PHYSICAL REVIEW E, VOLUME 65, 031506

Kinetics of formation of a phase with an arbitrary stoichiometric composition in a multicomponent solid solution

V. V. Slezov
National Science Center "Kharkov Institute of Physics and Technology," Academician Street 1, Kharkov 61108, Ukraine

J. Schmelzer
Department of Physics, University of Rostock, 18051 Rostock, Germany

(Received 13 December 2000; revised manuscript received 12 November 2001; published 6 March 2002)

A kinetic theory of nucleation and growth of a evolving phase with a given stoichiometric composition in a multicomponent solid solution is developed. It is assumed naturally that the phase grows as a result of individual atom incorporation into the phase domain in a stoichiometric ratio. As it is shown, for the case of phase formation in a multicomponent system the basic kinetic equations, describing the nucleation-growth process, can be reduced formally to the respective expression derived for nucleation-growth processes in one-component systems. However, the effective diffusion coefficients and the effective supersaturation are expressed as nontrivial combinations of the thermodynamic and kinetic parameters of the different components involved in the phase formation process. In the determination of these properties, the theory is not restricted in its applicability to perfect solutions but extended to phase formation in real mixtures. Thus, the theory may be applied directly towards the interpretation of experimental data. In the present paper, particular attention is devoted to the analysis of the two stages of the overall transformation process: (1) the stage of quasi-steady-state nucleation and (2) the transient stage of coarsening. As the results of this analysis, the quasi-steady-state nucleation rate, the number of clusters formed via nucleation and growth, and the time evolution of the cluster size distributions are established. Moreover, estimates are given for the duration of the different stages of the transformation process.

DOI: 10.1103/PhysRevE.65.031506 PACS number(s): 64.75.+g, 64.70.Kb

I. INTRODUCTION

A large number of studies, including several monographs, have been devoted to the investigation of the kinetics of first-order phase transitions [1–16]. Nevertheless, a number of problems remain unsolved as yet.

As a further restriction in the applicability of the theory to experiment, most of the previous analyses are devoted to single-component systems. Homogeneous binary nucleation is more complex as single-component nucleation. In part, these complications arise from uncertainties in the knowledge of the composition of the critical clusters and the related problem of the compositional dependence of the critical cluster surface tension. These limitations in the application of the theory to experiment are even more pronounced in the case of phase formation in multicomponent systems.

Moreover, in the majority of previous studies, attention is directed mainly towards the determination of the so-called steady-state nucleation rate or, in other words, the steady-state flux in cluster size space. Steady-state conditions can be realized in real systems, however, only for limited periods of time or when the state of the solution is artificially maintained constant by some appropriate real or supposed mechanism (cf., e.g., [1,12]).

In most cases of interest, the degree of metastability or the state of the ambient phase changes in the course of the phase transformation because of depletion effects due to cluster formation and growth. Different aspects of the effect of depletion on the course of first-order phase transitions have been studied by various authors (see, e.g., Tunitskij [17], Wakeshima [18], Binder and Stauffer [19,20], Rusanov [21], Gunton, San Miguel, and Sahni [22], Schmelzer [23], Wehner and Wolfer [24], Schmelzer and Ulbricht [25], Ulbricht *et al.* [26], Barrett and Clement [27], Tokuyama and Enomoto [28], Grinin [29], Kuni, Grinin, and Kurasov [30]). As it has been shown (cf. Schmelzer and co-workers [23,25,26]), depletion effects affect nucleation quantitatively and determine qualitatively the whole course of first-order phase transformations proceeding by nucleation and growth. As the result of such depletion effects, in particular, only a finite number of clusters develop in the system (cf. Schmelzer and co-workers [31,32], Slezov, Schmelzer, and Tkatch [33]).

An extended theoretical analysis of the kinetics of phase formation of single-component systems via nucleation and growth has been given previously in [34]. In the present paper these analyses are extended to multicomponent systems. In order to remedy various problems encountered in the description of phase formation an additional assumption is employed; it is assumed that the new phase has a well-defined but arbitrary composition. Using this assumption, the kinetic equations governing nucleation and growth, can be reduced to a relation identical in its form to the respective expression for phase formation in single-component systems [35–37]. However, as will be shown in the course of the analysis, the effective diffusion coefficients and the effective supersaturation have to be expressed as nontrivial combinations of the thermodynamic and kinetic parameters of the different components involved in the phase-formation process.

In the analyses, we assume (cf. [33,34]) that, for the whole course of the process of nucleation, at any instant in

1063-651X/2002/65(3)/031506(13)/$20.00

time a quasi-steady distribution function with respect to the size of the phase particles $f(n,t)$ is established in the range of cluster sizes $1 \leqslant n \leqslant n_c$. Here n denotes the number of structural units (or, quasimolecules) in an aggregate (or cluster) of the evolving phase, and n_c is the critical size of the aggregate. The critical cluster is an aggregate of phase particles in unstable equilibrium with the solid solution. Its size changes with variations in the state of the ambient phase.

Similarly, the quasi-steady-state distribution with respect to cluster size in the range $n \leqslant n_c$ is determined by the current state parameters of the solid solution. In other words, for the range of cluster sizes $n \leqslant n_c$, the time of adjustment t_r of the distribution function $f(n,t)$ and the flux $I(n,t)$ in cluster size space to the current state parameters of the solid solution is much less when compared to the characteristic times of variation of these parameters. Generally, these conditions are valid.

In line with the classical approach, we assume that the aggregation formation process of the evolving phase proceeds via incorporation and emission of individual structural units exclusively. This way, the smallest aggregate of the evolving phase corresponds to $n=1$. Further, we go over from a discrete description in terms of a set of kinetic equations to a continuous description in terms of the Frenkel-Zeldovich equation. In the domain of cluster sizes $n \geqslant n_c \gg 1$, we focus on the continuum description which is reasonable approximation. Moreover, the properties of the aggregates of the evolving phase approach the properties of their respective bulk phases.

The kinetic equations are applied to the region of cluster sizes $n \leqslant n_c$ as well but mainly in order to derive an estimate of the time to establish quasi-steady-state conditions and to obtain the boundary conditions at $n=n_c$. Thus, the approximations arising from the application of the kinetic equations to very small clusters are of minor importance for the results of the analysis outlined below.

Once the stage of nonsteady-state nucleation is over (the stage of approach of quasi-steady-state conditions in the range of cluster sizes $n \leqslant n_c$ in cluster size space), the further evolution can be divided into a stage of dominant quasi-steady-state nucleation followed by the stages of independent and competitive growth [13,14]. The present analysis is devoted mainly to the description of the stages of quasi-steady-state nucleation and independent growth. For these stages, the evolution in time of the basic characteristics of the nucleation-growth process is found in form of the distribution functions with respect to cluster sizes and the size-dependent flux in cluster size space. Further, the number of clusters of the phase and their average size at the end of the independent growth stage are determined as a function of the initial system supersaturation. Finally, estimates for the duration of the stages of quasi-steady-state nucleation and independent growth are provided.

The state of the cluster ensemble at the end of the nucleation and independent growth stages simultaneously represents the initial state for the process of competitive growth. The theory of competitive growth or coarsening was developed for the first time by one of the authors in cooperation with Lifshitz and Slezov [13,14]. Thus, the present analysis provides a complete quantitative description of the entire course of first-order phase transitions in multicomponent systems.

II. BASIC SET OF EQUATIONS

We consider processes of formation of a phase with a given stoichiometric composition. The stoichiometric coefficients specifying the composition of the evolving phase are denoted by ν_i and the number of basic structural units in the cluster or aggregate of the evolving phase given by n.

The volume V of an aggregate of the evolving phase is given then by $V = n\omega_s$ with $\omega_s = \Sigma_i \nu_i \omega_i$. Here ω_s is the volume of a structural element, ω_i is the volume of the ith component in the ambient solution and in the evolving phase (i.e., we do not consider differences in the respective volumes in both phases resulting from elastic stresses).

The basic system of equations, describing the kinetics of nucleation and growth, are given by (see [35–37] and Appendix)

$$\frac{\partial f(n,l)}{\partial t} = -\frac{\partial I(n,t)}{\partial n},$$

$$I(n,t) = -\nu_{n,n+1}\left(\frac{\partial f(n,t)}{\partial n} + \frac{1}{T}\frac{\partial \Delta\Phi}{\partial n} f(n,t)\right), \tag{1}$$

$$f(n,t)|_{n\to 0} = \prod_i c_i^{\nu_i}, \quad f(n,t)|_{t=0,n>1} \to 0, \tag{2}$$

$$c_{0;} = c_i(t) + \nu_i \int_0^\infty f(n,t)\, n\, dn. \tag{3}$$

The first set of equations Eqs. (1) describe the evolution of the cluster size distribution function $f(n,l)$ and the flux in cluster size space $I(n,t)$. The distribution function $f(n,t)$ has to obey the boundary and initial conditions as given by Eq. (2). Here it is assumed that the system can be brought suddenly into the respective metastable initial state. Aggregation phenomena and their effects on the phase formation process, which may occur in the course of the transfer of the system into the considered initial state, are excluded from consideration (for the account of such additional transient effects cf., e.g., [38,39] and references cited therein).

The number of nucleation sites is given by $f(n \to 0,t)$ and is determined by the number of configurations $\Pi_i c_i^{\nu_i}$ that may result in the evolution of the structural element of the evolving phase. T is the temperature in energetic units (i.e., $k_B T$).

Further, conservation of the total number of particles results in the set of balance equations Eqs. (3) for the different components forming the evolving phase. c_i is the actual concentration and c_{i0} the initial concentration of the ith component in the solution. Note that all concentrations c_i as well as the distribution function $f(n,t)$ refer to the respective numbers per single lattice site.

In order to solve the given system of equations, one has to specify the coefficients of aggregation $\nu_{n,n+1}$. As shown in

[35–37], these coefficients can be expressed via the macroscopic growth rates dn/dt and the derivative $(\partial\Delta\Phi/\partial n)$ as

$$\frac{dn}{dt}=-\nu_{n,n+1}\frac{\partial\Delta\Phi}{\partial n}. \tag{4}$$

Here $(\partial\Delta\Phi/\partial n)$ is partial derivative of $\Delta\Phi$. $\Delta\Phi$ is the change of the thermodynamic potential if in the solid solution an aggregate of the evolving phase with n structural elements is formed. Both the aggregate of the evolving phase as well as the solution are considered to be in a state of internal thermal equilibrium while the system as a whole is in a nonequilibrium state. The change of the characteristic thermodynamic potential $\Delta\Phi$, due to the formation of such an aggregate with n structural elements, can be expressed then as

$$\Delta\Phi=n\left(\mu^s-\sum_i \nu_i\mu_i\right)+4\pi a_s^2\sigma n^{2/3}. \tag{5}$$

We obtain then immediately

$$\frac{1}{T}\frac{\partial\Delta\Phi}{\partial n}=\frac{1}{T}\left(\mu^s-\sum_i \nu_i\mu_i\right)+\beta n^{-1/3},\quad \beta=\frac{8\pi}{3}\frac{\sigma a_s^2}{T}. \tag{6}$$

In above equations, μ^s is the chemical potential per structural element in the phase, μ_i is the chemical potential of the ith component in the solution, $a_s=(3\omega_s/4\pi)^{1/3}$ is the characteristic size parameter of the structural elements, σ is the specific interfacial energy of the aggregate of the phase in the solution. Note that, since the composition of the aggregates and the specific volumes of the different components are independent of cluster size, the surface energy σ has to be considered as independent of cluster size as well.

The size of the critical aggregate n_c for a cluster, being in unstable equilibrium with the ambient solution, is determined via $(\partial\Delta\Phi/\partial n)=0$ or via

$$n_c^{1/3}=\frac{\beta}{\sum_i \nu_i\mu_i-\mu^s}. \tag{7}$$

For a weak or perfect solution, where $\mu_i=\psi_i+T\ln c_i$ holds, we get, in particular,

$$r_c=n_c^{1/3}=\frac{\beta}{\ln\left(\frac{\Pi_i c_i^{\nu_i}}{k_\infty}\right)},\quad k_\infty=\exp\left(\frac{\mu_s-\Sigma_i\nu_i\psi_i}{T}\right). \tag{8}$$

Here with k_∞ the chemical equilibrium constant has been introduced.

For any arbitrary value of n we may write immediately

$$\frac{1}{T}\frac{\partial\Delta\Phi}{\partial n}=\beta(n^{-1/3}-n_c^{-1/3}),\quad \frac{\Delta\Phi(n)}{T}=-\frac{\beta n}{n_c^{1/3}}+\frac{3}{2}\beta n^{2/3},$$
$$-\frac{1}{2T}\frac{\partial^2\Delta\Phi}{\partial n^2}=\frac{\beta}{6n^{4/3}}, \tag{9}$$

resulting in

$$\frac{\Delta\Phi(n_c)}{T}=\frac{\beta}{2}n_c^{2/3},\quad \Delta\Phi(Sn_c)=-2\beta n_c^{2/3},\quad \delta n_c=\sqrt{\frac{6n_c^{4/3}}{\beta}}, \tag{10}$$

$$\frac{1}{2T}\left.\frac{\partial^2\Delta\phi(n)}{\partial n^2}\right|_{n=n_c}=-\frac{1}{\delta n_c^2}=-\frac{\beta}{6}n_c^{-4/3}. \tag{11}$$

The quantity δn_c describes the range of n values in the vicinity of the critical cluster size, where the relation $\Delta\Phi(n_c)-\Delta\Phi(n)\leqslant T$ holds.

The expressions for the aggregation coefficients $\nu_{n,n+1}$ can be found from the analysis of the mode of aggregation of the clusters. For the small-sized clusters, prevailing in the stage of nucleation, the growth is limited kinetically (e.g., [34,37]). In the transient stage, the aggregates of the evolving phase are sufficiently large, so that the growth rate dn/dt and the aggregation coefficients can be found from the solution of the diffusion equation.

In order to arrive at the respective expressions, we have to take into account first that the partial fluxes j_i of individual components have to fulfill the relations [35–37,40,41]

$$\frac{j_i}{\nu_i}=\frac{j_k}{\nu_k}=\cdots. \tag{12}$$

In addition, we may write down for any partial flux j_i [37,42]

$$4\pi R^2 j_i=-\nu_{n_i,n_i+1}\frac{1}{T}\frac{\partial\Delta\Phi^s}{\partial n_i}$$
$$=\frac{3\alpha_i D_i\tilde{c}_i n^{2/3}}{a_m^2 T}\left(\frac{\omega_s}{\omega_m}\right)^{2/3}[\mu_i(\overline{c_i})-\mu_i(c_{ni})], \tag{13}$$

$$\Delta\Phi^s=\sum_i n_i[\mu_i(c_{ni})-\mu_i(\tilde{c}_i)],\quad \mu^s=\sum_i \nu_i\mu_i(c_{ni}). \tag{14}$$

Here μ^s is the chemical potential of a structural element of the phase, $\mu_i(c_{ni})$ are the chemical potentials of the particles of the ith component in the solution in equilibrium with a cluster of size n, $\mu_i(\overline{c_i})$ are the chemical potentials of the particles of the ith component in the solution in the immediate vicinity of the aggregate, $\{c_{ni}\}$ represents a set of concentrations of the particles of the different components that result in an equilibrium with an aggregate of size n, while $\{\overline{c_i}\}$ represents the set of concentrations in the vicinity of the surface of the aggregate. We get

$$\frac{\partial\Delta\Phi^s}{\partial n_i}=-\frac{1}{T}[\mu_i(\overline{c_i})-\mu_i(c_{ni})],$$

$$\nu_{n_i,n_i+1}=\frac{3\alpha_i D_i}{a_m^2}\tilde{c}_i\left(\frac{\omega_s}{\omega_m}\right)^{2/3}n^{2/3}. \tag{15}$$

Here ν_{n_i,n_i+1} is the frequency of incorporation of particles of the component i into the phase aggregates, α_i is the sticking coefficient $(0\leqslant\alpha_i\leqslant 1)$, D_i is the partial diffusion coefficient of the component i, a_m is the lattice parameter of the matrix ($\omega_m = 4\pi a_m^3/3$). The radius R and the particle number in the aggregates are related via $n = (4\pi R^3/3\omega_s)$, $\omega_s = 4\pi a_s^3/3$.

For the rate of growth of an aggregate of size n, we get from Eq. (12) and equation $\omega_s = \Sigma_i \nu_i \omega_i$

$$\frac{dn}{dt} = \frac{4\pi R^2}{\omega_s} \sum_i \omega_i j_i = 4\pi R^2 \frac{j_i}{\nu_i}. \tag{16}$$

As the next step, we insert Eq. (13) into Eq. (16). Afterwards, we may divide the equation at the coefficient in front of the term $[\mu(\tilde{c}_i) - \mu_i(c_{ni})]$, multiply the resulting equation at ν_i, and take the sum over all values of i. As the result, we obtain

$$\frac{dn}{dt} = \frac{3D^*}{a_m^2}\left(\frac{\omega_s}{\omega_m}\right)^{3/2} n^{2/3} \sum_i \nu_i [\mu_i(\tilde{c}_i) - \mu_i(c_{ni})],$$

$$\frac{1}{D^*} = \sum_i \frac{\nu_i^2}{\alpha_i D_i \tilde{c}_i}. \tag{17}$$

In the limiting case of a weak solution, we get, in particular,

$$\Delta\Phi = -n \ln\left(\frac{\prod_i (c_i)^{\nu_i}}{k_\infty}\right) + 4\pi\sigma a_s^2 n^{2/3},$$

$$k_n = \prod_i (c_{in})^{\nu_i} = k_\infty e^{\beta/(n^{1/3})},$$

$$\frac{\partial \Delta\Phi}{\partial n} = -\ln\left(\frac{\Pi i (c_i)^{\nu_i}}{k_n}\right), \tag{18}$$

resulting in

$$\frac{dn}{dt} = -\nu_{n,n+1}\frac{\partial\Delta\Phi}{\partial n} = \frac{3D^*}{a_m^2}\left(\frac{\omega_s}{\omega_m}\right)^{3/2} n^{2/3} \ln\left(\frac{\Pi_i c_i^{\nu_i}}{k_n}\right), \tag{19}$$

$$\frac{dn}{dt} = \frac{3D^*}{a_m^2}\left(\frac{\omega_s}{\omega_m}\right)^{2/3} n^{2/3} \beta\left(\frac{1}{n_c^{1/3}} - \frac{1}{n^{1/3}}\right),$$

$$\nu_{n,n+1} = \frac{3D^*}{a_m^2}\left(\frac{\omega_s}{\omega_m}\right)^{2/3} n^{2/3}. \tag{20}$$

Equations (19) and (20) describe the flux of particles to the aggregates of the evolving phase in the immediate vicinity of the aggregate. The concentrations of the different components $\tilde{c}_i$ in this region are determined by the interplay of losses by aggregation and input fluxes due to the diffusion from the distant environment. For the determination of these concentrations, the respective diffusion problem has to be solved self-consistently [14,43].

If the concentrations of the different components in the phase and the ambient solution differ considerably, then, in order to find the rate of growth of the aggregates of the phase, one may employ the steady-state solution of the diffusion equation and the effects of the motion of the interface may be neglected [14,33] (with an accuracy of the order $c_i/c_i^s \ll 1$, where c_i^s are the concentrations in the solution in equilibrium with a macroscopic aggregate of the evolving phase). In such case, we have

$$\frac{dn}{dt} = 4\pi R^2 \frac{j_i}{v_i} = 3\left(\frac{\omega_s}{\omega_m}\right)^{2/3} \frac{D_i}{a_m^2} \frac{c_i - \tilde{c}_i}{\nu_i} n^{1/3}. \tag{21}$$

From Eqs. (13) and (21) we arrive at the following expression for the determination of the concentrations $\tilde{c}_i$ (for the case of a weak solution)

$$\ln\left(\frac{\tilde{c}_i}{c_{in}}\right) = \frac{1}{\alpha_i n^{1/3}} \frac{c_i - \tilde{c}}{\tilde{c}_i}. \tag{22}$$

Equations (13) and (22) and the equilibrium conditions at the interface of an aggregate completely determine the sets of concentrations $\{\tilde{c}_i\}$ and $\{c_{ni}\}$ for the stage of nucleation. In the limit $\alpha_i n^{1/3} \leqslant 1$ (which is usually fulfilled in the stage of nucleation), we get $\tilde{c}_i \cong c_i$ [cf. Eq. (22)]. In this case, it is more convenient to employ Eq. (19) for the determination of the growth rate dn/dt with the replacements $\tilde{c}_i \rightarrow c_i$, $\ln(\tilde{c}_i/c_{in}) \cong \ln(c_i/c_{in})$.

In the transient stage, when the size of aggregates is sufficiently large (i.e., the inequality $\alpha_i n^{1/3} \gg 1$ holds), the relation $\tilde{c}_i \cong c_{in}$ is fulfilled [cf. Eq. (22)]. In this case, one has to employ directly Eqs. (21) and (22) for the determination of dn/dt.

III. THE STAGE OF NUCLEATION OF CLUSTERS OF THE EVOLVING PHASE

The description of the kinetics of nucleation is significantly simplified after the time interval t_r when a quasi-steady-state flux in a cluster size space is established in the range $0 \leqslant n \leqslant n_c$ (e.g., [33–35,37,43]). Indeed, in this case it is possible to employ a simpler version of the basic equation Eq. (1) for the determination of the flux in cluster sizes space $I(n,t)$. The respective relation is valid in the whole stage of steady-state nucleation, $t_r \leqslant t \leqslant t_N$. Hereby, the boundary conditions for the flux in the range $0 \leqslant n \leqslant n_c$ may be expressed via the boundary conditions for the distribution function $f(n,t)$. Once the flux $I(n,t)$ is known, the distribution function $f(n,t)$ can be found straightforwardly.

An estimate of the time lag t_r can be derived in the same way as outlined in [33,34]. We get

$$t_r = \frac{5}{3} \frac{a_m^2}{D^*}\left(\frac{\omega_m}{\omega_s}\right)^{2/3} \frac{n_c^{2/3}}{\beta}. \tag{23}$$

An overview of different alternative attempts to estimate this quantity is given, e.g., in [12,44,45]. The results, obtained by different methods, deviate only slightly.

After the completion of the transient stage to steady-state nucleation, the equation for the determination of the flux in cluster size space may be written in the form [33–35,44]

$$\frac{\partial I(n,t)}{\partial t} = \nu_{n,n+1}\left\{\frac{\partial^2 I(n,t)}{\partial n^2} + \frac{1}{T}\frac{\partial \Delta\Phi}{\partial n}\frac{\partial I(n,t)}{\partial n}\right\} \tag{24}$$

with the boundary conditions $I(n,t)|_{n=n_c}=I(n_c)$. Hereby we chose the moment of time $t=0$ as corresponding to the beginning of the stage of steady-state nucleation, i.e., we make the replacement $t-t_r\rightarrow t$.

In the derivation of Eq. (24), terms of the order $(\dot{c}/c)I(\partial I/\partial t)^{-1}\simeq(t_N/t_c)\ll 1$ have been neglected, where t_c is the characteristic time of change of the concentration in the solution. During the time of steady-state nucleation t_N the change of the concentration in the solution is insignificant for the case $n_c|_{t=0}\gg 1$. Equation (24) is valid thus for any moment of time $t\leqslant t_N$ or when $I(n,t)>0$ holds for any value of n. In this stage, the number of supercritical clusters increases.

For $t\geqslant t_N$, the quantity $I(n_c)$ becomes practically equal to zero and the process of formation of clusters is terminated. Their number remains then nearly constant at the subsequent transient stage to coarsening for a time $t_f>t_N$. For $t\geqslant t_f$ the further evolution is governed by processes of competitive growth or coarsening [13,14].

In the considered stage of steady-state nucleation $t<t_N$, it is possible to express $f(n,t)$ via $I(n,t)$ as [33–35]

$$f(n,t)=\exp\left[-\frac{\Delta\Phi(n)}{T}\right]\int_n^{\infty}\exp\left(\frac{\Delta\Phi(n')}{T}\right)\frac{I(n',t)}{\nu_{n',n'+1}}\,dn'. \tag{25}$$

With $I(n,t)=I(n_c)$, $0\leqslant n\leqslant n_c+\delta n_c$ and the boundary condition for $f(n,t)$ at $n\rightarrow 0$ we get

$$\prod_i c_i^{\nu_i}=\int_0^{\infty}\exp\left(\frac{\Delta\Phi(n')}{T}\right)\frac{I(n',t)}{\nu_{n',n'+1}}\,dn',\quad \Delta\Phi(0)=0. \tag{26}$$

Since $\Delta\Phi(n)$ has a sharp extremum at $n=n_c$ $[\Delta\Phi(n)=\Delta\Phi(n_c)-T(n-n_c)^2\delta n_c^{-2}\gg 1]$, we get with Eq. (11)

$$I(n_c)=\sqrt{\frac{3\beta D^*}{2\pi a_m^2}}\left(\frac{\omega_s}{\omega_m}\right)^{2/3}\prod_i c_i^{\nu_i}\exp\left[-\frac{\Delta\Phi(n_c)}{T}\right]. \tag{27}$$

Equation (27) is reduced, evidently, to the respective expression for the steady-state nucleation rate in single-component systems in the limiting case of segregation of only one component.

For $n<n_c$, in Eq. (25) the maximum of $\Delta\Phi$ is located inside the limits of integration. Moreover, $I(n,t)=I(n_c)$ holds and we get

$$f(n)|_{n<n_c}=\prod_i c_i^{\nu_i}\exp\left[-\frac{\Delta\Phi(n)}{T}\right]\frac{1}{2}\left[1-\mathrm{erf}\left(\frac{n-n_c}{\delta n_c}\right)\right]. \tag{28}$$

Here $\mathrm{erf}(x)=-\mathrm{erf}(-x)$ is the error function.

In the limiting case of a saturated system, we have $n_c\rightarrow\infty$ and Eq. (28) is reduced to the well-known steady-state cluster size distribution in an equilibrium state.

In the stage of nucleation, we have $I(n,t)>0$ and for any given value of n this quantity is determined by the respective values at $n'<n$. In the later stages of the process, the situation is different. There we have $I(n,t)<0$ for $n<n_c$ and $I(n,t)>0$ for $n>n_c$. It follows that in the stage of nucleation one may determine the functions $I(n,t)$ for different ranges of n values by different methods and take as the boundary conditions the values determined via the solutions at the left hand side of the respective intervals.

In order to proceed with the analysis, we introduce the dimensionless time $\tau=t/\tilde{t}$ with $\tilde{t}^{-1}=D^*a_m^{-2}(\omega_s/\omega_m)^{2/3}$. Further, we note that in the range $1\leqslant n/n_c\leqslant 8$ the quantity $A=3[(n/n_c)^{1/3}+(n/n_c)^{-1/3}+1]^{-1}$ varies only in between the limits from 1 to 6/7 [34]. Consequently, in this range of cluster sizes we may set $3n^{2/3}(n^{-1/3}-n_c^{-1/3})=-(n-n_c)n_c^{-2/3}$ and $A\cong-(n-n_c)n_c^{-2/3}$.

The kinetic equation for $I(n,\tau)=I\tilde{t}$ can be written then in this range of cluster sizes as

$$\frac{\partial I}{\partial\tau}=-\frac{\beta}{n_c^{2/3}}(n-n_c)\frac{\partial I}{\partial n}+3n_c^{2/3}\frac{\partial^2 I}{\partial n^2}, \tag{29}$$

$$I|_{n=n_c}=I(n_c)=I_0\tilde{t},\quad I(n;\tau)|_{n>n_c,\tau=0}=0. \tag{30}$$

The replacement $n^{2/3}\rightarrow n_c^{2/3}$ in the second term on the right hand side of Eq. (29) decreases the diffusion contribution to the flux for $n>n_c$. However, in the considered range this contribution is small [33,34]. In the vicinity of $n\simeq n_c$, the replacement represents a quite accurate approximation.

In order to solve Eq. (29), we make the ansatz $(I(n,\tau)\rightarrow I[\psi(x,\tau),t(\tau)])$ and determine the functions ψ and $t(\tau)$ via

$$\psi=(n-n_c)\exp(-\delta\tau),\quad \delta=\beta n_c^{-2/3},$$

$$t(\tau)=\frac{3n_c^{2/3}}{2\delta}(1-e^{-2\delta\tau}). \tag{31}$$

After this substitution Eq. (29) takes the form

$$\frac{\partial I}{\partial t}=\frac{\partial^2 I}{\partial\psi^2},\quad I|_{n=n_c}=I(n_c),\quad I(n,\tau)|_{n>n_c,\tau=0}=0 \tag{32}$$

with the solution

$$I=I(n_c)\left[1-\mathrm{erf}\left(\frac{\psi}{2\sqrt{t}}\right)\right]=I(n_c)\left[1-\mathrm{erf}\left(\frac{e^{-\delta\tau}(n-n_c)}{2\sqrt{t(\tau)}}\right)\right]. \tag{33}$$

It follows that after a time $\tau_p\simeq 1/\delta\simeq\tau_r$ in the range $n_c\leqslant n\leqslant g=8n_c$ a steady state with the flux $I=I(n_c)$ establishes. Thus, the time of establishment of the steady-state conditions in the range $n\leqslant g=8n_c$ is of the same order as the time of establishment of the steady state during nucleation in the range $0\leqslant n\leqslant n_c$.

The distribution function over cluster size in the range $n_c\leqslant n\leqslant g\simeq 8n_c$ can be derived from Eq. (25) via a Taylor expansion of $\Delta\Phi(n)$ in the vicinity of n

$$f(n,\tau)=\frac{I_0}{\nu_{n,n+1}}\int_n^\infty \exp\left\{-\frac{1}{T}[\Delta\Phi(n)-\Delta\Phi(n')]\right\}dn'$$
$$=\frac{I_0}{2\nu_{n,n+1}}\sqrt{\frac{\pi}{b}}\left[1-\operatorname{erf}\left(\frac{a}{2b}\right)\right]e^{a^2/(4b^2)}, \tag{34}$$

$$a=-\frac{1}{T}\frac{\partial\Delta\Phi}{\partial n}\geqslant 0,\quad b=-\frac{1}{2T}\frac{\partial^2\Delta\Phi}{\partial n^2}>0,\quad n\geqslant n_c. \tag{35}$$

The function $f(n,\tau)$, determined via Eq. (34), goes over continuously into the expression derived via Eq. (28) for $n=n_c$. This way, the boundary conditions for $I(n,\tau)=I(n_c)$ hold after the time interval $\tau\simeq 2\tau$, at $g=8n_c$.

In the range $n\geqslant g$, it is also possible to simplify further the kinetic equation (29) describing the time evolution of $I(n,\tau)$ and obtain an exact analytic solution. However, one has to account for the decrease of the degree of metastability of the system due to the continuous formation and growth of the already formed supercritical clusters (depletion effects). In this way, an expression for the time interval of dominating steady-state nucleation may be obtained.

In the range of cluster sizes $n\geqslant g\simeq 8n_c$, we get for the case of a weak solution

$$\frac{\Delta\Phi(n_c)}{T}=\frac{\Delta\Phi(n_c(0))}{T}+n_c(0)\varphi,$$

$$\varphi(\tau)=-\ln\prod_i\left(\frac{c_i(\tau)}{c_i(0)}\right)^{\nu_i}. \tag{36}$$

Here $c_i(0)=c_{i0}$ is the initial concentration of the particles of the ith component in the solution. These quantities obey the inequality $c_{i0}\geqslant c_i$.

The boundary conditions at $n=g$ may be written in the form

$$I(n_c)=I(n_c(0))\exp[-n_c(0)\varphi(\tau)]. \tag{37}$$

As evident from Eq. (37), for $n_c(0)\gg 1$ a small change of the quantity φ results in a significant decrease of the nucleation rate. Processes of nucleation are terminated practically, if the condition $\varphi(\tau_N)=1/n_c(0)$ is fulfilled.

In the considered range of cluster sizes, the equation for the flux may be formulated most conveniently when the variable $r=n^{1/3}$ is employed [34–36]. We get

$$\frac{\partial I}{\partial\tau}=-\frac{\beta}{r_c}\frac{\partial I}{\partial r}+\frac{1}{3r_c^2}\frac{\partial^2 I}{\partial r^2}, \tag{38}$$

where the boundary condition is given by Eq. (37).

In Eq. (38) several terms are omitted that are small in comparison to $(\beta/2r_c)/(\partial I/\partial r)$ [i.e., $(2r^{-3}/3)(\partial I/\partial r)$ and $(\beta/r)(\partial I/\partial r)$ for $\beta>1$]. Moreover, the substitution $3r^{-2}\to 3r_c^{-2}$ is made (in the considered range the inequality $r>2r_c$ holds). Such approximation results in a sufficiently accurate description of the spectrum of the viable nuclei, which give the dominating contribution into the law of conservation of particle numbers. However, the mentioned approximations result in some additional broadening of the front of motion of the aggregates in cluster size space [34–36].

As a next step, we redefine the variable r via $r=n^{1/3}-g^{1/3}$. The solution for I is expressed further as

$$I=\exp\left(\frac{3}{2}\beta r r_c\right)\exp\left(-\frac{3}{4}\beta^2\tau\right)p(r,\tau). \tag{39}$$

A substitution of this expression into Eq. (38) results in the following equation for the function $p(r,\tau)$

$$\frac{\partial p}{\partial\tau}=(3r_c^2)^{-1}\frac{\partial p^2}{\partial r^2}. \tag{40}$$

The solution of Eq. (38) with the boundary conditions Eq. (37) reads then

$$I=I(n_c(0))e^{3\beta r r_c/2}\frac{r}{2}\left(\frac{\pi}{3r_c}\right)^{-1/2}\int_0^\tau \exp\{-n_c(0)\varphi(\tau')$$
$$-3\beta^2(\tau-\tau')/4-3r^2r_c^2/[4(\tau-\tau')]\}\frac{d\tau'}{(\tau-\tau')^{3/2}}. \tag{41}$$

With the variable $z=rr_c[4/3(\tau-\tau')]^{-1/2}$ we may write down the expression for I in the form

$$I=I(n_c(0))\frac{2}{\sqrt{\pi}}\int_{rr_c(4\tau/3)^{-1/2}}^\infty \exp[-n_c\varphi(\tau-3r^2r_c^2z^{-2}/4)]$$
$$\times\exp[-(3\beta rr_cz^{-1}/4-z)^2]dz$$
$$=I(n_c(0))\frac{2}{\sqrt{\pi}}\exp[-n_c\varphi(\tau-rr_c\beta^{-1})]$$
$$\times\int_{z(\tau'=0)}^\infty \exp[-(3\beta rr_cz^{-1}/4-z)^2]dz. \tag{42}$$

In Eq. (42), the second term in the first expression has a sharp maximum at $z=z_0$. In the vicinity of z_0 we may write down

$$f^2(z)=\left(\frac{3}{4}\frac{\beta rr_c}{z}-z\right)^2\simeq 4(z-z_0)^2,\ \ z_0=\sqrt{\left(\frac{3}{4}\beta rr_c\right)}. \tag{43}$$

With such approximation, we arrive at

$$I(n,\tau)=I(n_c(0))\exp[-n_c\varphi(\tau_0(n,\tau))]\frac{2}{\sqrt{\pi}}$$
$$\times\int_\xi^\infty \exp(-\xi'^2d\xi'), \tag{44}$$

$$\xi=2[z(\tau'=0)-z_0]=2\left(\frac{rr_c}{\sqrt{4\tau/3}}-z_0\right), \tag{45}$$

$$\tau_0(n,\tau)=\tau-rr_c\beta^{-1}=\tau-(r-r_g)\frac{r_c}{\beta},$$

$$\tau_0(r_{\max},\tau)=0,\quad \tau_0(q^{1/3},\tau)=\tau,\quad r_{\max}(\tau)=r_g+\beta r_c^{-1}\tau. \tag{46}$$

Here the redefinition of r has been taken into account ($r\rightarrow r-r_g$).

$r_{\max}(t)$ describes the motion of the cluster front in cluster size space along the characteristic solution of Eq. (44). The diffusiveness of the front is determined by the integral term in Eq. (44). This integral is practically equal to unity for $\xi\leqslant 0$ and equal to zero for $\xi\geqslant 0$. Approximately, we may write thus

$$I(n,\tau)=I(n_c(0))\exp[-n_c(0)\varphi(\tau_0(n,\tau))]\theta(r_{\max}(t)-r) \tag{47}$$

with

$$r_{\max}(t)=r_g+\frac{\beta\tau}{r_c}=r_g+\ln\left(\prod_i \frac{c_i^{\nu_i}}{k_\infty}\right)\frac{t}{\tilde{t}},$$

$$\theta(x)=1(x>0),\quad \theta(x)=0(x<0). \tag{48}$$

Since the broadening of the front of motion of the clusters in cluster size space is small, we may employ Eq. (47) for the application of the laws of conservation of the numbers of particles. These laws can be written as

$$\varphi=-\ln\prod_i\left(\frac{c_i}{c_{i0}}\right)^{\nu_i}=\sum_i \nu_i\ln\left(\frac{c_{i0}}{c_i}\right),$$

$$c_{i0}=c_i+\nu_i\int_0^\infty nf(n,\tau)dn, \tag{49}$$

$$\dot{c}_i=-\nu_i\int_0^\infty n\frac{\partial f}{\partial\tau}dn=-\nu_i\left(I(\tau)g-\int_0^\tau I(\tau_0)\frac{\partial n}{\partial\tau_0}d\tau_0\right). \tag{50}$$

By definition of the quantity $\tau_0(n,\tau)$ we may write down [employing Eq. (44)]

$$n(\tau-\tau_0)=\left[r_g+\ln\left(\prod_i\frac{c_i^{\nu_i}}{K_\infty}\right)(\tau-\tau_0)\right]^3. \tag{51}$$

With Eq. (51), we may go over in Eq. (49) from the variable n to the variable $\tau_0(n,t)$. We then get

$$\int_g^\infty I(\tau_0(n,\tau))dn=\int_g^{n_{\max}}I(\tau_0)dn$$

$$=\int_{\tau_0(g,r)=\tau}^{\tau_0(n_{\max},\tau)=0}I(\tau_0)\frac{dn}{d\tau_0}d\tau_0$$

$$=-\int_0^\tau I(\tau_0)\frac{dn}{d\tau_0}d\tau_0, \tag{52}$$

where $dn/d\tau=-dn/d\tau_0$ is the rate of growth at the moment of time τ of those aggregates of the phase, which have grown up to the size g at the moment of time τ_0, $n|_{\tau=\tau_0}=g$, $r|_{\tau=\tau_0}=r_g$. This way, we get the following expression for φ:

$$\frac{d\varphi}{d\tau}=-\sum_i\frac{\nu_i}{c_i}\frac{dc_i}{d\tau}=\left(\sum\frac{\nu_i^2}{c_i}\right)\left(Ig-\int_0^\tau I(\tau_0)\frac{dn}{d\tau_0}d\tau_0\right). \tag{53}$$

Equation (53) has a clear physical meaning (cf. also [34–36]). The decrease of the degree of metastability φ is due, both, to the formation of supercritical clusters [first term in Eq. (53)] as well as to the growth of already existing aggregates [second term in Eq. (53)].

Taking the integral in Eq. (53) by parts and employing additionally Eqs. (47) and (51), we obtain,

$$\frac{d\varphi}{d\tau}=\left(\sum\frac{\nu_i^2}{c_i}\right)I_0n(\tau);\quad I_0=I(n_c(0)). \tag{54}$$

Here $I(n_c(0))$ is determined by Eq. (27) and

$$n(\tau)=n(\tau-\tau_0)|_{\tau_0=0}=(r_g+a\tau)^3=r_{\max}^3(\tau), \tag{55}$$

$$a=\ln\left(\prod_i c_i^{\nu_i}/k_\infty\right),\quad \tau=\frac{t}{\tilde{t}}=\frac{D^*}{a_m^2}\left(\frac{\omega_s}{\omega_m}\right)^{2/3}t,$$

$$r_{\max}(\tau)=r_g+a\tau. \tag{56}$$

In Eq. (55) a small term of the second order in $I_0\ll 1$ has been neglected (remember, I_0 is by definition the flux per lattice site). Indeed, since we have $d\varphi/d\tau_0\simeq I_0$, we get

$$-n_c\int_0^\tau I_0e^{-n_c\varphi(\tau_0)}\frac{d\varphi}{d\tau_0}n(\tau-\tau_0)d\tau_0\simeq I_0^2. \tag{57}$$

In Eq. (55), we may set $c_i\simeq c_{i0}$ since the variations of the concentrations remain small in the stage of nucleation. An integration of this equation yields then (with $\varphi|_{\tau=0}=0$)

$$\varphi=\left(\sum\frac{\nu_i^2}{c_{i0}}\right)\frac{I_0}{4a}[(r_g+ar)^4-r_g^4],\quad \varphi(\tau_N)\simeq n_c^{-1},$$

$$0\leqslant\tau\leqslant\tau_N. \tag{58}$$

The time of steady-state nucleation [determined via $\varphi n_c(0)\cong 1$] is obtained then as

$$\tau_N^4=\left[\left(\sum\frac{\nu_i^2}{c_i}\right)I_0\frac{a_3}{4}\right]^{-1}\frac{1}{n_c}. \tag{59}$$

As evident, τ_N depends weakly on n_c^{-1}.

A substitution of the expressions for n_c and a [cf. Eq. (56)] yields in the limit $a\tau_N\gg r_g$,

$$\tau_N=\frac{t_N}{\tilde{t}}=4^{1/4}\beta^{-3/4}\left(\sum_i\frac{\nu_i^2}{c_{i0}}\right)^{-1/4}I_0^{-1/4}. \tag{60}$$

In order to determine the distribution function $f(r,\tau)$ in the considered range of cluster sizes, $r \geqslant g^{1/3} = 2r_c$, we have to find first the flux $I(r,t)$ given by Eq. (47). However, in order to get an explicite expression, we have to find first $\varphi(\tau_0(r,\tau))$ from Eq. (58). Using $r_g \ll a_\tau$, we have for $n_c\varphi(\tau_0(r,\tau))$,

$$n_c\varphi(\tau_0(r,\tau)) = \frac{\varphi(\tau_0(r,\tau))}{\varphi(\tau_N)} \simeq \left(\frac{\tau_0(r,\tau)}{\tau_N}\right)^4 = \left(\frac{r_{\max}(\tau)-r}{r_{\max}(\tau_N)-r_g}\right)^4. \tag{61}$$

It follows from Eq. (61) that in the considered time interval $(\tau \leqslant \tau_N)$ and cluster size range $[r \leqslant r_{\max}(\tau_N)]$, the quantity $n_c\varphi(\tau_0(r,\tau))$ is much less than unity. For this reason, Eq. (47) yields

$$I = I_0\,\theta(r_{\max}(\tau)-r), \quad \theta(x)=1 \;\; (x>0), \qquad \theta(x)=0 \;\; (x<0). \tag{62}$$

In the range $r > r_g$ and for $n_c \gg 1$, the interfacial effects as well as the influence of the diffusion term in the basic equation can be neglected. Then we get from Eq. (34) with $-T^{-1}(\partial\Delta\Phi/\partial n) \gg -0.5T(\partial^2\Delta\Phi/\partial n^2)$, $(n=8n_c=r_g^3)$,

$$f(r,\tau)\big|_{r \geqslant r_g} = I\left(\frac{dr}{dt}\right)^{-1} = \frac{I_0}{a}\,\theta(r_{\max}(\tau)-r)\,\theta(r-r_g). \tag{63}$$

Here $dr/dt = a$ holds at $r_g = 2r_c$, as it follows from Eq. (17). We took also into account in Eq. (63) the relation $f(r,\tau) = f(n,\tau)3n^{2/3}$.

This way, the distribution function in the stage of nucleation is determined in the range $0 \leqslant r \leqslant r_g$ via Eqs. (28) and (34), while for the range $r_{\max} \geqslant r > r_g$ this function is given by Eq. (63) for $\tau_N > \tau$.

The number of viable clusters per lattice site, formed at $\tau < \tau_N$, is given then by [cf. Eqs. (62) and (63), $r_{\max} = a\tau$ at $r \geqslant r_g$]

$$N = \int_0^\tau I(g,\tau')\,d\tau' = \int_{r_g}^{r_{\max}(\tau)} f(n,\tau)\,dn = I_0\tau. \tag{64}$$

The upper limit of N is given thus by

$$N_{\max} = I_0\tau_N = 4^{1/4}\beta^{-3/4}I_0^{3/4}\left(\sum_i \nu_i^2/c_{i0}\right)^{1/4}. \tag{65}$$

The largest size of the clusters, which may be formed in the stage of steady-state nucleation, is given by

$$n_{\max}^{1/3} = r_{\max} = a\tau_N = \ln\left(\frac{\Pi_i c_{i0}^{\nu_i}}{k_\infty}\right)\tau_N\,. \tag{66}$$

Further, the amount of matter J concentrated in the evolving phase, is given at $a\tau_N = r_{\max} \gg r_g$ by

$$J = \int_{g^{1/3}}^{r_{\max}} f(r,\tau)r^3\,dr = \frac{I_0 r_{\max}^4}{4a} = \frac{1}{n_c}\left(\sum \frac{\nu_i^2}{c_{i0}}\right)^{-1}. \tag{67}$$

For the change of the concentrations of the different components, we get, consequently,

$$\frac{\Delta c}{c_{i0}} = \frac{c_{i0}-c_i(\tau_N)}{c_{i0}} = \frac{\nu_{i0}}{c_{i0}}J = \frac{1}{n_c}\,\frac{\nu_{i0}}{c_{i0}}\left(\sum \frac{\nu_i^2}{c_{i0}}\right)^{-1} < n_c^{-1} \ll 1. \tag{68}$$

This way, at $n_c(0) \gg 1$, the stage of steady-state nucleation is terminated at relatively small variations of the concentrations of the components forming the phase. On physical grounds, this result is a consequence of the exponential decay of the flux in dependence on $n_c\varphi$ [cf. Eq. (47)]. It follows further that all quantities in the preexponential factors may be set equal to the respective values in the initial state.

IV. THE TRANSIENT STAGE

After the completion of the stage of intensive nucleation of clusters of the evolving phase, a transient stage of the phase transition begins (for $\tau \geqslant \tau_N$). In order to find the cluster size distribution function in the transient stage, we have to take into account the following circumstances. First, the initial state for the cluster size distribution is given by the distribution function formed in the nucleation to the moment $\tau = \tau_N$. Second, in the transient stage we may neglect the diffusion term in the basic equation due to the high degree of smoothness of the function $f(n,\tau)$ for $\tau \geqslant \tau_N$. As will be shown below, in the range $r > r_g = 2r_c$ (most of the matter of the phase is concentrated in clusters having sizes in this range) one can neglect the effect of surface energies as well. This way, in the transient stage, similar to the late stage [13,14] of the process of phase separation, we may write

$$\frac{\partial f}{\partial\tau} + \frac{\partial}{\partial\tau}\left[\left(\frac{dr}{dt}\right)f(r,t)\right] = 0, \quad r = n^{1/3}, \tag{69}$$

$$f(r,\tau)\big|_{\tau=\tau_N} = f_H(\tau;\tau_N)\,\theta(r_g-r) + f_H(r,\tau_N) \times \theta(r-r_g)\,\theta(r_{\max}(\tau_N)-r). \tag{70}$$

Here $f_H(r_0,\tau_N)$ is determined by Eqs. (28) and (34) for $r \leqslant r_g$ and by Eq. (63) for $r \geqslant r_g$. The growth rate dr/dt is given by Eq. (19). The solution of Eqs. (69) and (70) reads $f(r,\tau) = f(r_0,0)(\partial\tau_0/\partial\tau)$ or

$$f(r,\tau) = [f_H(r_0,\tau_N)\,\theta(r_g-r_0) + f_H(r_0,\tau_N) \times \theta(r_0-r_g)\,\theta(r_{\max}(\tau_N)-r_0)]\,\frac{\partial r_0}{\partial r}. \tag{71}$$

Here $r_0 = r_0(r,\tau)$ is the characteristic solution of Eqs. (69) and (70) determined by Eq. (19). The time $\tau = 0$ corresponds, by definition, to the beginning of the transient stage.

The characteristic equation is determined from the system of equations, Eq. (21), and the conservation law, Eq. (3), as

$$\frac{dr^2}{dt}=2\left(\frac{\omega_s}{\omega_m}\right)^{2/3}a_m^{-2}B_{in}\,,\quad r|_{\tau=0}=r_0\,, \tag{72}$$

$$B_{in}=\frac{D_i}{\nu_i}(c_i-c_{in})=B_{jn}=\cdots=B,$$

$$\prod\ (c_{in})^{\nu_i}=k_\infty\exp\left(\frac{\beta}{n^{1/3}}\right), \tag{73}$$

$$c_{i0}=c_i+\nu_iJ,\quad J=\int_0^\infty fn dn. \tag{74}$$

In the transient stage, for $n>n_c$, we may replace $\beta_{in}\rightarrow\beta_{i\infty}$ or $c_{in}\rightarrow c_{i\infty}$, and $k_\infty\exp(\beta n^{-1/3})\rightarrow k_\infty$.

For $n\leqslant n_c$, an analytic solution for the characteristic equation cannot be found in the general case for arbitrary $c_i(\tau)$. However, this range of cluster sizes is not important in the transient stage. The degree of metastability is decreased mainly by the growth of the large clusters, $n\gg n_c(0)$. Small clusters, with $n\leqslant n_c$, present in the system at the initial moment of time, disappear and give only a small contribution to the supersaturation. The range $n\leqslant n_c(t)$ will be characterized by the growth of $n_c(t)$ and by the dissolution of clusters with sizes $n_c(\tau)\geqslant n\geqslant n_c(0)$.

From Eqs. (72)–(74), we get

$$c_{in}=c_{i0}-\nu_iJ-\frac{\nu_i}{D_iA}\frac{dr^2}{dt},\quad A=\left(\frac{\omega_s}{\omega_m}\right)^{2/3}a_m^{-2}, \tag{75}$$

$$\prod_i\ (c_{i0}-\nu_iJ)^{\nu_i}\prod_i\ \left(1-\frac{\nu_i}{D_iA(c_{i0}-\nu_iJ)}\frac{dr^2}{dt}\right)^{\nu_i}=k_\infty e^{\beta/r}. \tag{76}$$

The main contribution to the characteristic time of the transient stage gives the time interval when $dr^2/dt\rightarrow 0$ and $r\gg\beta$, $J\leqslant J_{\max}$. Here $J_{\max}$ is the maximum amount (at the given conditions) of the evolving phase per lattice site. This effect is particularly well expressed for a sufficiently high degree of metastability in the initial state (e.g., for the limit $\Pi_i c_{i0}^{\nu}\gg k_\infty$ in the case of a weak solution). In this case, the clusters of the evolving phase as well as the degree of metastability are sufficiently large, and surface effects may be neglected. The late stage is reached, when the degree of metastability tends to zero. Here surface effects become of importance, again, and determine the asymptotic behavior [13,14].

Taking into account above comments, we obtain from Eq. (76) (employing a Taylor expansion and the condition $dr^2/dt\rightarrow 0$) the following sufficiently accurate expression

$$\frac{dr^2}{dt}=\left[1-\frac{k_\infty}{\Pi_i(c_{i0}-\nu_iJ)^{\nu_i}}\right]\left[\sum_i\ \frac{\nu_i^2}{D_i}\,\frac{1}{A(c_{i0}-\nu_iJ)}\right]^{-1}. \tag{77}$$

At $J\leqslant J_{\max}$, Eq. (77) can be written in the form

$$\frac{dr^2}{dt}=-D_{\text{eff}}A(J-J_{\max}),\quad t_N\leqslant t\leqslant t_f \tag{78}$$

with

$$D_{\text{eff}}A=\left[\sum_i\ \frac{\nu_i^2}{D_iA}\,\frac{1}{(c_{i0}-\nu_iJ_{\max})}\right]^{-1}\left[\sum_i\ \frac{\nu_i^2}{(c_{i0}-\nu_iJ_{\max})}\right], \tag{79}$$

$$\prod_i\ (c_{i0}-\nu_iJ_{\max})^{\nu_i}=k_\infty\,.$$

Here l_f is the length of the transient stage of the process.

Note that the precise expression for dr^2/dt for a single-component system is obtained from Eq. (77) in the limiting case $r\gg\beta$. A similar limiting result may be derived if one of the components has a diffusion coefficient or a concentration much less as compared with the other components. In these latter cases, the process of phase formation is determined mainly by the behavior of this particular component. In contrast to the single-component case, each growth step remains to be characterized by the addition of one structural element.

The number of particles of the evolving phase is given, again, by [cf. Eqs. (65) and (71)]

$$N_{\max}=\int_0^\infty f(r_0,r)\frac{\partial r_0}{\partial r}dr\simeq\int_{r_c}^{r_{\max}(\tau_N)}f(r_0,0)dr_0\,, \tag{80}$$

$$J=\int_0^\infty f(r_0,0)\frac{\partial r_0}{\partial r}r^3(r_0,\tau)dr$$

$$\simeq\int_{r_c}^{r_{\max}(\tau_N)}f(r_0,0)r^3(r_0,\tau)dr_0=N_{\max}r^3(t). \tag{81}$$

Here we took into account that, in the transient stage, for the main part of the distribution the inequality $r\gg r_{\max}(\tau_N)$ holds. By this reason, r^3 practically does not depend on r_0.

With Eqs. (80) and (81), we may reformulate Eq. (78) as

$$\frac{dr^2}{dt}=-D_{\text{eff}}AN_{\max}(r^3-r_{\max}^3),\quad r|_{t=t_N}=r_0\,,\quad t_N\leqslant t\leqslant t_f \tag{82}$$

with

$$r_{\max}=(J_{\max}/N_{\max})^{1/3}=n_{\max}^{1/3}\,. \tag{83}$$

$J_{\max}$ is given by Eqs. (80) and (81).

In Eq. (82), the variables may be separated and we arrive at a solution in the implicit form

$$\int_{y_0}^{y}\frac{ydy}{1-y^3}=\frac{1}{3}\Bigg[\ln\frac{1-y_0}{1-y}+\frac{1}{2}\ln\frac{y^2+y+1}{y_0^2+y_0+1}-\sqrt{3}\left(\arctan\frac{2}{\sqrt{3}}(y+1/2)-\arctan\frac{2}{\sqrt{3}}\times(y_0+1/2)\right)\Bigg]=\frac{t}{t_0}, \tag{84}$$

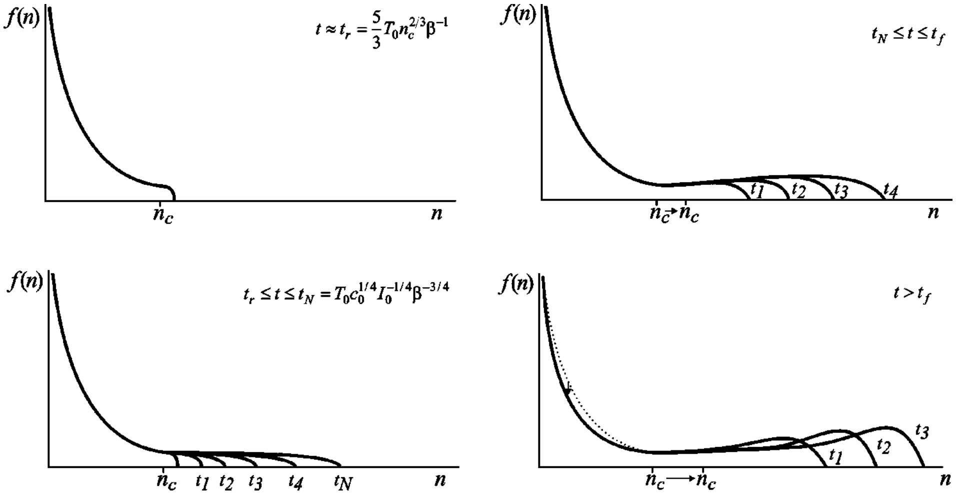

FIG. 1. Evolution of the cluster size distribution function $f(n,\tau)$ for different stages of the process: (a) Establishment of a quasi-steady-state nucleation for the range of cluster sizes $n \leqslant n_c$ for $\tau \leqslant \tau_r$ (left top) in the stage of nonsteady-state nucleation; (b) evolution in the stage of quasi-steady-state nucleation (right top); (c) evolution in the transient stage to coarsening (left bottom); (d) evolution in the late stage of coarsening (right bottom).

$$y_0 \leqslant y = \frac{r}{r_{\max}} \leqslant 1; \quad y_0 = \frac{r_0}{r_{\max}} \ll 1; \quad t_0^{-1} = \frac{D_{\text{eff}}}{2} A N r_{\max}. \tag{85}$$

After the substitution of the expression for the quantity A, we have

$$l = a_m N^{-1/3}, \quad t_0^{-1} = D_{\text{eff}} l^{-2} (\omega_s / \omega_m)^{2/3} J_{\max}^{1/3}. \tag{86}$$

The parameter l has the meaning of the average distance between the particles of the phase. N is determined via Eq. (65) and $J_{\max}$ via Eq. (81).

Equation (84) shows that, in the main part of the spectrum of phase particles r (for $y < 1$), the term y^3 may be neglected in the denominator. This way, we get

$$y^2 = y_0^2 + 2\frac{t}{t_0}, \quad t_0 = t_f. \tag{87}$$

In the close vicinity of unity the relative size y exponentially goes with time to unity, $y \to 1$. Consequently, in the time interval $t_N \leqslant t \leqslant t_0$ a distribution of phase particles is formed that represents the initial state for the late stage of the process, the so-called coarsening [13,14]. The distribution function is given in the transient state, in dependence on r, by Eqs. (71) with a value of r_0 determined by Eq. (87). We get

$$f = \frac{I_0 r_0}{a r} \theta(r_{\max}(\tau_N) - r_0) \theta(r_0 - r_g). \tag{88}$$

The parameter a is given by Eq. (56).

It follows from Eq. (87) that the range of cluster sizes Δ, which gives the basic contribution to the phase in the transient stage of the transformation, is significantly narrower than the range of cluster sizes that is formed in the stage of steady-state nucleation and that serves as the initial distribution in the transient state. Denoting the width of this initial distribution by $r_{\max}(\tau_N) - \tau_g = \Delta r_0$, we may write

$$\Delta = \frac{r_0 \Delta r_0}{\sqrt{2 r_{\max}^2 t / t_0}} \simeq \frac{r_{\max}(\tau_N)}{r_{\max}(\tau_f)} \Delta r_0 \ll \Delta r_0. \tag{89}$$

In other words, the ratio of the widths of the intervals is determined by the ratio $r_{\max}(\tau_N)/r_{\max}(\tau_f)$, where $r_{\max}$ is determined by Eqs. (66) and (83), respectively, for the both considered cases.

V. DISCUSSION

The present paper is devoted to the description of the entire course of the evolution of a phase transformation process encompassing both the quasi-steady-state nucleation stage and the transient stage to coarsening in a multicomponent solid solution. An approach to the theoretical treatment of this problem is proposed and a complete set of equations is formulated describing this process. The expression for the effective diffusion coefficient is derived, which determine the flux of structural units of the phase through the boundaries of the aggregates of the evolving phase. This coefficient can be written as a combination of the partial diffusion coefficients of the different components in the solid solution.

All the basic characteristics of the phase transformation process are determined analytically including the following: the distribution function of particles with respect to cluster size, the cluster flux in size space, the maximal number of phase particles, and estimates of the duration of the different stages of the process.

The degree of dispersity of the system is shown to grow essentially in the initial, nucleation stage of the process of phase separation. However, at the transient stage, the width of the distribution with respect to cluster sizes is reduced, but increases again at the later stage, approaching (in reduced variables) a constant value [13,14]. These results allow one to vary the dispersity of the evolving phase by terminating the phase separation at some definite stage of the process.

In addition, the analytic expressions can be utilized toward the determination of the interfacial free energy (which can hardly be measured otherwise) by comparing the theoretical results with experimental data. Of course, one has to be sure that the process is dominated, as assumed here, by homogenous nucleation.

Numerical solutions of the basic kinetic equations show an excellent agreement with the results of the theory (see [12,15,24,32,46–50] and Fig. 1).

The proposed theory can be applied toward the description of phase transitions in the liquid as well as for the case of droplet formation with a given stoichiometric composition.

ACKNOWLEDGMENTS

The work was performed as a part of a project financed by the German Ministry for Science and Higher Education (BMBF). One of the authors (J.S.) also acknowledges a grant given by the Deutsche Forschungsgemeinschaft (DFG).

APPENDIX: DERIVATION OF BASIC KINETIC EQUATION

Primarily, the theoretical description of the kinetics of first-order phase transitions, proceeding via the mechanism of nucleation and growth, can be given based on a set of kinetic equations of the form

$$\frac{\partial f(n,t)}{\partial t} = -[I(n,t) - I(n-1,t)], \tag{A1}$$

$$I(n,t) = \nu_{n,n+1} f(n,t) - \nu_{n+1,n} f(n+1,t)$$
$$= \nu_{n,n+1}\left[f(n,t) - \frac{\nu_{n+1,n}}{\nu_{n,n+1}} f(n+1,t)\right].$$

Here $I(n,t)$ denotes the flux of phase particles in cluster size space.

In order to employ these equations, the rates of aggregation and emission have to be determined. The rates of aggregation can be evaluated based on the analysis of the mechanism of growth of the aggregates. Conventionally, the rates of emission are determined then utilizing the principle of detailed balancing. We avoid here the application of this principle and use an alternative general method we denoted as the method of virtual media (see, e.g., [36,51,52]). This method can be employed in systems, where the ambient phase is in a state of local thermodynamic equilibrium. Here we will summarize the basic ideas of this method in application to clusters of supercritical sizes. The alternative range of cluster sizes can be treated similarly (see, e.g., [36,51,52]).

Let us consider two different closed systems, one of them being the phase particle in the real medium and the other one a phase particle in virtual medium. This virtual medium (or this partly artificial alternative state of the ambient) is defined in such a way that the aggregate of the phase is in thermal equilibrium with the ambient phase. For supercritical clusters, this virtual state can be constructed by freezing in the position of a certain ratio of the different ambient phase particles in the solution [36,51,52]. For any aggregate of any given size (number of structure elements *n*) such virtual state of the ambient phase or such virtual medium may be constructed [36,51,52].

The motion of the mobile particles of the different components proceeds in the same way as for the real state of the system since the potential energy landscape is the same for both states. During the time of transfer of atoms from one location in the solution to a neighboring one, or to the aggregate of the phase, the environment of these particles does not change. This way, the kinetic coefficients, which determine the transition velocity from the real ($\beta_{n,n+1}$) and the virtual ($\overline{\beta}_{n,n+1}$) media to the phase aggregate, coincide. Thus, we get

$$\beta_{n,n+1} = \tilde{\beta}_{n,n+1}. \tag{A2}$$

The ratio of atoms of the different components, allowed to move in the virtual medium, is determined by the equilibrium conditions (equality of chemical potentials) with the phase aggregate of size *n*. The frequencies of aggregation to an aggregate of size *n* in the real and virtual media have the form

$$\nu_{n,n+1} = \beta_{n,n+1} W_{n,n+1}, \quad \tilde{\nu}_{n,n+1} = \tilde{\beta}_{n,n+1} \tilde{W}_{n,n+1}. \tag{A3}$$

Here W and $\tilde{W}$ denote the number of favorable configurations allowing the respective process to proceed.

Since the aggregate is, in the virtual medium, in equilibrium with the ambient phase, we have $\tilde{W}_{n,n+1} = \tilde{W}_{n+1,n}$ and $\tilde{\beta}_{n,n+1} = \tilde{\beta}_{n+1,n}$. For the real system, we may write [36,51,52]

$$\frac{\nu_{n,n+1}}{\nu_{n+1,n}} = \frac{\beta_{n,n+1} W_{n,n+1}}{\beta_{n+1,n} W_{n+1,n}} = \frac{\beta_{n,n+1} W_{n,n+1}}{\tilde{\beta}_{n+1,n} \tilde{W}_{n+1,n}} = \frac{W_{n,n+1}}{\tilde{W}_{n,n+1}}$$
$$= \exp(\Delta S_n). \tag{A4}$$

Here ΔS_n is given by $\Delta S_n = \Delta S_p - \Delta S$. It denotes the change of the total entropy when a structural unit is added to the aggregate. ΔS_p is the change of entropy per structural unit for the phase aggregate and ΔS the respective quantity for the ambient phase. ΔS_n may be expressed further as

$$\Delta S_n = -\frac{1}{T}[\Delta\Phi(n+1) - \Delta\Phi(n)]. \tag{A5}$$

Such replacement can be made if the temperature is not changed in the course of transfer of one structural unit from the ambient phase to the aggregate. Thus, this replacement can be made in condensed matter only where the thermal conductivity is high.

Thus, using $\tilde{W}_{n,n+1} = 1$ and Eqs. (A2)–(A6) we get

$$\frac{\nu_{n+1,n}}{\nu_{n,n+1}}=W^{-1}_{n,n+1}=\exp\left(\frac{1}{T}\right)[\Delta\Phi(n+1)-\Delta\Phi(n)]. \tag{A6}$$

Here $\Delta\Phi(n)$ denotes the difference of the thermodynamic potential, if a phase aggregate of size n is formed in the solution.

A substitution of Eq. (A6) into Eq. (A1) yields

$$I(n,t)=\nu_{n,n+1}\exp\left(-\frac{\Delta\Phi(n)}{T}\right)\left[\exp\left(\frac{\Delta\Phi(n)}{T}\right)f(n,t)-\exp\left(\frac{\Delta\Phi(n+1)}{T}\right)f(n+1,t)\right]. \tag{A7}$$

By a Taylor expansion of the second term in the brackets in the right-hand side of Eq. (A7), we get in a first approximation and for $n \gg 1$, Eq. (1) is used as the basic equation for the analysis presented above.

[1] M. Volmer, *Kinetik der Phasenbildung* (Steinkopff, Dresden, 1933).

[2] R. Becker and W. Döring, Ann. Phys. (Leipzig) **24**, 719 (1935).

[3] R. Kaischew and I. Stranski, Z. Phys. Chem. Abt. A **170**, 295 (1934).

[4] H. Reiss, J. Chem. Phys. **18**, 840 (1951).

[5] D. Stauffer, J. Aerosol Sci. **7**, 319 (1976).

[6] K. Binder and D. Stauffer, Adv. Phys. **25**, 343 (1976).

[7] H. Trinkaus and H. Yoo, Philos. Mag. A **55**, 269 (1987).

[8] H. Wiedersich and J. Katz, Adv. Colloid Interface Sci. **10**, 33 (1979).

[9] F. M. Kuni and A. P. Grinin, Kolloidn. Zh. **46**, 460 (1984).

[10] F. M. Kuni and A. P. Grinin, Teor. Mat. Fiz. **80**, 418 (1989).

[11] J. Katz and M. Donohue, Adv. Chem. Phys. **40**, 137 (1979).

[12] I. Gutzow and J. Schmelzer, *The Vitreous State. Thermodynamics, Structure, Rheology, and Crystalization* (Springer, Berlin, 1995).

[13] I. M. Lifshitz and V. V. Slezov, J. Phys. Chem. Solids **19**, 35 (1961); Zh. Eksp. Teor. Fiz. **35**, 475 (1958) and references cited therein.

[14] V. V. Slezov, *Theory of Diffusive Decomposition of Solid Solutions*, Sov. Scientific Reviews, Vol. A17 (Gordon and Breach, London, 1995).

[15] J. Schmelzer, G. Röpke, and R. Mahnke, *Aggregation Phenomena in Complex Systems* (Wiley-VCH, Weinheim, 1998).

[16] J. W. P. Schmelzer, G. Röpke, and V. B. Priezzhev, in *Nucleation Theory and Applications*, edited by J. W. P. Schmelzer (Joint Institute for Nuclear Research Publishing House, Dubna, Russia, 1999) (further information can be received via email, juern-w.schmelzer@physik.uni-rostock.de).

[17] N. N. Tunitskij, Zh. Fiz. Khim. **15**, 1061 (1941) (in Russian).

[18] H. Wakeshima, J. Phys. Soc. Jpn. **9**, 400 (1954); **9**, 407 (1954).

[19] K. Binder and D. Stauffer, Adv. Phys. **25**, 343 (1976).

[20] K. Binder, Phys. Rev. B **15**, 4425 (1977).

[21] A. I. Rusanov, *Phasengleichgewichte und Grenzflächenerscheinungen* (Akademic-Verlag, Berlin, 1978).

[22] J. D. Gunton, M. San Miguel, and P. S. Sahni, *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic Press, London, 1983), Vol. 8.

[23] J. Schmelzer, D.Sc. thesis, Universität Rostock, 1985.

[24] M. F. Wehner and W. G. Wolfer, Philos. Mag. A **52**, 189 (1985).

[25] J. Schmelzer and H. Ulbricht, J. Colloid Interface Sci. **117**, 325 (1987).

[26] H. Ulbricht, J. Schmelzer, R. Mahnke, and F. Schweitzer, *Thermodynamics of Finite Systems and the Kinetics of First-Order Phase Transitions* (Tuebner, Leipzig, 1988).

[27] J. C. Barrett and C. F. Clement, J. Aerosol Sci. **22**, 327 (1991).

[28] M. Tokuyama and Y. Enomoto, Phys. Rev. Lett. **69**, 312 (1992); Phys. Rev. E **47**, 1156 (1993).

[29] A. P. Grinin, D.Sc. thesis, St. Petersburg State University, 1993 (in Russian).

[30] F. M. Kuni, A. P. Grinin, and V. B. Kurasov, *Lectures on Kinetic Theory of Condensation Under Dynamical Conditions* (St. Petersburg State University Press, St. Petersburg, 1996).

[31] F. P. Ludwig and J. Schmelzer, J. Colloid Interface Sci. **181**, 503 (1996).

[32] J. W. P. Schmelzer, G. Röpke, J. Schmelzer, Jr., and V. V. Slezov, in *Nucleation Theory and Applications* (Ref. [16]), pp. 82–129.

[33] V. V. Slezov and J. Schmelzer, and Ya. Y. Tkatch, J. Chem. Phys. **105**, 8340 (1996).

[34] V. V. Slezov and J. W. P. Schmelzer, in *Nucleation Theory and Application* (Ref. [16]), pp. 6–81.

[35] V. V. Slezov and J. Schmelzer, Fiz. Tverd. Tela (S.-Peterburg) **36**, 353 (1994); **39**, 2210 (1997).

[36] V. V. Slezov and J. Schmelzer, J. Phys. Chem. Solids **55**, 243 (1994).

[37] V. V. Slezov, J. Schmelzer, and Ya. Y. Tkatch, J. Mater. Sci. **32**, 3739 (1997).

[38] J. W. P. Schmelzer and J. Schmelzer, Jr., J. Colloid Interface Sci. **215**, 345 (1999).

[39] F. M. Kuni, A. P. Grinin, and V. B. Kurasov, in, *Nucleation Theory and Applications* (Ref. [16]), pp. 160–193.

[40] V. V. Slezov, Fiz. Tverd. Tela (S.- Peterburg) **37**, 2879 (1995); **38**, 433 (1996).

[41] V. V. Slezov and V. V. Sagalovich, Fiz. Tverd. Tela (Leningrad) **17**, 1497 (1975).

[42] V. V. Slezov, J. Phys. Chem. Solids **39**, 367 (1978).

[43] V. V. Slezov and V. V. Sagalovich, J. Phys. Chem. Solids **38**, 943 (1977).

[44] K. Binder, in *Stochastic Nonlinear Systems in Physics, Chemistry and Biology*, edited by L. Arnold and R. Lefever (Springer, Berlin, 1981), p. 62.

[45] I. Gutzow, J. Schmelzer, and A. Dobreva, J. Non-Cryst. Solids **219**, 1 (1997).

[46] P. Mirold and K. Binder, Acta Metall. **25**, 1435 (1977).
[47] J. Bartels, U. Lembke, R. Pascova, J. Schmelzer, and I. Gutzow, J. Non-Cryst. Solids **136**, 181 (1991).
[48] R. Kampmann, Th. Ebel, M. Haese, and R. Wagner, Phys. Status Solidi B **172**, 295 (1992).
[49] F.-P. Ludwig and J. Schmelzer, J. Colloid Interface Sci. **181**, 503 (1996).
[50] T. Olson and P. Hamill, J. Chem. Phys. **104**, 210 (1996).
[51] V. V. Slezov and J. Schmelzer, J. Phys. Chem. Solids **59**, 1507 (1998).
[52] V. V. Slezov, Phys. Rep. **288**, 389 (1998).