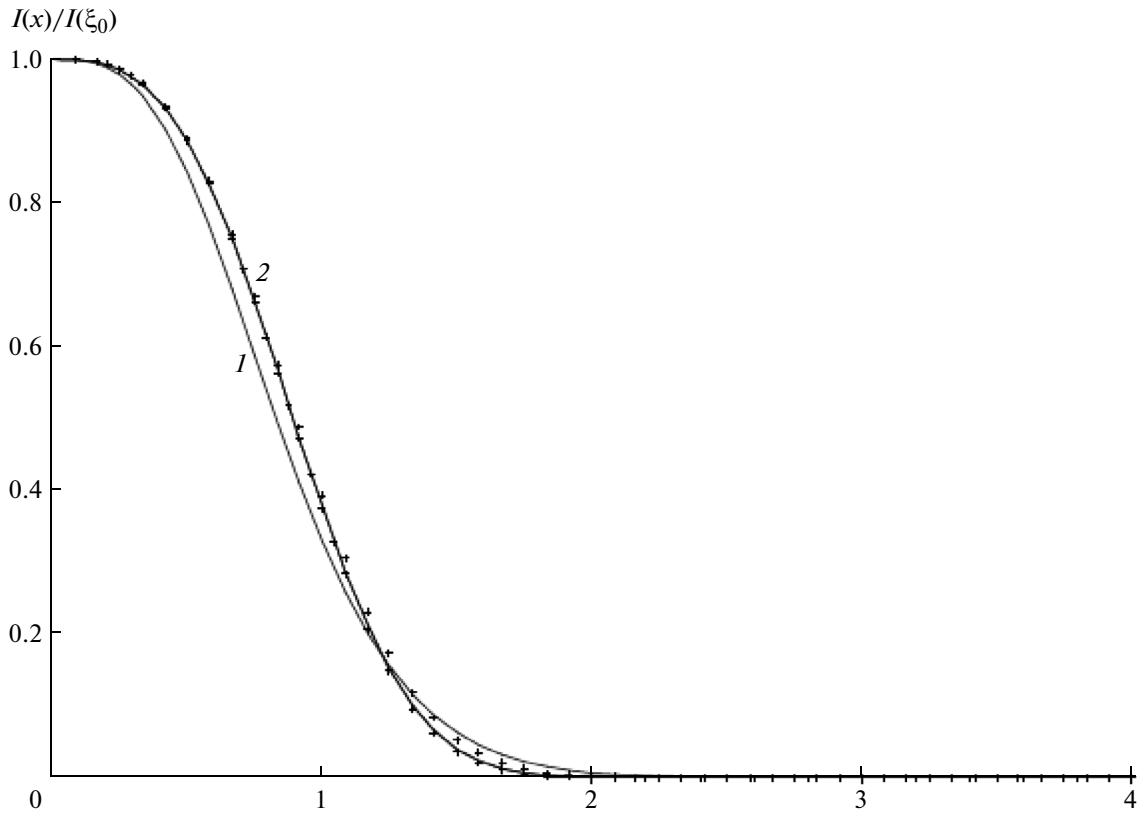
Fig. 1. Patterns of spectra at $k = 0$: (*1*) solution obtained in terms of the perturbation theory and (*2*) the combined exact solution, monodisperse approximations, and iterative solution.
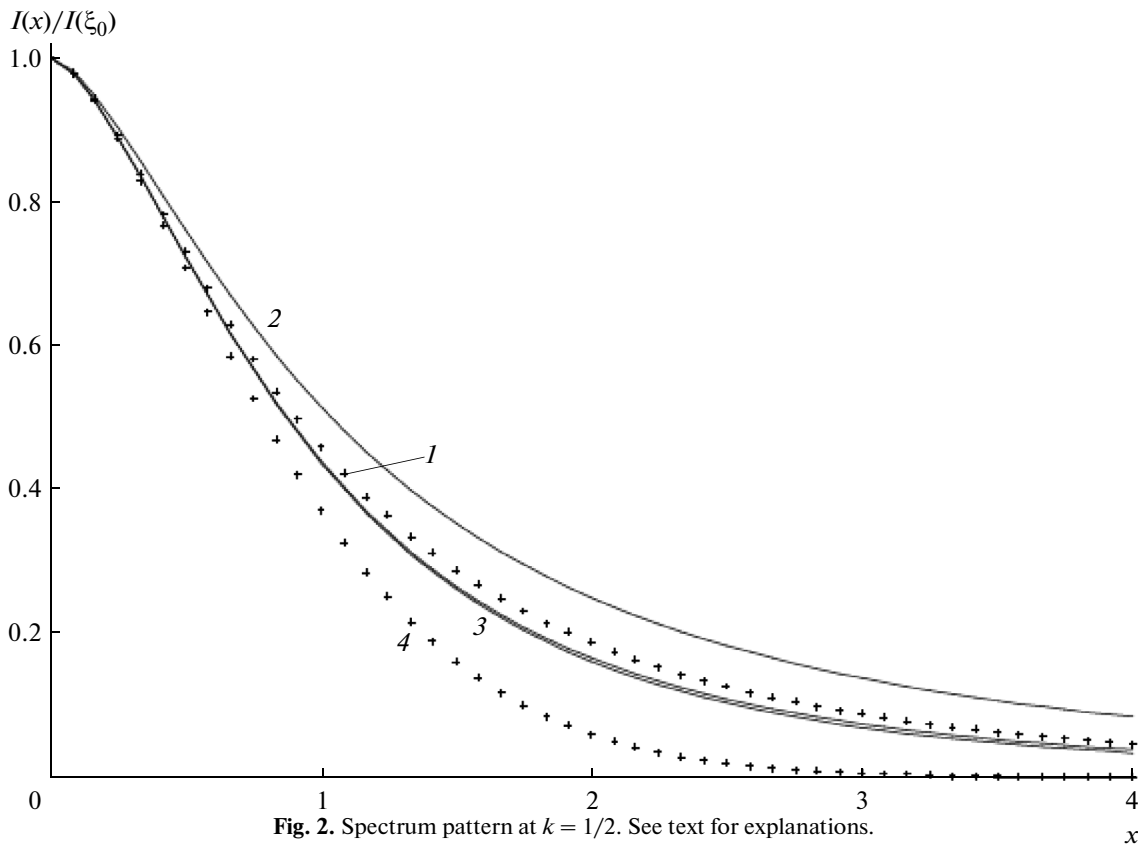

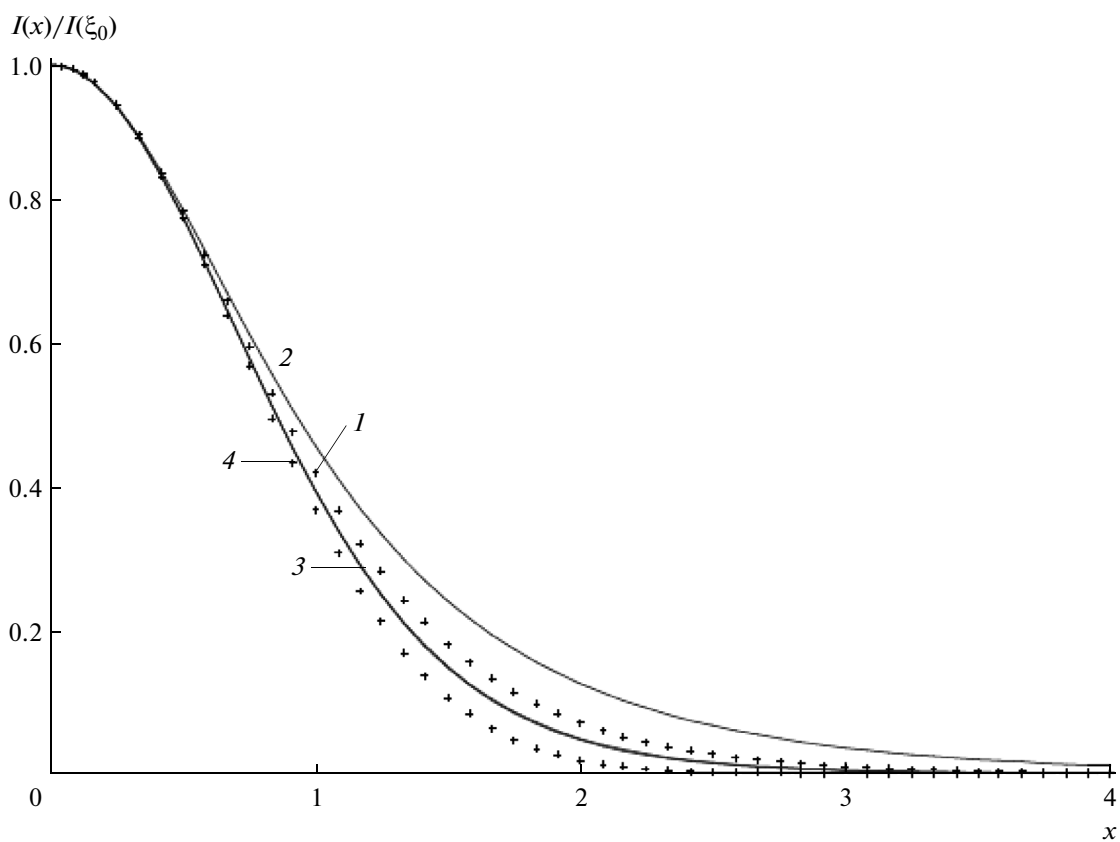**Fig. 2.** Spectrum pattern at $k = 1/2$. See text for explanations.

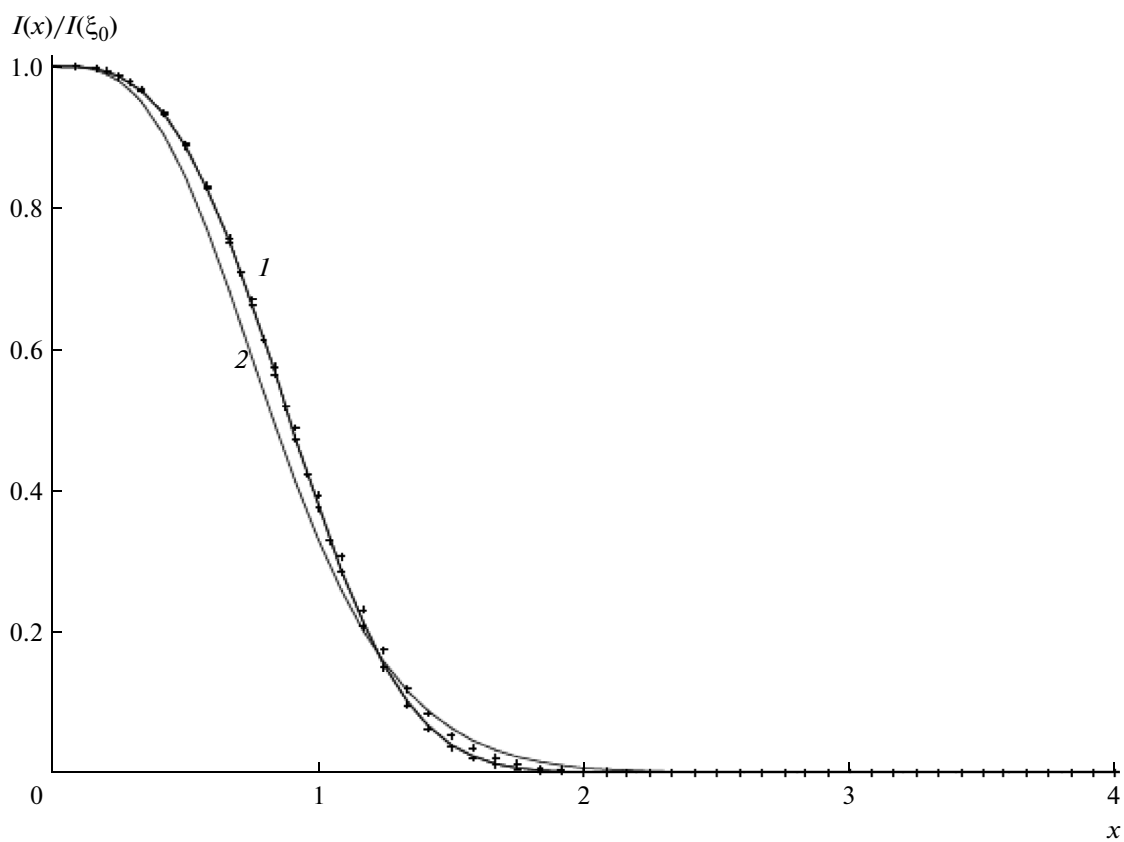**Fig. 3.** Spectrum pattern at $k = 1$. See text for explanations.

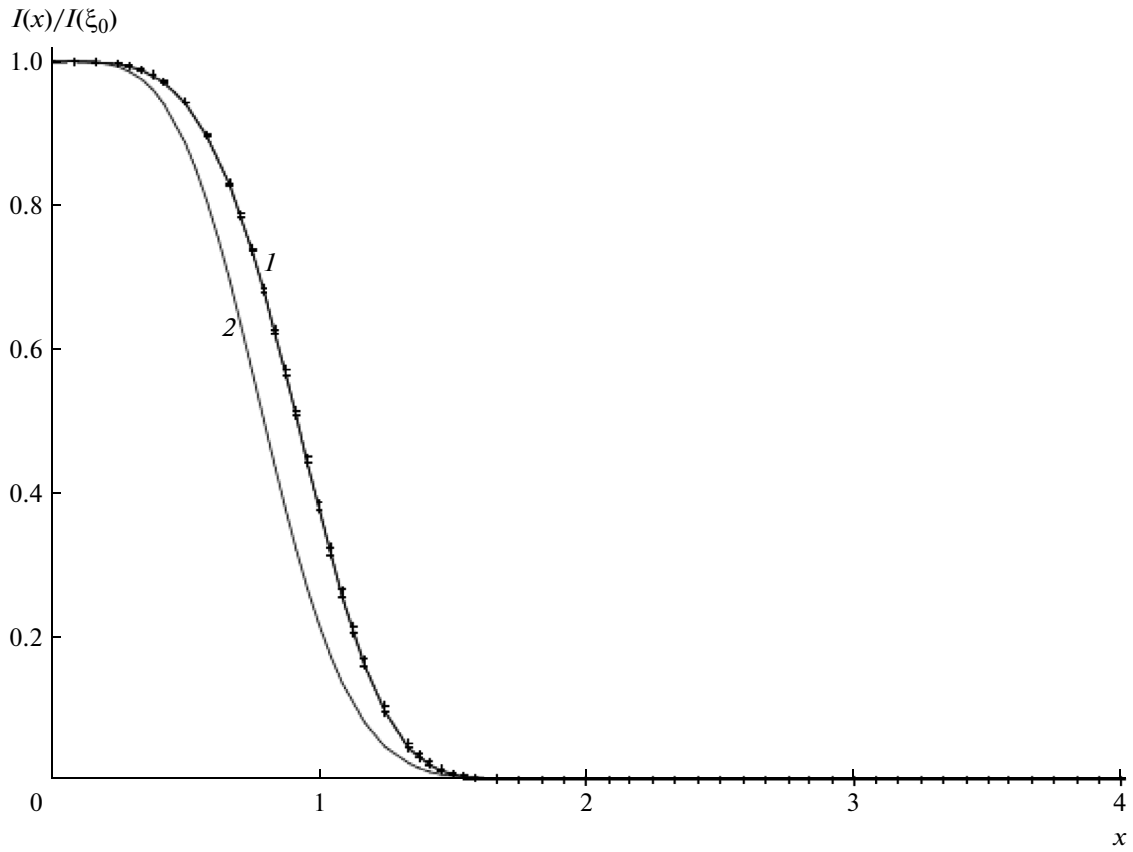**Fig. 4.** Spectrum pattern at $k = 2$. See text for explanations.

$I(x)/I(\xi_0)$

Fig. 5. Spectrum pattern at $k = 3$. See text for explanations.

ΔI

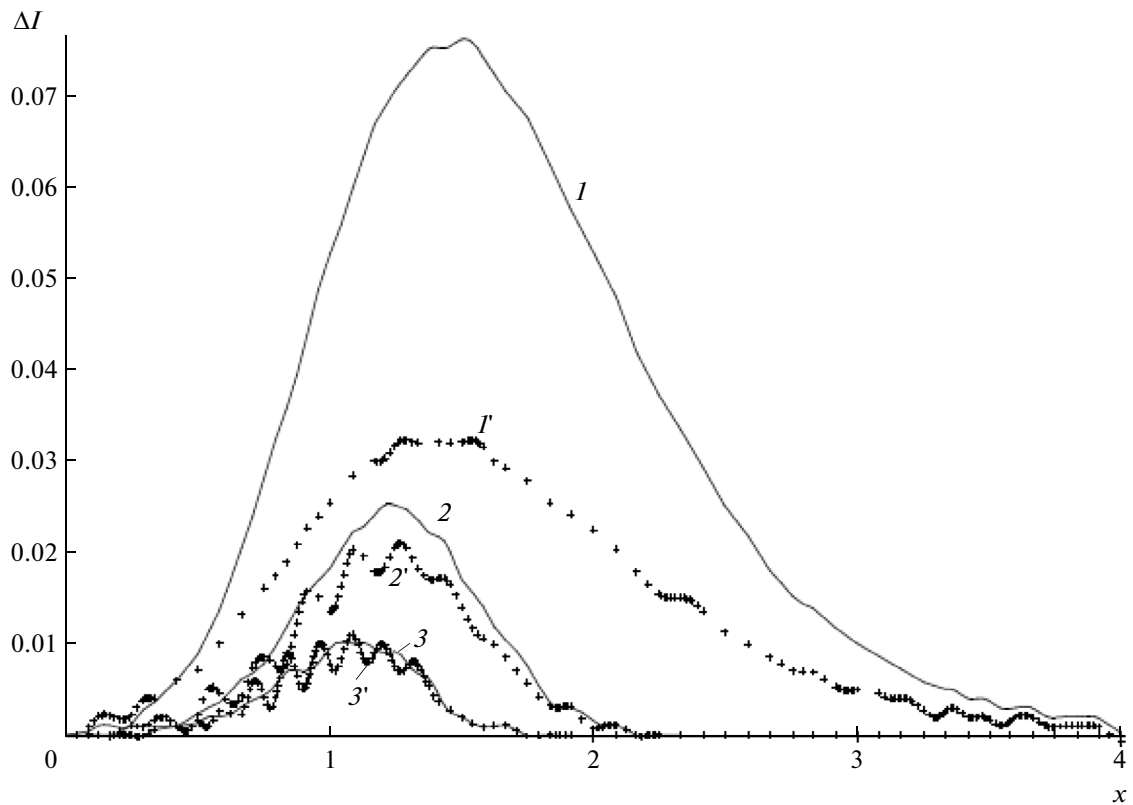**Fig. 6.** Errors ΔI of different approximations as functions of x: $k = (1, 1')$ 1, $(2, 2')$ 2, and $(3, 3')$ 3.

under the exponential approximation of the nucleation rate.

In this case, the main characteristic of the nucleation process (the total number of droplets) is surprisingly easy to calculate. Indeed, total number N_{tot} of droplets will be just equal to number $\zeta_0 n_\infty$ of excess substance molecules divided by total number v_{fin} of molecules in a droplet (in this case, it must be used as an external parameter):

$$N_{\text{tot}} = \frac{\zeta_0 n_\infty}{v_{\text{fin}}}.$$

Here, we deal with an obvious defect of the model for $k = 0$, because the growth rate appears to be zero and the droplets will never become supercritical. It is necessary to use the global nucleation model, and the appropriateness of the introduction of external parameter v_{fin} becomes evident.

The case of small k values is most complex, because, on the one hand, there is no balance equation analogous to the last one, and, on the other hand, all droplets play almost equal roles in vapor absorption, and the number of droplets formed at already decreased supersaturation is rather large.

Let us consider the case of $k = 1/2$. Nucleation rates determined under different approximations are presented in Fig. 2. Here, we can see two dashed and two solid lines. Curve 1 reflects the exact solution. The solution with the expansion of the kernel cannot be distinguished from the exact solution in the scale of the figure. Curve 2 represents the approximation obtained in terms of the perturbation theory. This curve is located rather close to the exact solution; however, there is some deviation.

Curve 3 illustrates actually joined approximations (8) and (9). The solution resulting from the first iteration of approximation (10) is shown by curve 4. It can be seen that the error of the last approximation is essential.

Let us consider the case of $k = 1$, for which the solutions are shown in Fig. 3. This case implies an analytical solution, because it is consistent with a second-order autonomous differential equation. In this figure, curve 1 represents the exact solution. Curve 2 illustrates the approximation based on the perturbation theory. Curve 3 reflects combined monodisperse approximations (8) and (9). Curve 4 shows the solution resulting from the first iteration of approximation (10).

Now, let us represent the solutions obtained for the case of $k = 2$. They are illustrated in Fig. 4. Only two curves are seen here. All dependences corresponding to the exact solution, monodisperse approximations (8) and (9) and the first iteration of approximation (10) are combined into one curve (curve 1). Curve 2 is an approximation based on the perturbation theory. Although it obviously deviates from the exact solution, this deviation seems to become insignificant at a very large value of k. However, this is no more than an illusion.

For the case of $k = 3$, we have obtained the numerical results shown in Fig. 5. Here, we also obtain in fact two curves. Curve 2 has been obtained in terms of the perturbation theory. "Curves" 1 correspond to the exact solution and all other approximations. Comparison of the presented dependences with the curves in Fig. 4 shows that the solution obtained in terms of the perturbation theory for $k = 3$ deviates farther from the exact solution. This tendency resulted from the number of droplets being nucleated within the framework of the perturbation theory being incorrectly taken into account.

Now, let us find the accuracy of the new approximations. Since the errors of the perturbation theory are obvious, there is no need to discuss them. The errors of the approximations for $k = 1$, 2, and 3 are presented in Fig. 6. Three pairs of dotted and solid lines are shown in the figure. Curves 1–3 illustrate the errors of approximation (10) for different k values. Curves $1'$–$3'$ show the errors of approximations (8) and (9) (they almost coincide with each other for all k values at the selected calculation accuracy). Curves 3 and $3'$ actually coincide with one another; hence, in the case of $k > 3$, monodisperse approximations, such as (8) and others, have no advantages over the approximation of the first iteration of approximation (10). The comparison between curves 1, $1'$ and 2, $2'$ shows that, for $k = 1$, the advantage of approximations (8) and (9) over the first iteration of approximation (10) is significant.

An important consequence may be drawn from approximation (10). For example, if we plot the curves corresponding to approximation (10) for all values $k = 1/2$, 1, 2, and 3 in the same figure, we shall see a focus, i.e., the point of the intersection of all curves. The existence of the focus may be proven analytically by simple differentiation. Indeed, the pattern of the curve for the first iteration is surprisingly simple—it is proportional to $\exp(-x^{k+1})$, and, at $x = 1$, the nucleation rate decreases by $\exp(1)$ times. This enables us to raise the issue of the unified length of the nucleation stage.

Since the first iteration insignificantly deviates from the exact solution, we may note a common property of an approximate character. This property consists of the fact that the lengths of the decay of the size spectra are nearly the same. This enables us to say that

there is a common duration of nucleation under external conditions of decay.

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The Interference of Fluctuations
in the Kinetics of Metastable State Decay

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Abstract—The interference of nucleation-rate fluctuations during metastable state decay has been considered. The effects have been shown to be always weak; therefore, averaged parameters may be used to construct the kinetics of the process.

INTRODUCTION

The kinetics of metastable state decay is a significant factor in the theory of first-order phase transitions. It is commonly studied in terms of the mean-field approximation or by explicitly constructing the density profiles of various thermodynamic parameters in the vicinity of an already-formed new phase nucleus. In this situation, the description of the formation of supercritical nuclei of a new phase is based on the classical expression for a steady-state nucleation rate [1], which should be interpreted as the probability that a supercritical nucleus of the new phase is formed rather than as the exact number of formed nuclei. Hence, this value should be considered to be a random parameter in order to properly construct the phase transition kinetics. This fact noticeably complicates the construction of the process kinetics. The use of averaged parameters to construct the dynamics of the process implies that the number of droplets ΔN nucleated over an elementary interval of evolution is much larger than unity. In this situation, the elementary calculation of a variance shows that relative deviation $\delta \Delta N / \Delta N$ of the number of nuclei formed over the elementary interval is on the order of $\Delta N^{-1/2}$. This statement seems to completely solve the problem of substantiating the description of the process kinetics in terms of averaged parameters. However, a more detailed consideration reveals a number of problems, e.g., correct interpretation of the elementary interval of evolution. The deviation of the nucleation rate from an average value can qualitatively change the pattern of the process, and it is insufficient to simply state that the elementary interval is a small portion of the total duration of an intense nucleation process. A question arises as to the truly adequate construction of the process kinetics.

This problem appears to be related to a much narrower problem concerning the description of condensation at a small total number of formed supercritical nuclei (droplets). Attention to this problem was, for the first time, drawn in [2]. Later, it was considered in [3, 4]. However, it should be noted that the authors of these studies focused on corrections to the total number of formed droplets rather than the interaction between instant fluctuating values of the nucleation rate. The substantiation of considerations based on averaged values implies the justification of the weakness of the interference between the deviations of the nucleation rate from the averaged values. This property is not self-evident, since it is the interference of the droplets formed at different time moments that terminates the nucleation during the decay of a metastable state.

This problem is quite complex, because we cannot directly use equations based on the theory of averaged parameters (TAP). In [2, 3], the statistical parameters of the total number of droplets were determined in terms of TAP. In fact, we should initially substantiate the validity of using TAP for our considerations. This study is devoted to this substantiation.

We consider the decay of a metastable state under the conditions of interference between the fluctuations. The description of the interference of fluctuations in nucleation rate appears, to a great extent, to be similar to the discussion of the deviations of the total number of nucleated droplets from the value calculated in terms of TAP. Let us discuss this similarity.

Indeed, the total number of droplets can be counted in terms of TAP, in particular, on the basis of the avalanche-like absorption of a metastable phase by all droplets of a new phase. This property leads us to state that, in terms of TAP, the total number of droplets is just the duration of the nucleation stage taken in reciprocal units of the ideal (initial) intensity of nucleation. In this case, a certain similarity of nucleation conditions takes place up to the end of the intense nucleation. This allows us to hope that the methods

that were previously employed to find fluctuations in the total number of droplets may be successfully applied for calculating the interference of fluctuations at different time moments.

However, two specific circumstances emerge in this case. The former is that, when performing asymptotic expansion of a parameter of this effect as a function of the number of droplets nucleated within an elementary interval, this number being a priori unknown, it is necessary to take into account all expansion terms with positive exponents N_{el}, i.e., the numbers of droplets in the elementary interval. All expansion coefficients must be small. The entire polynomial, which is a part of the series at positive exponents N_{el}, must also be small at all values of physical parameters. Otherwise, there will be some N_{el} value at which the interference becomes strong, and it is this value that will be the number of droplets starting from which the interference between the droplets should be regarded to be strong.

The latter fact complicating the problem is the necessity of considering the interference of fluctuations in the number of droplets formed during an arbitrary portion of the period whose statistical parameters are to be determined. Indeed, although the effect of a quarter of the period should be considered in terms of TAP (which has been substantiated in [5]), but, since the appropriateness of using TAP is questionable here, it is reasonable to examine the effect of fluctuations and show its smallness at any value of the portion of the period under consideration. Two exceptions may be made in this case: when the portion of the period is close to unity (the period cannot have a noticeably strong effect on itself; this effect is close to the identical one) and when the portion is close to zero (this situation is inverse to the previous one). Even if the constructions are based on the averaged nucleation rate, a new additional parameter (the total number of droplets nucleated according to the TAP) disturbs the universal character of the solution, which has been shown in [6] for the theory based on averaged parameters. This fact complicates the solution of the problem.

1. FEATURES OF THE DECAY KINETICS

Let us start our constructions by analyzing the theory based on averaged parameters. It is known [6] that, after certain renormalizations, the behavior of supersaturation is determined by the equation

$$\psi(z) = \int_0^z dx(z-x)^3 \exp(-\psi(x))$$

for function ψ, which represents a renormalized relative deviation of supersaturation from its initial value. The $f = \exp(-\psi)$ function may be interpreted as the
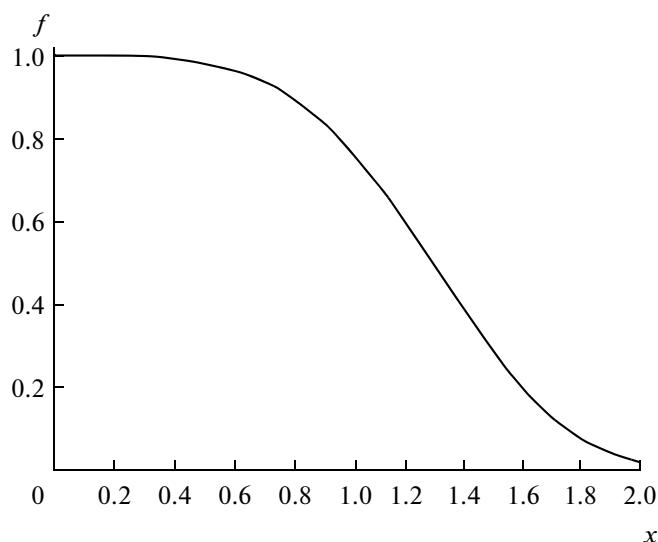

Fig. 1. The pattern of the function approximating the spectrum of droplet sizes.

spectrum of droplet sizes. This spectrum can be adequately approximated by the following distribution:

$$f_1 = \exp(-z^4/4). \tag{1}$$

The pattern of f_1 is shown in Fig. 1. It can be seen that intense nucleation stops at approximately $z_0 = 1.25$.

Approximation (1) is based on the following law of substance absorption for the renormalized number of molecules G in a new phase:

$$G = z^4/4 = \int_0^z (z-x)^3 dx = \int_0^z g(z,x)dx.$$

For further considerations, it will be of importance that, at any time moment t or z, the $g(z, x)$ function has the same pattern. We shall refer to this property as "self-similarity of nucleation conditions." This property demonstrates that droplets that have been formed during the final one-third of the period from the onset of nucleation to the current moment will accumulate a negligibly small amount of a substance. The relative amount of this substance has an order of $1/27$ and is so small that it will still remain small even if some fluctuations emerge. As can be seen from the pattern of f_1, below $z = 0.5–0.7$, all droplets do not substantially absorb vapor. This fact will be of importance for subsequent analysis.

Another important property is the possibility of describing the kinetics in terms of TAP using a monodisperse approximation (see [5]). This property allows one to use the monodisperse approximation [5] not only after the nucleation is completed but also at each current time moment within the intense nucleation period.

Let $t(G)$ be the moment at which the droplets contain G number molecules (in renormalized units). The

use of monodisperse approximation [5] yields the following form of the G value:

$$G = N_m(z)z^3,$$

where $N_m(z)$ is the number of droplets nucleated before the moment corresponding to z. Then,

$$N_m(z) = N(z/4) = z/4$$

and

$$N_m(z) = N(z)/4.$$

2. INTERACTION OF ARBITRARY RANDOM FLUCTUATIONS

Allowance for the interaction of fluctuations at each time moment is of importance for substantiating the smallness of random corrections. In the course of nucleation period, an arbitrary value of z corresponds to an arbitrary value of G (in renormalized units (see [6]), the G value belongs to the (0, 1) interval). It appears to be possible to repeat, to a certain extent, the approach described in [2] with arbitrary parameter G instead of unity (in renormalized units; before the renormalization, it would be $1/\Gamma$ (see [6])).

Let $t(z)$ be a current time moment (z is the coordinate of the rising edge of the size spectrum and t is proportional to z). We assume that, before the time moment corresponding to az (a is a certain parameter), the droplets were formed with no interferences and the Poisson distribution could be used for them. These droplets make up the first group.

The second group is composed by all droplets nucleated within the period from az to z. A natural constraint is imposed on parameter a, namely, $a < 0.7$. Furthermore, assuming that there is an inversion, we take $a > 1 - 0.7 = 0.3$. We believe that the effects of the droplets of the second group on their own formation can be neglected (this follows from the fact that $2 \times 0.7 = 1.4 > 1.25$ and from the remark about the final one-third of the nucleation period). In this situation, we may write down the Poisson distribution for the second group of droplets, but with parameters depending on random values characterizing droplet distribution in the first group. Strictly speaking, we need to use the first four (the first three and the zero) distribution-function moments of the droplets in accordance with [6]; however, to simplify the formulas, we shall present the results for the zero moment alone (the results for the remaining three moments are similar but the formulas are more cumbersome). Sometimes we shall, for simplicity, give expressions only for $a = 1/4$, which corresponds to the monodisperse approximation. Generalization may evidently be performed here; however, since G is an arbitrary value, the above expressions are quite sufficient for our purpose. Of course, we cannot state that it is four distribution function moments that play the key role in vapor absorption. This statement can only be made based on

TAP. Thus, we have to consider the interactions of random fluctuations for all a values that are not too small compared with 1/4; in addition, $1 - a$ must not be too small compared to 1/4. This will be performed below.

At the next step, it will be necessary to pass from the Poisson distribution to the Gaussian distribution and integrate it with regard to the relationship between the stochastic-distribution parameters in the first and second groups (Poisson distributions are much more difficult to integrate). A similar procedure was performed in [2] for the dominant term. The necessity of considering all of the increasing terms in the expansions becomes clear from the analysis of the behavior of the function of interference at all a values. The presence of, at least, one coefficient with a large absolute value means that there is a size of a group for which the interaction provides a strong effect. This could make this interaction the main motive force of the process, while these groups could be regarded as quasi-particles.

In contrast to [2], we need to take into account all correction terms that emerge upon passing from the Poisson distribution to the Gaussian one, as well as the corrections resulting from the nonlinear relationship between the distributions in the considered groups. We have to take into account all the contributions that increase with the total number of nucleated droplets. Then, we obtain the droplet distribution in the following form:

$$P = P_\infty(1 + y),$$

where

$$P_\infty = \left(\frac{9a}{2\pi N(3a + 1)} \right)^{1/2} \exp\left(\frac{-9aD_s^2}{2(3a + 1)} \right),$$

$$D_s = \frac{\hat{N} - N}{\sqrt{N}},$$

$\hat{N}$ is some random value of the total number of droplets, N is the average number of droplets, and y is the correction for the distribution.

At $a = 1/4$, we have

$$y = y_1 s + y_2 s^2,$$

$$y_1 = \frac{1}{74088} D_s(8087 D_s^2 - 10269),$$

$$y_2 = -\frac{4}{9} + \frac{305}{1176} D_s^2$$
$$- \frac{85903}{12446784} D_s^4 + \frac{65399569}{10978063488} D_s^6,$$

where $s = 1/\sqrt{N}$ is a small expansion parameter. In order to obtain contributions that increase with N, we must perform the expansion to s^2.

Why do we have to retain all of the increasing contributions in the expansion? The answer consists in the

specific interaction that is observed at the nucleation stage. A droplet that has been formed at the first time moment creates "external" conditions for the formation of a next droplet; then, the first and the second droplets impose certain conditions on subsequent nucleation, etc. If N number of droplets appeared in the system, for which corrections are large, this very number would be critical for the entire kinetics.

At arbitrary a values, the following expression is derived for P/P_∞ (here, P_∞ is the limiting value at $N \to \infty$):

$$P/P_\infty = 1 + w_1 s + w_2 s^2. \tag{2}$$

Here,

$$w_1 = -\frac{w_{11} + w_{21} + w_{31} + w_{41}}{d(1 + 3l^2)^3(l+1)(l^2-1)} D_s,$$

$$w_{11} = 486l^{12}(1 + D_s^2) - 972l^{11}D_s^2$$
$$+ l^{10}(342 - 648D_s^2) + 756l^{10},$$

$$w_{21} = 810l^9 D_s^2 - l^8(459 - 297D_s^2)$$
$$- l^7(387 + 135D_s^2) + 90l^6 D_s^2,$$

$$w_{31} = -153l^6 + (27D_s^2 - 213)l^5 - (66D_s^2 + 3)l^4 + 27l^3,$$

$$w_{41} = -3l^3 D_s^2 + (16D_s^2 - 3)l^2 + (D_s^2 + 9)l + D_s^2,$$

$$l = \sqrt{a}$$

and

$$w_2 = w_{02}/[(l+1)^2(l^2-1)(1+3l^2)^6 l^2],$$

$$w_{02} = \sum_{i=0}^{3} q_{(2i)} D_s^{(2i)},$$

$$q_0 = q_{01} + q_{02}, \quad q_2 = \sum_{i=1}^{4} q_{2i}, \quad q_4 = \sum_{i=1}^{4} q_{4i}, \quad q_6 = \sum_{i=1}^{5} q_{6i},$$

$$q_{01} = -\frac{1}{12} - \frac{1}{6}l + \frac{243}{4}l^{16} - \frac{135}{2}l^7$$
$$- 90l^8 - \frac{87}{2}l^6 + \frac{243}{2}l^{14} + \frac{81}{2}l^{12} - \frac{153}{2}l^{10},$$

$$q_{02} = -392l^5 - \frac{67}{6}l^4 - \frac{225}{2}l^9 - \frac{3}{2}l^2$$
$$- 812l^{11} + 2432l^{13} - \frac{243}{2}l^{13} - 2432l^{15} - \frac{17}{6}l^3,$$

$$q_{21} = \frac{5265}{4}l^{12} + \frac{51}{2}l^6 + 117l^{10} + \frac{333}{2}l^{11} + \frac{31}{8}l^4,$$

$$q_{22} = \frac{17}{2}l^5 + \frac{5049}{2}l^{14} - \frac{15309}{2}l^{19} + 2079l^{13},$$

$$q_{23} = 31l^8 - 8748l^{18} + 42l^9$$
$$+ \frac{24057}{2}l^{21} + \frac{103}{2}l^7 + \frac{16767}{8}l^{20} + 6561l^{22},$$

$$q_{24} = \frac{4617}{2}l^{15} - 3159l^{16} - 8262l^{17},$$

$$q_{41} = -\frac{4413}{2}l^{13} - \frac{447}{2}l^{15} + 7047l^{21} - \frac{1161}{4}l^{18},$$

$$q_{42} = \frac{361}{6}l^8 + \frac{105}{2}l^{11} - \frac{104247}{4}l^{22}$$
$$- \frac{3}{4}l^4 + 17091l^{20} - 5103l^{23},$$

$$q_{43} = 436l^5 - 311854l^{19} + 7965l^{17}$$
$$- \frac{3213}{4}l^{12} - \frac{475}{3}l^{10} + 510l^{14} - \frac{49}{6}l^7 + \frac{23}{4}l^6,$$

$$q_{44} = \frac{1}{12}l^3 + 444694l^{24} - \frac{1}{12}l^2 - \frac{6903}{4}l^{16} + \frac{74}{3}l^9,$$

$$q_{61} = -13122l^{25} - \frac{40419}{8}l^{18}$$
$$+ \frac{17253}{2}l^{20} - \frac{24057}{2}l^{22} + 4374l^{24} + \frac{6561}{2}l^{26},$$

$$q_{62} = -\frac{48843}{2}l^{21} - \frac{623}{24}l^8 + \frac{59}{36}l^6 - \frac{3609}{4}l^{14},$$

$$q_{63} = -\frac{57}{8}l^{12} + \frac{411}{4}l^{10} + \frac{11}{24}l^4$$
$$+ \frac{1}{72}l^2 - \frac{29}{12}l^7 - \frac{345}{4}l^{11} + \frac{1}{36}l^3,$$

$$q_{64} = \frac{13}{36}l^5 + \frac{65}{4}l^9 + \frac{2421}{4}l^{13} - \frac{7857}{4}l^{15}.$$

Having integrated expression (2), we obtain corrections to the number of droplets. The term comprising s vanishes after integration; the first nonzero correction has an order of s^2 and is independent of the total number of droplets. At $s^2 = 1/4$, the coefficient at a is

$$d_0 = 311/3024 \ll 1.$$

At arbitrary a values, the coefficient at s^2 in the correction to the total number of droplets looks as follows:

$$d_{01} = 108a^6 + 540a^{11/2} - 72a^5 - 203a^{9/2} - 335a^4,$$

$$d_{02} = 713a^{7/2} + 158a^3 + 4a^2$$
$$- 203a^{5/2} - 5a + 39a^{3/2} - 3a^{1/2},$$

$$d_a = (d_{01} + d_{02})/[72a^{3/2}(1-a)^2(1+3a)].$$

It is of interest to compare the results obtained with and without the correction appearing as a result of the passage from the Poisson to the Gaussian distribution. Let us discuss this case in greater detail. The dominant term remains unchanged. For the correction terms, we have the following:
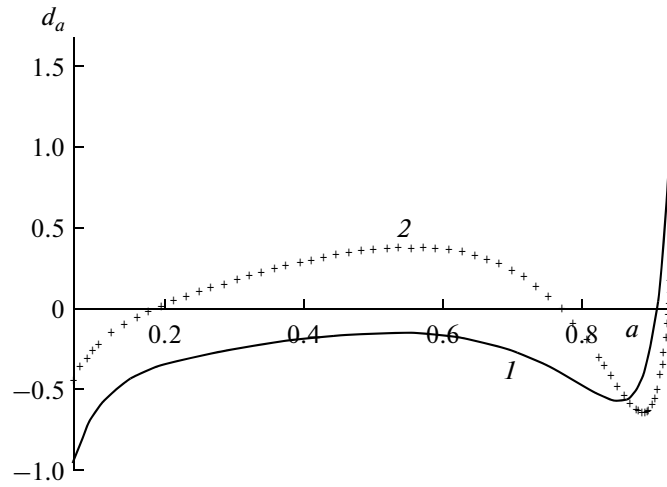
$$y = y_1 s + y_2 s^2,$$

Fig. 2. The $d_a(a)$, functions obtained (*1*) without and (*2*) with allowance for the transition from the Poisson and Gaussian distribution.

$$y_1 = -\frac{17}{71088} D_s(-2331 + 289D_s^2),$$

$$y_2 = \frac{17}{196} D_s^2 + \frac{732037}{12446784} D_s^4 + \frac{24137569}{10978063488} D_s^6 - \frac{13}{36},$$

$$d_0 = -37/126,$$

$$d_a = (d_{a1} + d_{a2})/[72a^{3/2}(1-a)^2(1+3a)],$$

$$d_{a1} = 648a^{11/2} - 216a^5$$
$$- 1062a^{9/2} + 108a^4 + 753a^{7/2} - 30a^3,$$

$$d_{a2} = -195a^{5/2} - 126a^2 + 19a^{3/2} + 6a - 7a^{1/2}.$$

The corrections are seen to be small. At arbitrary values of a, with the exceptions of ones that are too small and too close to unity (these values are unrealistic), we obtain values shown in Fig. 2. All corrections have the same order and are small. There is a plateau for all a values except for $a \ll 1/4$ and $1 - a \ll 1/4$. Thus, the smallness of the corrections for interaction between random peaks is quite obvious here.

However, even small corrections can lead to significant changes in the total number of droplets via consecutive effects. The conclusion regarding the smallness of the corrections in the total number of nucleated droplets can be drawn from specific kinetic features of the process (e.g., the effect of the first droplet can turn out to be crucial). This process should be considered separately.

It must be noted that we did not take into account the corrections for the passage from summation to integration. This passage must be made, because the number of droplets is a discrete value. Indeed, as we can see, the transition from summation in the formula

$$P(N) = \sum P_1(\hat{N}_1, N_1)P_2(N - \hat{N}_1 - \hat{N}_2(\hat{N}_1))$$

to integration (here, N is the total number of droplets; $\hat{N}_1$ is a random number of droplets in the first group; $\hat{N}_2$ is a random number of droplets in the second group; N_1 is the average number of droplets in the first group; N_2 is the average number of droplets in the second group, which is a function of the random number of droplets in the first group $\hat{N}_1$; and N remains to be a random value)

$$P(N) = \int d\hat{N}_1 P_1(\hat{N}_1, N_1)P_2(N - \hat{N}_1 - \hat{N}_2(\hat{N}_1))$$

can be performed using the Euler–Maclaurin expansion. This yields an asymptotic series that can be included in the final result. This passage is a formal solution of the problem. However, the discrete nature of the nucleation process cannot be completely excluded from consideration. The nucleation process cannot start without the formation of the first droplet. A condensing system will be waiting for the first droplet during an indefinitely long period of time. This fact indicates that the discrete nature must be taken into account in a special manner. At least, the initial moment must be taken equal to the moment at which the first droplet arises and the nucleation must be considered under external conditions created by the first droplet, the effect of which is explicitly described as being proportional to z^3. This effect of the first droplet is rather interesting; however, allowance for it gives rise to appreciably small corrections. Nevertheless, these corrections are comparable with the correction obtained above for the total number of droplets. Furthermore, the contribution of the first-droplet effect may be significant when considering the nucleation dynamics.
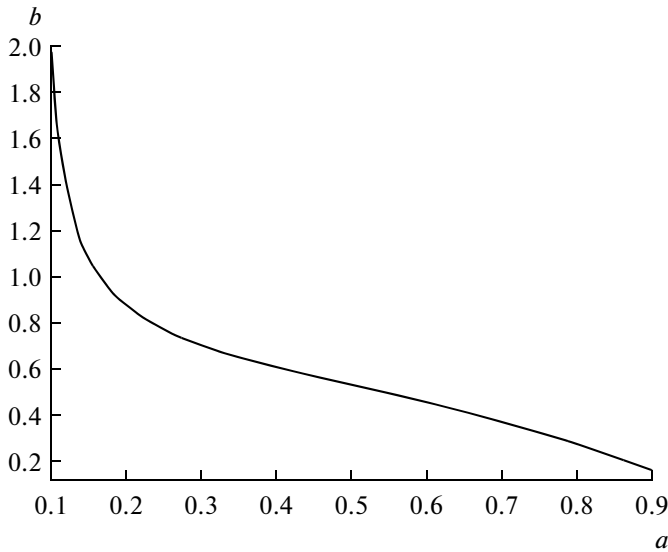
Fig. 3. The pattern of the $b(a)$ function.

Fig. 4. The pattern of the $r(a)$ function.

3. SELF-SIMILARITY OF GAUSSIAN DISTRIBUTIONS

In order to use the Poisson distribution for the first group of droplets, the following circumstance must be taken into account. In reality, nucleation conditions for the first group are identical to those for nucleation of the entire group of droplets. Then, distribution P_1 with another half-width should be used as the distribution in the first group. However, it is impossible to assign a half-width to the Poisson distribution as simply as it can be done for the Gaussian distribution. This is why we have discussed the observed effects without the passage from the Poisson to the Gaussian distribution above. Thus, the Gaussian distribution may be used as the initial one. The half-width of the Gaussian distribution can be easily renormalized. Then, for the distribution of the first group of droplets P_1, it may be taken that

$$P_1 \to \exp[-(\hat{N}_1 - N_1)^2/(2bN_1)],$$

where b is the renormalizing factor. The distribution of the second group of droplets P_2 remains unchanged:

$$P_2 \to \exp[-(\hat{N}_2 - N_2)^2/(2N_2)].$$

Here, N_2 is specified as

$$N_2 = \left(1 - \frac{1}{3}s + \frac{2}{9}s^2 - \frac{14}{81}s^3 + \frac{35}{243}s^4 - \frac{91}{279}s^5 - a\right)N,$$

where N is the average value of the total number of droplets and

$$s = \frac{\hat{N}_1 - aN}{aN}$$

is a small parameter on the order of $N^{-1/2}$. After the integration, we arrive at the following distribution:
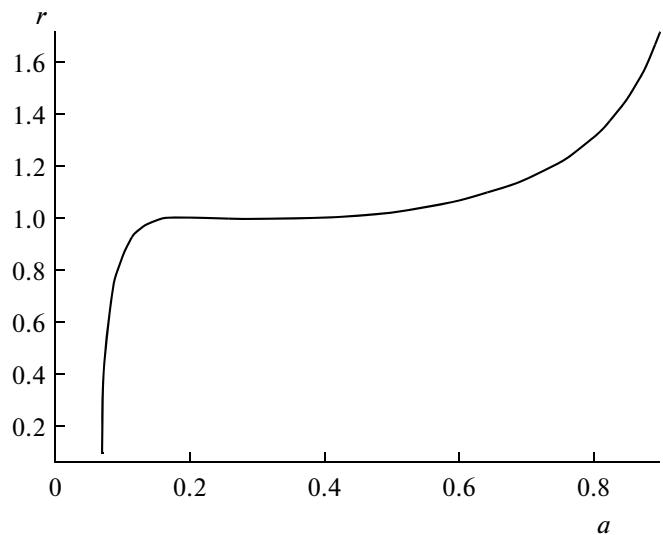
$$P \to \exp\left[-\frac{9ad^2}{2(9a + b - 6ba + 9ba^2 - 9a^2)}\right],$$

where $d = (\hat{N} - N)/\sqrt{N}$. The half-width of distribution P_1 must be equal to the half-width of distribution P, which results in the following relationship:

$$b = 9\frac{a(1-a)}{-9a^2 + 15a - 1}.$$

The pattern of function $b(a)$ is shown in Fig. 3.

Now, let us discuss the effects of renormalization. The ratio between the half-widths of the Gaussian distributions determined with and without the renormalization has the following form:

$$r = \frac{1}{9}\frac{\sqrt{-9a^2 + 15a - 1}\sqrt{3a + 1}}{a\sqrt{1-a}}.$$

The $r(a)$ function is shown in Fig. 4. For all reasonable a values, the $r(a)$ function is approximately equal to unity. At $a = 1/4$, we obtain $r(a) = 1.0041$. The smallness of the variations takes place only due to the use of the monodisperse approximation; in other situations, the deviations can be much more significant. Instead of taking into account all of the considerable (the first four) moments of the distribution, we may directly calculate the effects from the explicit pattern of the spectrum using the iteration procedure.

The result of this consideration can be summarized as follows. It has been confirmed that the effects of random emergence of droplets are rather weak. The condensation kinetics may also be considered using the expression for the averaged nucleation rate.

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