

Approximate Methods for Constructing a Solution of Balance Equation with a Known Number of Nuclei of a New Phase in the Kinetics of First-Order Phase Transitions

V. B. Kurasov

St. Petersburg State University, 13B Universitetskaya nab., St. Petersburg, 199034 Russia

e-mail: victor_kurasov@yahoo.com

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A reasonably accurate solution of the balance equation for a substance is obtained for a predetermined number of nuclei of a new phase in the nucleation kinetics. This solution is necessary for the adequate description of secondary nucleation and accurate determination of the number of nuclei of a new phase. The approximation is constructed by studying the characteristic properties of the solution at various stages of evolution. In particular, iterations, quadratic approximation, asymptotic formula, relaxation solution, and deformed relaxation are constructed. As a result, a solution that is accurate for the time intervals up to the beginning of precondensation is obtained.

Keywords: nucleation, supersaturation, secondary nucleation

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1. INTRODUCTION

The nucleation process [1] is a complex multi-stage process of phase transformation. An adequate description of each stage is necessary due to the fact that the previous stage affects the course of the subsequent evolution of the system. Indeed, in some cases it is possible to observe a reduction in the description of the system, however, in almost all cases the number of nuclei of a new phase is the most important parameter governing subsequent evolution.

An example of such a situation is also demonstrated by the evolution of the system after the formation of new phase nuclei including solid nucleation centers on substrates and in free space. At first glance, it seems that the process of nucleation is completed and there is no need to describe further evolution. However, if there is a small number of active centers (heterogeneous centers) in the system, then after the end of nucleation, the process of homogeneous nucleation occurs on the heterogeneous centers. To describe homogeneous nucleation in this case, it is necessary at least to know the solution of the balance equation with a known number of nuclei of a new phase (in this case, it is equal to the number of heterogeneous centers). Some effective methods for constructing such a solution are given below. In fact, the process of homogeneous nucleation of a new phase deforms the pure evolution of the system with a known number of nuclei. However, it is possible to show that this deformation is quite small [2]. The problem of constructing a description for homogeneous nucleation (or nucleation at heterogeneous centers with significantly lower activity) can be divided into two steps: describing a supersaturation without homogeneous nucleation and constructing a solution that describes homogeneous nucleation for the previously constructed solution as in the case of external supersaturation [3]. Thus, the problem on constructing a solution for balance equation with a known number of nuclei of a new phase is relevant. We consider this problem in the present article.

2. THE WORST POSSIBLE CASE FOR DESCRIBING

In the case of a small number of heterogeneous centers (and it is this situation that is important when studying the evolution of the system), it is quite easy to describe the initial conditions for further evolution of system. The number of nuclei of a new phase coincides with the total number of heterogeneous centers η . It can be shown that the size spectrum for nuclei of a new phase is almost monodisperse (the arguments are similar to those presented in [4]). The ideal supersaturation Φ (that is, the supersaturation that would

occur in the system if there was no consumption of the metastable phase by the nuclei of a new phase) is a quantity characterizing the external conditions. Φ is a known function of time t . We use the simplest approximation with a constant coefficient t :

$$\Phi[t] = At$$

The form of the function $\Phi[t]$ can be different. It is obvious that $d\Phi/dt > 0$. Since Φ is the function of time, its generalization to an arbitrary law is formal and the advantage of the methods given below is that they generalize the dependence of ideal supersaturation on time to a rather arbitrary law. These methods turn out to be effective for dependencies without avalanche-like increase of supersaturation in time even when particles of a new phase are nucleated. It is easy to define limit laws for such dependencies. If we assume that the spectrum of the nuclei of a new phase is finite, then the time raised to the third power is the limit dependence, and if we assume that the nucleation of particles of a new phase continues, then time raised to the fourth degree is the limit dependence. Hereinafter, the nucleus growth mode is considered to be free-molecular.

The balance equation can be written as follows

$$\Phi = \zeta + \eta z^3 \quad (2.1)$$

where ζ is the actual supersaturation and the term ηz^3 is the number of molecules in the nuclei of a new phase. In the last term, z is the linear size of a new phase nuclei, and η is the total number of nuclei of a new phase that does not change with time and is equal to the total number of heterogeneous centers. Under various types of external conditions, factors may appear before the last term. These factors are caused by the evolution type imposed by external conditions. For example, there are two different factors for nucleation processes caused by isothermal cooling and adiabatic expansion of the system. In any case, this factor is a known; for such a factor we adopt the notation $W[t]$. Then, we have

$$\Phi = \zeta + W[t]\eta z^3$$

We can consider a situation when $W[t] = 1$ (this is a case for a vapor source), other physically significant cases are considered similarly. When spraying on a substrate, we naturally have a pure source of vapor and there is no need to introduce this factor.

In dimensionless time, the supersaturation ζ is associated with a change in the linear size as follows

$$\zeta = dz/dt$$

This expression closes the relation (2.1) and it becomes an ordinary first-order differential equation (or non-linear Abel equation in the absence of a factor corresponding to the type of external conditions). It is necessary to set the initial condition, which has a form: $z(t_{init}) = 0$ where t_{init} is time of heterogeneous nucleation (we mean exactly the moment of heterogeneous nucleation, since the size spectrum for nuclei of a new phase is monodisperse). It is clear that $t_{init} > 0$ (since $t = 0$ is the moment when Φ becomes positive and before this moment phase is stable and no nucleation occurs). Now we consider the worst situation for applying the methods presented below, namely, when $t_{init} = 0$. The higher t_{init} , the stronger the estimates underlying the approximate methods presented below. This part of the analysis was performed in [2] and there is no need to repeat it here. The major point of the analysis is the determination of the parameter

$$Q = (\Phi[t_{max}]/\zeta_{max}) - 1$$

Here t_{max} is the moment at which the maximum of supersaturation is reached, ζ_{max} is the maximum value of supersaturation. The parameter Q turns out to be sufficiently small. It is the smallness of this parameter that plays a key role in the fast convergence of the iterations given below. It can be shown that this parameter controls the accuracy of expressions up to the onset of the asymptotic period of evolution. It is possible to write down all the formulas presented below also for an arbitrary value of t_{init} , but they are quite cumbersome. Therefore, we write the formulas only for the worst-case situation. Paradoxically, they have the most compact form. It is clear that the simplest way to verify the applicability of formulas for an arbitrary case is to write them explicitly for an arbitrary t_{max} .

3. ANALYSIS FOR $t_{init} = 0$

We consider the worst possible case. In this case, the evolution equation is written as

$$At = \frac{dz}{dt} + z^3 \eta$$

with initial condition

$$z(t=0) = 0$$

We call dz/dt simply the supersaturation ζ . By renormalization, we obtain

$$t = \frac{dz}{dt} + z^3$$

with the same initial condition.

3.1. Determination of Maximum Supersaturation

In this case, the construction of iterations is logical and natural. Iterations are determined by recurrence formulas

$$zt = \left(\frac{dz}{dt} \right)_{i+1} + z_i^3$$

$$z_{i+1} = \int_0^t \left(\frac{dz}{dt} \right)_{i+1} dt$$

with an initial approximation in the form

$$z(0) = 0$$

Iterations and the exact solution (it tends to the abscissa axis for long moments of time) are shown in Fig. 1. The higher the iteration number, the more precisely it approaches the solution. We note that the first iteration sufficiently well describes the qualitative behavior of the solution, but cannot give a sufficiently accurate value for the supersaturation amplitude. The second iteration can already ensure that a sufficiently accurate amplitude value of the supersaturation is found (for the case of intense nucleation). All iterations of a higher order that can more accurately describe the solution at the stage of increasing supersaturation and more accurately determine the position of the supersaturation maximum and its value can be analytically calculated. However, it is not possible to precisely and effectively describe the stage of the fall of supersaturation using this method. The reason for this lies in the change in the rate of convergence of iterations. Indeed, the essence of the iterative procedure is based on the smallness of the parameter

$$\frac{\Phi - \zeta}{\Phi} \ll 1$$

After the significant decrease in supersaturation, we have the opposite situation

$$\Phi \ll \zeta$$

which shows the inefficiency of the iterative approach to the description of the reverse side of supersaturation hump.

3.2. Reverse Side of the Supersaturation Hump in the Vicinity of the Maximum

The problem for obtaining a solution over the entire period of decrease in supersaturation is unnecessarily difficult to offer an approximation suitable over this period. Therefore, we divide this period into several sub-periods. The first sub-period is limited by the decrease in supersaturation to three quarters of the maximum value

$$\zeta(t_{dec}) = \frac{3}{4} \zeta(t_{max})$$

There are at least two effective approaches in this sub-period. The first consists in renormalizing the first iteration for obtaining the correct (exact) position of the maximum (this position is determined in the framework of the second initial iteration). Then, based on the renormalized first iteration, the second iter-

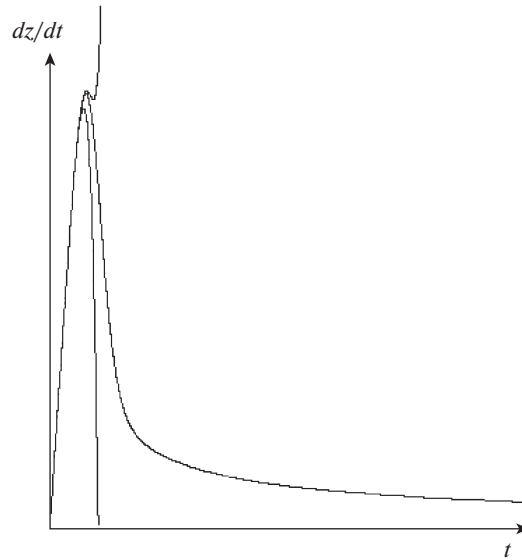


Fig. 1.

ation is constructed. The second approach is even simpler. We determine the position of the maximum t_{max} and the amplitude value ζ_{max} based on the initial iterations. For the second derivative $d^2\zeta/dt^2$ we obtain

$$\frac{d\zeta}{dt} = A - 3\eta z^2 \zeta \tag{3.1}$$

$$\frac{d^2\zeta}{dt^2} = -6\eta z \zeta^2 - 3\eta z^2 \frac{d\zeta}{dt}$$

Near the maximum of ζ , the second term on the right-hand side of the previous expression should be small and the first term is approximately proportional to z , since ζ changes slightly near its maximum. Thus, $d^2\zeta/dt^2$ is proportional to z

$$|d^2\zeta/dt^2| \sim (6\eta \zeta^2) z \tag{3.2}$$

The first initial iteration is a good lower bound for t_{max} , ζ_{max} , z_{max} . Explicit calculations give

$$\zeta = At - \eta A^3 t^6 / 8 \tag{3.3}$$

The condition for the maximum is written as

$$1 = 6\eta A^2 t^5 / 8$$

and then

$t_{max} = (8/(6\eta A^2))^{1/5}$. This means that in the renormalized quantities, the following estimate is valid

$$t_{max} \approx 1\bar{x}$$

Then, in order to significantly deviate $d^2\zeta/dt^2$, it is necessary to substantially change z as well. But according to (3.3) for $z > 1$ we get that a significant deviation of z means a critical decrease in ζ . Then $d^2\zeta/dt^2$ can be considered as a quasi-integral of evolution over period after t_{max} and until the complete loss in value of ζ (in fact, up to a significant decrease, and not until the complete loss in ζ , since according to (3.2) it is the change in ζ that deviates $d^2\zeta/dt^2$ from the maximum supersaturation). Note that it is impossible to integrate (3.1) directly by setting $z = z_{max}$

$$d\zeta/dt = A - 3\eta z_{max}^2 \zeta$$

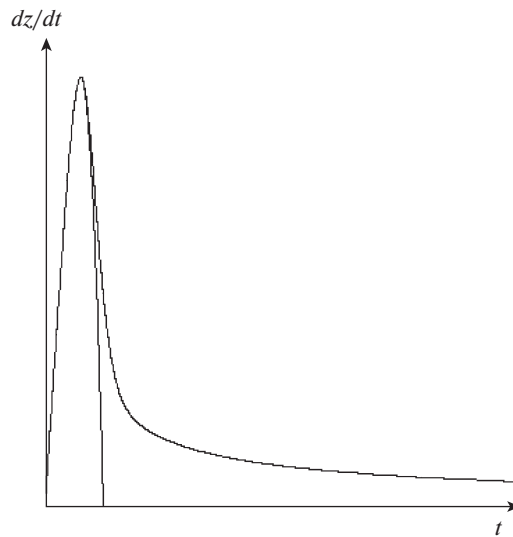


Fig. 2.

since it is precisely the deviation of z from z_{max} that causes the deviation of ζ from ζ_{max} at the beginning of the decrease immediately after t_{max} . As a result, we arrive at a verification of the approximation applicability

$$\zeta = \zeta_{max} + (1/2) (d^2\zeta/dt^2)_{max} (t - t_{max})^2$$

for $t > t_{max}$ and up to the significant decrease in ζ . In fact, this approximation works well up to $t_{3/4}$ determined from

$$\zeta_{3/4} = \frac{3}{4} \zeta_{max}$$

The quadratic approximation (lower curve) and the exact solution (upper curve) are shown in Fig. 2.

3.3. Asymptotics

A set of methods can be proposed to describe the evolution after $t_{3/4}$. Different sub-periods should be described by different methods. First, we describe the asymptotic sub-period that corresponds to $t \rightarrow \infty$. In this case, we can approximately write

$$At = \eta z^3$$

Then, we have

$$z_{(as0)} = (A/\eta)^{1/3} t^{1/3}$$

The recursive procedure is as follows:

$$dz/dt|_{(asi+1)} = dz_{(asi)}/dt$$

and

$$z_{(asi)} = ((At - dz/dt|_{(i)})/\eta)^{1/3}$$

The calculations result in

$$dz/dt|_{(as1)} = (1/3)(A/\eta)^{1/3} t^{-2/3}$$

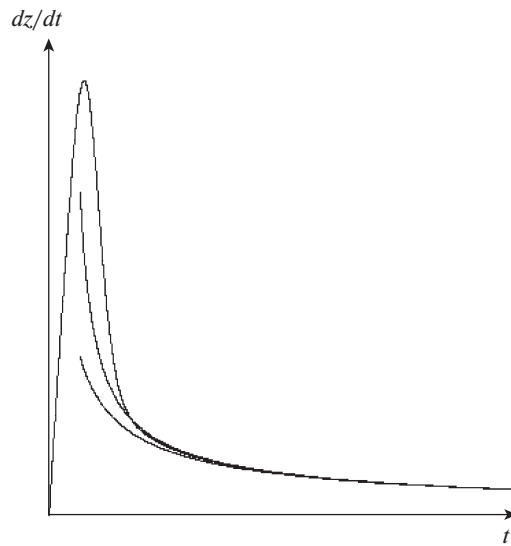


Fig. 3

and

$$z_{(as1)} = \left(\left(At - \frac{1}{3} (A/\eta)^{1/3} t^{-2/3} \right) / \eta \right)^{1/3}$$

as a first approximation and in

$$\frac{dz}{dt}_{(as2)} = \frac{1}{3} \left(\left(At - \frac{1}{3} (A/\eta)^{1/3} t^{-2/3} \right) / \eta \right)^{-2/3} \eta^{-1} \left(A + \frac{2}{9} (A/\eta)^{1/3} t^{-5/3} \right)$$

as a second approximation, the first and second asymptotic approximations and the exact solution (curve having onset at origin) are shown in Fig. 3. The higher the approximation number, the more accurate it is.

It can be seen that even the first approximation for dz/dt works well, the second approximation is even more accurate. Together with the quadratic approximation, we can assume that the solution is a combination of the asymptotics and the quadratic approximation, and the quadratic approximation is used where it is higher than the asymptotics, and the asymptotic is used where it is higher than the quadratic approximation. The resulting solution is valid, but it has one obvious drawback. It cannot provide smooth relaxation of the solution to asymptotics. To see this relaxation, it is necessary to consider the sub-period of effective relaxation and use other specific features of the solution.

3.4. Relaxation and Deformed Relaxation

Even the first initial iteration turns out to be able to describe the process qualitatively and show one important feature of the process. This feature is the rapid decrease in $|dz/dt|$ shortly after reaching a maximum. This behavior is ensured by a high 6th power (namely, $6 \gg 1$) in the law for dz/dt . We consider moments of time that are greater than $t_{3/4}$. Then the moments of time t at which dz/dt deviates from the asymptotic value $dz/dt|_{as}$ satisfy the inequality

$$t - t_{3/4} \ll t_{3/4}$$

The last inequality allows one to approximately consider the action of the source At as $At_{3/4}$. Then the evolution equation acquires the following form

$$At_{3/4} = dz/dt + \eta z^3$$

$$t - t_{3/4} = \int_{z_3/4}^z dz (At_{3/4} - \eta z^3)^{-1}$$

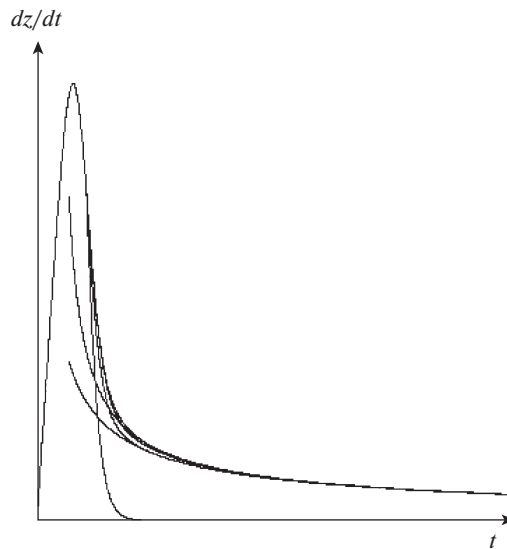


Fig. 4.

The last expression allows us to analytically calculate the integral. This allows us to obtain the curves $z_{rel}(t)$ and $(dz/dt)_{rel}(t)$. It is clear that $(dz/dt)_{rel}$ approaches zero. In Figure 4, there is curve approaching the zero level. This is $(dz/dt)_{rel}$.

The weakest point in the constructed solution $(dz/dt)_{rel}$ is that it tends exactly to zero. In fact, it should tend to $(dz/dt)_{as}$. To obtain the necessary property, it is necessary to propose an approximate deformation of the solution. We write relaxation not to zero, but to asymptotics. After such a deformation, the relaxation curve is denoted by $(dz/dt)_{relas}$. It has the following form

$$\left. \frac{dz}{dt} \right|_{relas} = \left. \frac{dz}{dt} \right|_{as} + \left(\left. \frac{dz}{dt} \right|_{\frac{3}{4}} - \left. \frac{dz}{dt} \right|_{as} \right) \left(\left. \frac{dz}{dt} \right|_{\frac{3}{4}} \right)^{-1} \left. \frac{dz}{dt} \right|_{rel}$$

In this case, we can set the asymptotics of any order. In fig. 4, there are curves approaching $(dz/dt)_{(as1)}$ and $(dz/dt)_{(as2)}$. These curves correspond to relaxation solutions $(dz/dt)_{relas(1)}$ and $(dz/dt)_{relas(2)}$ (solutions are known from the previous figure). It can be seen that the agreement between the present solution (curve starting from origin) and the approximations are ideal (it means they cannot be distinguished at scales of the figure).

An approximate calculation of the integral can also be proposed.

$$\int dz (At_{3/4} - \eta z^3)^{-1} = \eta^{-1} \int dz \left(\frac{At_{3/4}}{\eta} - z \right)^{-1} S(z)^{-1}$$

$$S(z) = \left(\frac{At_{3/4}}{\eta} \right)^2 + \left(\frac{At_{3/4}}{\eta} \right) z + z^2$$

It is easy to see that the quantity

$$S(z) = \left(\frac{At_{3/4}}{\eta} + z \right)^2 - \left(\frac{At_{3/4}}{\eta} \right) z$$

does not equal to zero for $z > z_{3/4}$. Then we can set $S(z_{3/4})$ instead of $S(z)$ and the integral reduces to the pure logarithm. This circumstance gives an expression for the relaxation time t_{rel} . The deformation

method is based on the fact that the asymptotics for $t > t_{3/4}$ have a sufficiently small derivative $(dz/dt)_{as}$, namely,

$$\frac{d}{dz}(dz/dt)_{as,t_{rel}} \leq (dz/dt)_{3/4} - (dz/dt)_{as}[t = t_{3/4}]$$

This method is effective to build a solution of the evolution equation.

4. CONCLUSION

The approaches presented above allow us to construct an adequate solution of the balance equation for all time instants. This allows a reasonably accurate description of the stage of subsequent nucleation (homogeneous nucleation). Indeed, homogeneous nucleation can take place only with an increase in ideal supersaturation. In this case, it is sufficient to describe the period of increasing supersaturation that is achieved by constructing the initial iterations. However, nucleation can occur at heterogeneous centers, which can be injected into the system at any moment (for example, one can illuminate a chamber with a supersaturated phase and create ions for condensation). Thus, it is important to be able to find a solution of the balance equation for all time points. The advantage of the methods presented above is that they can be used for rather arbitrary functional dependences of ideal supersaturation on time, and not just for linear function used above only for illustrative purposes.

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SPELL:OK

An Approximate Method for Describing Evolution Prior to Coalescence

V. B. Kurasov*

St. Petersburg State University, St. Petersburg, Russia

*e-mail: victor_kurasov@yahoo.com

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Abstract—A new approximate method is proposed for describing the evolution of the system at the stage after the end of substantial consumption of the metastable phase and before the start of coalescence. The properties of evolution during this period are analyzed and the reasons why the Lifshitz–Slezov asymptotic behavior is achieved so quickly are shown.

Keywords: first-order phase transitions, kinetics, coalescence

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1. INTRODUCTION

The famous Lifshitz–Slezov (LS) asymptotic theory [1] describes the behavior of a system of a first-order phase transition at the final stage when large nuclei consume a metastable phase so actively that small particles begin to dissolve. The universal nature of the first two terms in the asymptotic expansion is a remarkable fact. Later, Osipov and Kukushkin found regular asymptotics [2] for the asymptotic behavior of the characteristics of the system at the final stage of its evolution.

The question of how the system reaches the LS asymptotics is of particular interest. Experiments show that this happens rather quickly [3], but there was no explanation for this. The aim of this study is to give an approximate analytical model that shows the way in which the approximation to the asymptotic solution is achieved. This model is an obvious simplification of the approach begun in [4] and developed in [5–8]. But a recent revision of these approaches allows us to generalize the theory and give a new recipe for choosing a variable that leads to the correct behavior of the critical size. The analysis is structured as follows:

—first, we highlight the necessary features from the theoretical description of the nucleation stage;

—next, we determine the size continuum shape at the stage of diffusion blurring;

—after that, we compare the obtained shape with the shape of the size continuum in the LS theory and see approximate similarity;

—to complete the theory, we analyze the structure of the solution in the LS theory and see the path of choosing the appropriate variable in our approximate solution.

2. CHARACTERISTIC SCALE LEVEL

We begin the analysis with the stage of formation of the main part of supercritical nuclei of a new phase (nucleation stage). Our goal is to show that the size continuum of new nuclei in variables that provide independence of the shape of the size continuum while the nuclei continue to grow as supercritical objects of a new phase will be rather narrow at the end of substantial consumption of excess metastability. Despite the fact that a quantitative description of the kinetics of nucleation is well known [9] (though other approaches also exist [10]) an analysis can be performed in a fairly general case via relatively simple estimates.

The number of molecules in a critical nucleus, i.e., v_c , where the index denotes the critical nucleus, will be a large parameter at the nucleation stage. Otherwise, the thermodynamic description of the critical nucleus will be invalid, and, in this case, the work of critical nucleus formation cannot be analytically determined. Moreover, it is possible to propose a fairly apparent approximation for nucleation intensity I in the range, in which I varies e times:

$$I(\zeta_1) = I(\zeta_2) \exp\left(-\frac{\partial F}{\partial \zeta}(\zeta_1 - \zeta_2)\right). \quad (1)$$

Here, $\partial F/\partial \zeta$ is a derivative of free energy F of nucleation with respect to supersaturation ζ (see [9]) taken for the critical nucleus, ζ_1 and ζ_2 are two values of supersaturation, and it is assumed that $I \sim \exp(-F_c)$ in the leading term. Given that $F \sim \ln(\zeta + 1)v + \dots$ the in leading term, we come to

$$I(\zeta_1) = I(\zeta_2) \exp(v_c(\zeta_1 - \zeta_2)/(\zeta + 1)). \quad (2)$$

Hence, relative decrease $d_c/\zeta = (\zeta v_c/(\zeta + 1))^{-1} \approx v_c^{-1}$ of the supersaturation means the cessation of nucleation. This range also corresponds to a change in the supersaturation at the nucleation stage, since this means that already formed nuclei cannot overcome the external effect and the nucleation stage cannot be ceased if the intensity of variation of the external conditions during this period changes substantially. Thus, the amount of substance in the nuclei of a new phase at the time of nucleation cessation can be estimated as $q_n = \zeta v_c^{-1}$. At the end of consumption of excess metastability, i.e., when supersaturation ζ drops to almost zero and the critical size begins to substantially increase, the amount of substance in the nuclei of the new phase can be estimated as $q_s = \zeta$. To see what this means for the size continuum coordinate, we must look at what will be a variable that ensures the independence of the growth rate of the nucleus on its size. Despite the fact that a number of different modes of nucleation growth were considered in [11], it should be accepted that it is variable $y = v_c^{1/\alpha}$ with $\alpha \in [3/2, 3]$ that is such a variable in most cases. All other cases are quite rare. We will call the mentioned interval the “essential interval” (EI).

If the width of the size continuum is designated via d_y and its amplitude via f_m , then we can estimate q_n as $f_m d_y^{\alpha+1}$. Since $q_s/q_n \sim v_c \gg 1$, the q_s value can be estimated as $y_s^\alpha N$, where y_s is the size continuum coordinate at the end of significant consumption of excess metastability and $N = f_m d_y$ is the number of drops. Then we come to $y_s/d_y = v_c^{1/\alpha} \gg 1$, which means that the size continuum is relatively narrow by the end of consumption of excess substance. The main necessary result just consists in the fact that the size continuum of the nuclei is narrow at the end of the stage of consumption of excess substance.

3. MODEL

Relatively soon (in comparison with the characteristic coalescence times), the coordinate of the narrow continuum of sizes reaches the vicinity of the critical size. To see relaxation, it is enough to solve a first-order differential equation or to undertake an asymptotic analysis, as is fully described in the mentioned publications. Nevertheless, the obvious result is that a narrow size continuum stops at a coordinate equal to the critical nucleus size. The regular velocity is zero at this coordinate and the spreading of a size narrow continuum due to diffusion can be seen.

Based on the solution of the diffusion equation, the transformation of the size continuum can be seen. We know the form of the solution with a narrow peak at the initial point. This is the Green function of the dif-

fusion equation, which is a Gaussian in the following form:

$$G(v, t) \sim \exp(-(v - v_c)^2/(4Dt)). \quad (3)$$

Here D is the diffusion coefficient, which looks like $W^{\text{inside}} + W^{\text{outside}}$ (the sum of the forward and reverse flows) on the scale. Thus, we get a solution.

The continuum looks like a Gaussian, and according to the balance condition, v_c is close to the head of the Gaussian. Then it is clear that an essential part of the continuum will sooner or later reach the boundary of the region of droplets that dissolve quite quickly by now.

Initially, an essential part of the continuum lies in the range of $|v - v_c| \ll 1$. Then it makes no difference whether the diffusion equation is written in the scale of $S = v^{2/3}$ or $\rho = v^{1/2}$. Time that takes for an essential part of the continuum to reach v_l (a size that dissolves quickly enough in a regular way) can be merely calculated from $4Dt = (v_c - v_l)^2$. Here, the time is counted from the end of the previous period.

Later, condition $f(v_l) = 0$ becomes important for the continuum of droplet sizes f . It can be approximately taken that $v_l^{1/3} \approx 0.5v_c^{1/3}$. Functional dependence $W^{\text{inside}} \sim v^{2/3}$ (we consider here the free-molecular mode of matter exchange, in which there is no need to pay attention to the influence of the nearest neighbors) makes it preferable to use $S = v^{2/3}$ as a variable for writing and solving the diffusion equation.

The solution of the diffusion equation with the mentioned boundary condition clearly is as follows:

$$f(S) = 0 \quad \text{for} \quad S < S_l$$

and

$$f(S) = G_{\text{positive}} + G_{\text{negative}} \quad \text{for} \quad S > S_l.$$

Here, $G_{\text{positive}} = \frac{N}{\sqrt{4\pi Dt}} \exp\left(\frac{-(S - S_c)^2}{4Dt}\right)$, $G_{\text{negative}} = \frac{-N}{\sqrt{4\pi Dt}} \exp\left(\frac{-(S + S_0)^2}{4Dt}\right)$, and S_0 is determined by condition $S_c - S_l = S_l - S_0$ at the initial point.

In contrast to the unbounded solution with a half-width of $d_s \sim t^{1/2}$, in which the amplitude (and mean) value stays unmoved at $S_{\text{max}} = \text{const}$, the new solution has, as can be seen, a moving amplitude coordinate of $S_{\text{max}} \sim t^{1/2}$, a moving mean value $S_{\text{mean}} \sim t^{1/2}$, and a growing half-width of $d_s \leq t^{1/2}$, which ensures relative localization of the continuum. The supersaturation value is determined from

$$\int_0^\infty 3\rho^2 f(\rho) \left(\frac{d\rho}{dt}\right) d\rho = 0.$$

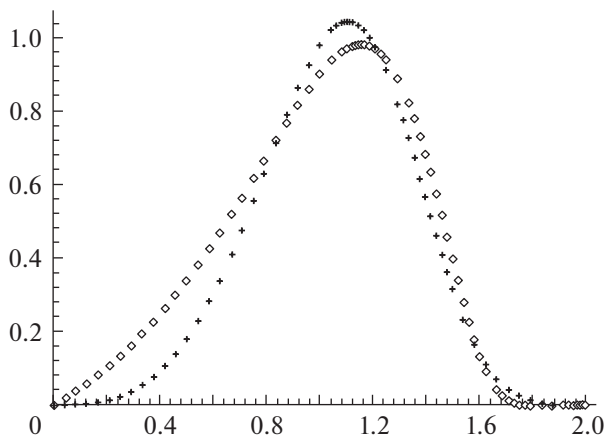


Fig. 1. Double Gaussian (diamonds) and Lifshitz–Slezov (crosses) distributions in the $v^{1/3}/v_c^{1/3}$ scale.

Then we get ρ_c and supersaturation. It is clear that critical size S_c must be in the essential part of the continuum in accordance with the previous formula. The size continuum is well localized on the size scale and cannot escape from the critical size. We will call the new size continuum the “double Gaussian (DG) continuum of sizes.”

4. RESEMBLANCE TO THE LS FORM

The surprising fact is that the DG distribution is very similar to the LS distribution. This can be seen from Fig. 1, which shows the DG and LS distributions in case of the free-molecular mode. Similar patterns are observed in the diffusion mode.

The frontal edge of the size continuum is determined with some error due to the discreteness of the number of molecules in the nucleus. In any case, the small region is not important in the material balance; it cannot experimentally be measured with good accuracy, since the nuclei in this region have a substantial rate of dissolution (not a relative dissolution rate, but a physical one). So, a conclusion can be drawn that the DG and LS continuums cannot be distinguished within the accuracy of a modern experiment. It should be noted that we did not normalize the half-widths, but only partitioned the distributions into their amplitude values.

The proximity of the LS and DG continuums explains why there is no long relaxation to the LS asymptotics in the experiments. This proximity is important for substantiating the LS asymptotics, since we are not able to analytically solve the evolutionary equation with diffusion terms and problems arise in the absence of diffusion terms. Furthermore, now we see that diffusion does not substantially change the size continuum shape.

5. VARIABLE SELECTION

Everything is fine in the DG solution except for the main feature that the functional dependence of the critical size does not correspond to that given by the LS asymptotics. We have already noted, though, that the size continuum remains moderately narrow and concentrated near the critical size, at which the regular velocity is absent and the diffusion equation can be written in any of the ρ , v , or S scales, or in any variable v^β with moderate power β . This is a property of the relative independence of the DG model.

Now, we give a recipe for selecting the power in an appropriate way. The structure of the LC asymptotic solution has one nice feature, which has not yet been explicitly identified until now, but has been the reason for establishing the correct power in the power dependence of the critical size since the time of Todes [12]. Namely, the power in the power dependence of the critical size can be obtained by imposing the requirement that supercritical nuclei must have the same power in the time dependence as the critical size has (asymptotic balance property). Otherwise, the critical size will exceed the size of droplets and make it negligible, or the droplets will make the critical size relatively negligible, which is also meaningless. This comment is similar to the LS analysis, which allows one to find a specific value of the γ parameter (see [1]), but a much more rough one. We will call this property the “possibility of rough analysis.” The LS solution decays into the following two steps: establishing the time dependence of the critical size and determining the size continuum (decomposition property). The first step can be performed in a rough approximation.

In the free-molecular mode, linear size $\rho = v^{1/3}$ of supercritical nuclei grows regardless of size and is proportional to supersaturation. So, choosing $\zeta \sim t^\alpha$ with some α , we get $\rho \sim t^{\alpha+1}$. For critical size $\rho_c \sim \zeta^{-1}$, we have $\rho_c \sim t^{-\alpha}$. Hence, the equivalence of the dependences gives $\alpha = 1/2$. Since the size of the selected variable in the DG solution grows as $t^{1/2}$, it is clear that $y = \rho$ is a variable that provides a correct dependence. It is this variable that should be chosen as S in the solution given above.

In the diffusion mode of matter exchange, $v^{2/3} = S$ increases without size dependence of the velocity and is proportional to supersaturation ζ . Choosing $\zeta \sim t^\alpha$, we get $S \sim t^{\alpha+1}$. For the critical size, we arrive at $v_c^{1/3} \sim \zeta^{-1} \sim t^{-\alpha}$. The asymptotic behavior balance leads to $\alpha = -1/3$. The agreement between $y \sim t^{1/2}$ and the growth of the critical size means that we have to select $y = v^{1/2}$ as a variable in the DG solution. The DG model with the above recipe for selecting a variable is a useful tool in describing the evolution of the system at a stage that precedes the coalescence.

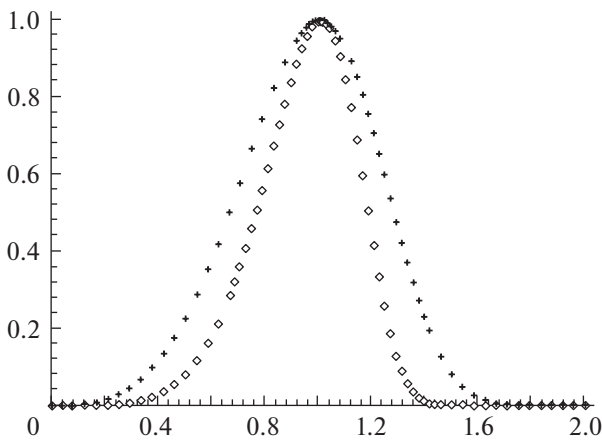


Fig. 2. DG distributions for the diffusion (diamonds) and free-molecular (crosses) cases as functions of the $v^{1/3}/v_c^{1/3}$ -scaled argument.

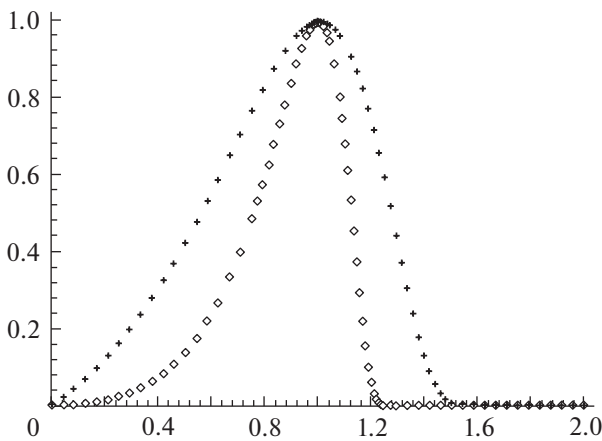


Fig. 3. LS distributions for the diffusion (diamonds) and free-molecular (crosses) cases as functions of the $v^{1/3}/v_c^{1/3}$ -scaled argument.

6. DISCUSSION OF RESULTS AND CONCLUSIONS

As we have seen, the DG solution in different modes differs only in the selection of variables. We mentioned that the DG is insensitive to variable selection in a certain sense. Hence, it should be expected that the difference in the size continuum shape will be insignificant. We show the size continuums at the EI boundaries and expect that the size continuums in all

cases that relate to the EI lie inside the boundary cases. Thus, we obtain Fig. 2, in which the DG distributions are plotted for the free-molecular and diffusion modes, and see a rough resemblance. The already mentioned proximity of the LS and DG size continuums allows us to expect that the LS continuums from the entire EI will be similar as well. This can be seen from Fig. 3, which shows the LS continuums for the free-molecular and diffusion modes.

So, we can talk about a rough resemblance of the LS and DG size continuums within the EI. This resemblance is confirmed by the approach described in [13], which is based on the method of steepest descent in constructing size continuums at the coalescence stage.

CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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