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The kinetics of decomposition of solid solutions

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The influence of solute–solute interactions on segregation processes in multi-component solid solutions leading to the formation of a new phase with a given stoichiometric composition, has been investigated for the first time. Expressions for the nucleation and growth rates have been derived. Estimates were developed for the time required to establish a steady-state nucleation rate in the system and the time interval for which such a steady-state can be sustained. Based on these results, it is anticipated that a method for an experimental determination of the parameters describing the interaction of the solute components, could be developed. The kinetic equation describing the evolution of the cluster size distribution function has been generalized to account for stochastic effects due to both fluctuations in the growth rate and possible spatial correlations of the evolving clusters in the matrix. The possible influence of such stochastic effects (thermal noise and random coalescence) on coarsening described by such additional terms has been discussed briefly.

1. Introduction

Phase transformation processes in solid solutions are known to determine a large variety of properties of materials [1–3]. In particular, this statement refers to segregation processes in solid solutions. A detailed investigation of such processes is, therefore, of outstanding technological and (owing to the number of difficult problems involved in such investigations) scientific importance.

The description of the initial stages of segregation processes in solids is carried out commonly based on classical nucleation theory (see [4–8]). This theory is supplemented by theoretical descriptions of the late stages of the transformation developed first by Lifshitz and Slezov [9] and extended later by different authors to account for the influence of a finite volume fraction of the evolving phase (diffusional interaction of the clusters, see, for example, [10]), elastic fields evolving during the course of growth (cluster–matrix interactions [7, 11], interactions between the different clusters [12]), spatial correlations of the clusters and other possible effects on coarsening (for example, [13]), and analyses giving a description of the whole course of the transformation (see, for example, [7]).

As is well-known, the classical nucleation theory was developed in the 1920–1930s by several workers (e.g. Volmer, Becker, Düring, Stranski, Kaischew, Zeldovich, Frenkel) first for one-component systems and then generalized by Reiss to binary nucleation ([4–7]). Subsequently, a number of attempts have been made to extend the results to nucleation processes in multi-component solid or liquid solutions, however, a final solution of all the various problems involved in such a task has been missing until now.

In a recent publication, the formation process of a new phase in a multicomponent solid solution was analysed for the case where clusters of a definite stoichiometric composition are formed [8]. It was shown that, for this particular situation, a consistent theory of nucleation and growth can be formulated. Moreover, in addition, a novel method for the determination of the relations connecting the rates of aggregation and dissolution of clusters of different sizes, was developed, by avoiding the application of the concept of detailed balancing for supercritical clusters, i.e. in the range of cluster sizes where its application is particularly questionable. This method is applicable far beyond the special problem considered.

Based on the general relations derived, special cases were considered for an illustration. Hereby it was assumed that the different solute components do not interact with each other, i.e. only the solute–matrix interaction was taken into account. This assumption is in line with classical investigations of segregation processes in solutions where, generally, the case of a weak (perfect) solution is considered.

In the present paper, as a generalization of the earlier results obtained for the first time, such interactions are taken into account in a comprehensive manner (for first attempts in this direction see [14]). It is shown that the general form of the basic equations remains the same, but in these equations the concentrations of the different components have to be replaced by chemical activities which are determined both by the concentrations and the type of interactions between the different components. A method is developed allowing an experimental determination of the interaction parameters of the solute

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components and, thus, of the chemical activities of the solute components.

The outlined theory may also be used to study nucleation processes in other fields of application where interactions between the basic building units of the evolving phase in clustering are essential for an understanding of the kinetics of nucleation and growth.

As a next step, a generalization of the kinetic equation is given, which is used commonly for the description of the evolution of the cluster size distribution. It contains, in addition to the regular hydrodynamic term describing the deterministic motion in cluster size space, a term proportional to the first derivative of the cluster size distribution function. This additional term reflects diffusion-like processes in cluster size space due to the influence of stochastic effects on the growth kinetics.

Moreover, another type of stochasticity is accounted for, connected with a possible touching and merging of clusters in the nucleation–growth process. Such effects are described by a collision integral. The influence of both effects on the different stages of the segregation process is investigated.

2. Basic kinetic equations

The time evolution of an ensemble of clusters in nucleation–growth processes is usually described in terms of the cluster size distribution function, $f(n, t)$. As shown in detail elsewhere [8], the evolution of the distribution $f(n, t)$ of aggregates consisting at time t of n structural elements in the process of formation of a phase with a given stoichiometric composition, may be calculated by a Fokker–Planck type equation of the form

$$\frac{\partial f(n,t)}{\partial n} = \frac{\partial}{\partial n}\left\{ w_{n,n+1}\left[\frac{\partial f(n,t)}{\partial n} + \frac{f(n,t)}{k_B T}\frac{\partial \Delta\Phi(n)}{\partial n}\right]\right\} + J_c(n,t) \qquad n \gg 1 \tag{1}$$

where k_B is the Boltzmann constant, T the absolute temperature, and Φ the Gibbs free energy. The kinetic coefficient $w_{n,n+1}$ describes here the probability that, per unit time, a primary building unit is incorporated to an aggregate consisting initially of n such units. Its specific form is determined by the mechanism of growth underlying the temporal evolution of the cluster size distribution and thermodynamic properties of the considered system.

In addition to earlier considerations, in Equation 1 a "collision integral" term J_c is introduced accounting for processes of touching and merging of the aggregates in the course of the segregation process. In the initial stages of the transformation process, the probability of such collisions is small, at least, if the volume fraction of the solute is sufficiently low. Therefore, as was done earlier and also in the present paper, for the consideration of nucleation, this term may be neglected. However, it may have a major impact on the late stages of the transformation accounting, at least in part, for a deviation of the cluster size distributions observed experimentally from the original Lifshitz–Slezov theoretical predictions (cf. [13, 15, 16]).

On the contrary, the second additional term in the kinetic equation is of basic importance in this stage, being the only source for processes of the formation of supercritical clusters. As will be shown later, its influence on the late stages of the process, however, ceases with time, although at intermediate times it may also have an important influence on the shape of the size distribution [17].

To generalize results earlier obtained to segregation processes in solutions, both the kinetic coefficients and the boundary conditions have to be reformulated. The respective relations depend on the thermodynamic properties and the type of interaction between the solute particles. Its thermodynamic description will be discussed in the next section.

3. Solute–solute interactions: thermodynamic relationships

The Helmholtz free energy, F, and the chemical potentials, μ_i, of the different components in a solid solution, taking into account possible interactions between them, can be calculated easily, if, as it is assumed commonly, only configurational contributions for the determination of the entropy are taken into consideration. Generally we have

$$F = -k_B T \ln Z \tag{2}$$

$$Z = \sum_n \exp\left(-\frac{E_n}{k_B T}\right) \tag{3}$$

k_B is the Boltzmann constant, T the absolute temperature, Z the partition function of the system and E_n are the different values of the energy of the system in a canonical ensemble.

With the above-mentioned assumption, we may write, approximately

$$Z \cong \left\{\exp\left[-\frac{E_0(S,V)}{k_B T}\right]\Delta\Gamma(T,V)\right\} \times \left\{\exp\left[-\frac{\Delta E(N,(n_i))}{k_B T}\right]\Delta\Gamma[N,(n_i)]\right\} \tag{4}$$

where S is the entropy, V is volume, $E_0(S, V)$ is the thermodynamic (most probable value) energy of the matrix not containing solute components, while $\Delta E(N, (n_i))$ is the correction term accounting for the change in the energy if solute components are introduced into the solid solution.

The statistical weight, $\Delta\Gamma$, is determined by the product of the respective quantities for the pure matrix ($\Delta\Gamma(T, V)$) and the configurational part of the solute components ($\Delta\Gamma[N,(n_i)]$). N is the total number of lattice sites where solute components may be introduced into the matrix, (n_i) describes the set of solute components in the matrix.

The thermal contributions to the entropy depend only weakly on the concerntration and distribution of solute particles in the matrix; therefore, they can be neglected in the calculation of the chemical potentials.

The energy term $\Delta E[N,(n_i)]$ may be written in a first approximation [18] as

$$\Delta E[N,(n_i)] = \Delta E^{(0)}[N,(n_i)] + \frac{1}{2}\sum_{i,k} \beta_{ik}\left(\frac{n_i n_k}{N}\right) \tag{5}$$

where β_{ik} is constant which accounts for interaction of the solute components; $E^{(0)}[N,(n_i)]$ (the energy contribution of the solute components) is denoted, taking into account only solute–matrix interactions. The interactions between the solute components themselves are described in a first approximation by the second term in Equation 5.

The configurational statistical weight has the same value independent of whether the interaction of the solute particles with each other is or is not accounted for; it depends only on the number of distributions of (n_i) solute particles on N lattice sites in the matrix.

Equation 2–5 yield

$$F = F^{(0)} + \frac{1}{2}\sum_{ik} \beta_{ik}\left(\frac{n_i n_k}{N}\right) \tag{6}$$

$$\mu_i = \frac{\partial F}{\partial n_i} = \mu_i^{(0)} + \sum_k \beta_{ik} c_k \tag{7}$$

$$c_k = \frac{n_k}{N} \tag{8a}$$

$$\mu_i^{(0)} = \psi_i + k_\mathrm{B} T \ln c_i, \tag{8b}$$

where c_k is the concentration of component k, $F^{(0)}$ and $\mu_i^{(0)}$ are the Helmholtz free energy and the chemical potential of the ith component for the case where the segregating components do not interact with each other.

As the result we obtain

$$\mu_i = \psi_i + k_\mathrm{B} T \ln c_i + \sum_k \beta_{ik} c_k \tag{9}$$

or

$$\mu_i = \psi_i + k_\mathrm{B} T \ln \left\{ c_i \exp\left(\frac{\sum_k \beta_{ik} c_k}{k_\mathrm{B} T}\right)\right\} \tag{10}$$

ψ_i is the excess enthalpy of the ith solute component in the matrix.

Equation 10 indicates that it is reasonable to introduce the notation

$$\varphi_i = c_i \exp\left(\frac{\sum_k \beta_{ik} c_k}{k_\mathrm{B} T}\right) \tag{11}$$

resulting with Equation 10 in

$$\mu_i = \psi_i + k_\mathrm{B} T \ln \varphi_i, \tag{12}$$

It is easily verified (cf. Equations 8 and 12) that the expression for the chemical potential has the same form as for a weak (perfect) solution with the difference that the concentrations, c_i, are to be replaced by the chemical activities φ_i. Moreover, in the outlined approach, the chemical activities are well-defined quantities expressed through the interaction parameters β_{ik}. A method of experimental determination of these parameters and thus of the activities will be discussed somewhat later.

As the next step we consider the change $\Delta\Phi$ of the Gibbs free energy, Φ, connected with the formation of an aggregate of a definite stoichiometric composition consisting of n structural elements. We have [8]

$$\Delta\Phi(n) = n\left(\mu_\mathrm{s}^{(\infty)} - \sum_i \nu_i \mu_i\right) + 4\pi\sigma\left(\frac{3\omega_\mathrm{s}}{4\pi}\right)^{2/3} n^{2/3} \tag{13}$$

where ν_i are stoichiometric coefficients; $\mu_\mathrm{s}^{(\infty)}$ is the chemical potential of a structural element of the aggregate, μ_i the chemical potentials of the different solute components in the solid solution, σ is the specific interfacial energy, and ω_s is the volume of one structural element of the evolving phase.

Assuming that both the aggregate and the structural element are of spherical shape, the radius, R, of the aggregate and radius a_s, of the structural element may also be introduced as parameters. They are connected by the equations

$$\omega_\mathrm{s} = \frac{4\pi}{3} a_\mathrm{s}^3 \tag{14a}$$

$$R = a_\mathrm{s} n^{1/3} \tag{14b}$$

Equation 14a may be considered also as the definition of the parameter a_s.

A derivation of Equation 13 with respect to n yields

$$\frac{\partial \Delta\Phi(n)}{\partial n} = \left(\mu_\mathrm{s}^{(\infty)} - \sum_i \nu_i \mu_i\right) + \frac{8\pi}{3}\sigma\left(\frac{3\omega_\mathrm{s}}{4\pi}\right)^{2/3} n^{-1/3} \tag{15}$$

By setting the derivative equal to zero, Equation 15 may be used to determine either the equilibrium concentrations of the different solute components (for a given value of n) or the critical size, n_c, of the aggregate (for given values of the solute concentration in the matrix). The resulting equation reads

$$\sum_i \nu_i \mu_i = \mu_\mathrm{s}^{(\infty)} + \frac{8\pi}{3}\sigma\left(\frac{3\omega_\mathrm{s}}{4\pi}\right)^{2/3} n_\mathrm{c}^{-1/3} \tag{16}$$

With Equation 12 we obtain

$$\sum_i \nu_i \psi_i + k_\mathrm{B} T \ln \prod_i \varphi_i^{\nu_i} = \mu_\mathrm{s}^{(\infty)} + \frac{8\pi}{3}\sigma\left(\frac{3\omega_\mathrm{s}}{4\pi}\right)^{2/3} n_\mathrm{c}^{-1/3} \tag{17}$$

If we introduce, in addition, the constant $K_\infty(p,T)$ of the chemical reaction equilibrium for a bulk system $(n_\mathrm{c}^{-1/3} \to \infty)$ as

$$K_\infty(p,T) = \exp\left(\frac{\mu_\mathrm{s}^{(\infty)} - \sum_i \nu_i \psi_i}{k_\mathrm{B} T}\right) \tag{18}$$

and a similar relation for the respective equilibrium constant for the reaction taking place near an aggregate consisting of n structural elements

$$K_n(p,T) = K_\infty(p,T)\exp\left[\frac{8\pi}{3}\left(\frac{\sigma}{k_\mathrm{B} T}\right)\left(\frac{3\omega_\mathrm{s}}{4\pi}\right)^{2/3} n^{-1/3}\right] \tag{19}$$

then Equation 17 may be rewritten as

$$\prod_i \varphi_i^{\nu_i} = K_\infty(p,T)\exp\left[\frac{8\pi}{3}\left(\frac{\sigma}{k_B T}\right)\left(\frac{3\omega_\mathrm{s}}{4\pi}\right)^{2/3} n_\mathrm{c}^{-1/3}\right] = K_{n_\mathrm{c}}(p,T) \tag{20}$$

It follows that, as a special case, the equilibrium values of φ_i in the bulk (denoted as $\varphi_i^{(\infty)}$) obey the following relation

$$\prod_i (\varphi_i^{(\infty)})^{\nu_i} = K_\infty(p, T) \tag{21}$$

For given values of the quantities φ_i, Equations 16 or 17 allow estimation of the critical number of structural elements in an aggregate as

$$n_c^{1/3} = \frac{2\sigma\omega_s}{a_s k_B T \Delta} \tag{22}$$

where the supersaturation, Δ, is determined by

$$\begin{aligned}\Delta &= \ln\left[\prod_i \left(\frac{\varphi_i}{\varphi_i^{(\infty)}}\right)^{\nu_i}\right] \\ &= \ln\left(\frac{\prod_i \varphi_i^{\nu_i}}{K_\infty(p, T)}\right)\end{aligned} \tag{23}$$

By using the same notations we may also write

$$\frac{1}{k_B T}\left[\frac{\partial \Delta\Phi(n)}{\partial n}\right] = -\ln\left(\frac{\prod_i \varphi_i^{\nu_i}}{K_n(p, T)}\right) \tag{24}$$

of applying Equations 19 and 20

$$\begin{aligned}\frac{1}{k_B T}\frac{\partial \Delta\Phi(n)}{\partial n} &= -\ln\left(\frac{K_{n_c}(p, T)}{K_n(p, T)}\right) \\ &= -\frac{8\pi}{3}\left(\frac{\sigma}{k_B T}\right)\left(\frac{3\omega_s}{4\pi}\right)^{2/3}\left(\frac{1}{n_c^{1/3}} - \frac{1}{n^{1/3}}\right)\end{aligned} \tag{25}$$

These expressions are needed in the subsequent derivations.

4. Rate of change of the number of structural elements of an aggregate of the newly evolving phase: the diffusion coefficient in the space of structural elements

The flux of particles of the ith component to an aggregate of the new phase consisting of n structural elements may be written, similarly to the case of segregation of one solute component in the matrix (c.f. [8]), in the form

$$4\pi R^2 j_i = -w_{n_i, n_{i+1}} \frac{1}{k_B T}\left[\frac{\partial \Delta\Phi^{(s)}}{\partial n_i}\right] \tag{26}$$

In this equation $w_{n_i, n_{i+1}}$ denotes the probability per unit time that particles of the ith component are incorporated into an aggregate consisting of n structural elements (and characterized sometimes also by a radius $R(n)$). This quantity may be expressed in the following way [19]

$$w_{n_i, n_{i+1}} = \left(\frac{\alpha_i D_i}{a_m^2}\right)\left(\frac{4\pi R^2 a_m \tilde{c}_i}{\omega_m}\right) \tag{27}$$

where $\tilde{c}_i$ is the concentration (molar fraction) of the ith component in the surface layer. The parameter α_i describes the degree of inhibition of the diffusion process in the immediate vicinity of the aggregate. It has values in the range $0 \leqslant \alpha_i \leqslant 1$. D_i denotes the partial diffusion coefficient of the ith component in the immediate vicinity of the aggregate, and a_m is the lattice constant of the matrix. With these notations it becomes evident that the first part of the right-hand side of Equation 27 ($\alpha_i D_i / a_m^2$) means the frequency of jumps of particles of the ith component in the interfacial layer near the aggregate in the direction of the aggregate.

Thus, the total number of particles in the surface layer can be written as $(4\pi R^2 a_m / \omega_m)$, where ω_m is the average volume per particle in the matrix. By multiplying this ratio with the concentration (molar fraction), $\tilde{c}_i$, of the ith component in the surface layer, we obtain the total number of particles of the ith component in the layer. Consequently, $w_{n_i, n_{i+1}}$ has, indeed, the meaning as specified above.

In addition to the number of jumps, the diffusional fluxes to the surface of the aggregate are determined by the change of the thermodynamic potential $\Delta\Phi^{(s)}$. Let n_i be the number of particles of the ith component in an aggregate of size n. $\Delta\Phi^{(s)}$ is the change of the thermodynamic potential, required to transfer all particles, n_i, of the different components required for the formation of an aggregate of size n from the solution with values of the concentration $\tilde{c}_i$ to a solid state for which an aggregate of size n is in equilibrium with the surrounding solution. The value of the chemical potential of the ith component, being in thermodynamic equilibrium with an aggregate of size n, is denoted by $\mu_i(c_{ni})$, and c_{ni} specifies the respective values of the equilibrium concentrations of the components in the matrix. As will be shown later, a determination of these concentrations, although possible, is not required for a formulation of the kinetic equations describing nucleation and growth.

To distinguish such a type of change of the characteristic thermodynamic potential from the change due to the formation of an aggregate of size n, the superscript (s) in $\Delta\Phi^{(s)}$ is introduced. According to the given definition, $\Delta\Phi^{(s)}$ may be written as

$$\Delta\Phi^{(s)} = \sum_i n_i[\mu_i(c_{ni}) - \mu_i(\tilde{c}_i)] \quad \mu^{(s)} = \sum_i n_i \mu_i(c_{ni}) \tag{28}$$

A derivation of Equation 28 with respect to n_i yields

$$\left(\frac{\partial \Delta\Phi^{(s)}}{\partial n_i}\right) = -[\mu_i(\tilde{c}_i) - \mu_i(c_{ni})] \tag{29}$$

and after a substitution into Equation 26 we obtain

$$4\pi R^2 j_i = \frac{3\alpha_i D_i \tilde{c}_i}{a_m^2}\left(\frac{\omega_s}{\omega_m}\right)^{2/3} n^{2/3}\left[\frac{\mu_i(\tilde{c}_i) - \mu_i(c_{ni})}{k_B T}\right] \tag{30}$$

In the derivation of Equation 30, in addition, the relations

$$n = \frac{4\pi}{3}\frac{R^3}{\omega_s} \tag{31a}$$

$$\omega_m = \frac{4\pi}{3} a_m^3 \tag{31b}$$

where applied. ω_s is the volume per primary building unit in the segregating phase.

The rate of change of the number n of structural elements may then be written as

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{4\pi R^2 \sum_i \omega_i j_i}{\omega_s} \tag{32}$$

where the parameters ω_i denote the volume of a particle of the ith component in an aggregate of the newly evolving phase.

In application of Equation 29 to the description of the process of formation and growth of aggregates of stoichiometric composition, it has to be taken into account that the different fluxes are connected by the additional condition

$$\frac{j_1}{\nu_1} = \frac{j_2}{\nu_2} = \cdots = \frac{j_i}{\nu_i} \tag{33}$$

where ν_i denotes the molar fractions of the different components in the newly evolving phase. This relation allows expression of the rate of growth of the aggregate through the density of fluxes of only one of the components, e.g. the ith component as

$$\frac{\mathrm{d}n}{\mathrm{d}t} = 4\pi R^2 \frac{j_i}{\nu_i} \frac{\sum_i \nu_i \omega_i}{\omega_s} = 4\pi R^2 \frac{j_i}{\nu_i} \tag{34}$$

from which the identity $\sum_i \nu_i \omega_i = \omega_s$ was taken into account.

A substitution of Equation 30 into Equation 34 yields

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{3\alpha_i D_i \tilde{c}_i}{\nu_i a_m^2} \left(\frac{\omega_s}{\omega_m}\right)^{2/3} n^{2/3} \left[\frac{\mu_i(\tilde{c}_i) - \mu_i(c_{ni})}{k_B T}\right] \tag{35}$$

By dividing Equation 35 through the difference of the chemical potentials as well as by ν_i, and taking as the next step the sum over all components, the equation may be rewritten in the form

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{3n^{2/3}}{a_m^2} \left(\frac{\omega_s}{\omega_m}\right)^{2/3} \left[\sum_i \left(\frac{\nu_i^2}{\alpha_i D_i \tilde{c}_i}\right)\right]^{-1} \times \sum_i \nu_i \left[\frac{\mu_i(\tilde{c}_i) - \mu_i(c_{ni})}{k_B T}\right] \tag{36}$$

Introducing the notation

$$\frac{1}{D^*} = \sum_i \frac{\nu_i^2}{\alpha_i D_i \tilde{c}_i} \tag{37}$$

and taking into account the following identities (cf. Equations 12 and 20)

$$\sum_i \nu_i \frac{\mu_i(\tilde{c}_i) - \mu_i(c_{ni})}{k_B T} = \sum_i \nu_i \ln\left(\frac{\varphi_i(\tilde{c}_i)}{\varphi_i(c_{ni})}\right) = \ln\left(\frac{\prod_i [\varphi_i(\tilde{c}_i)]^{\nu_i}}{K_n}\right) \tag{38}$$

we obtain, finally

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{3D^* n^{2/3}}{a_m^2} \left(\frac{\omega_s}{\omega_m}\right)^{2/3} \ln\left\{\frac{\prod_i [\varphi_i(\tilde{c}_i)]^{\nu_i}}{K_n}\right\} \tag{39}$$

For the rate of change of the number of structural elements we may write alternatively, an expression similar to Equation 26 as

$$v(n) = \frac{\mathrm{d}n}{\mathrm{d}t} = 4\pi R^2 j = -w_{n_i,n+1} \frac{1}{k_B T} \left(\frac{\partial \Delta\Phi}{\partial n}\right) \tag{40}$$

where v denotes velocity, nuclei growth rate; $\Delta\Phi$ is determined by Equation 13. With Equation 24 we may rewrite this relation in the form

$$\frac{\mathrm{d}n}{\mathrm{d}t} = w_{n,n+1} \ln\left(\frac{\prod_i [\varphi_i(\tilde{c}_i)]^{\nu_i}}{K_n}\right) \tag{41}$$

A comparison between Equations 41 and 39 shows that the rate coefficient $w_{n,n+1}$ may be written as

$$w_{n,n+1} = \frac{3D^* n^{2/3}}{a_m^2} \left(\frac{\omega_s}{\omega_m}\right)^{2/3} \tag{42}$$

In this way, the coefficients $w_{n,n+1}$ required for an application of Equation 1 are determined. However, in Equation 41 the activities $\tilde{\varphi}_i = \varphi_i(\tilde{c}_i)$ occur which have to be replaced later by the known average activities $\varphi_i(c_i)$ of the matrix. This replacement will lead to some further revision of the expression for $w_{n,n+1}$.

Moreover, as is evident from Equation 37, the effective diffusion coefficient, D^*, is a function of the concentration and depends, therefore, also on the interactions between the solute components. Therefore, as a next step, these dependencies have to be specified and expressed through the interaction parameters β_{ik}.

5. The coefficient of mass transfer of the *i*th component $D_i[(c_j)]c_i$

Taking into account the interaction between the solute particles the partial diffusion coefficients, D_i, depend on the concentration of the different components (c_j). This dependence is weak for the pre-factor D_{i0} in Equation 43

$$D_i = D_{i0} \exp\left(-\frac{Q_i}{k_B T}\right) \tag{43}$$

but may be of significant importance with respect to the activation energy of the diffusion process, Q_i.

This activation energy may be written as a sum of two terms, the first accounting for the contribution only due to solute–matrix interactions, $Q_i(0)$, while the second one, $\Delta Q_i[(c_j)]$, reflects solute–solute interactions, i.e.

$$Q_i[(c_j)] = Q_i(0) + \Delta Q_i[(c_j)] \tag{44}$$

Note that the solute–solute interaction is of significance only for distances not exceeding several times the respective lattice constants. Moreover, it is evident that the activation energy of the diffusion increases ($\Delta Q_i > 0$) if the solute particles attract each other and decreases ($\Delta Q_i < 0$) is the interaction leads effectively to a repulsion of the dissolved components. If the different solute particles have nearly the same size as the matrix building units (for the cases where they are occupying vacant lattice nodes) or if they are sufficiently small (occupying interstitial positions) then the solute interaction changes exclusively the potential well for the positions where the solute particles are bound to the lattice without changing the general shape of the energy relief.

The change of the activation energy is given for such cases by the energy of interaction of the solute particles as

$$\Delta Q_i = -\sum_k \beta_{ik} c_k \tag{45}$$

resulting in

$$Q_i[(c_j)] = Q_i(0) - \sum_k \beta_{ik} c_k \tag{46}$$

The partial diffusion coefficient of the ith component may be written then in the form

$$D_i[(c_j)] = D_{i0} \exp\left[-\frac{Q_i(0) - \sum_k \beta_{ik} c_k}{k_B T}\right] \tag{47}$$

For an application of the equations describing nucleation and growth of a stoichiometric multicomponent phase and not the partial diffusion coefficients themselves, but the so-called coefficients of mass transfer, $D_i c_i$ have to be known (cf. Equation 37). Denoting the partial diffusion coefficient in the absence of solute–solute interactions by $D_i^{(0)}$ we obtain from Equation 47

$$D_i[(c_j)]c_i = D_i^{(0)} c_i \exp\left(\frac{\sum_k \beta_{ik} c_k}{k_B T}\right) \tag{48}$$

or (cf. Equation 11)

$$D_i[(c_j)]c_i = D_i^{(0)} \varphi_i. \tag{49}$$

This result allows Equation 37 to be rewritten as

$$\frac{1}{D^*} = \sum_i \frac{\nu_i^2}{\alpha_i D_i^{(0)} \varphi_i}. \tag{50}$$

In this way, it turns out that the effective diffusion coefficient is, again, determined by the values of the chemical activities of the different components φ_i.

With Equation 49 the relation for the density of fluxes of particles of the ith component

$$\boldsymbol{j}_i = -\frac{D_i c_i}{k_B T} \operatorname{grad} \mu_i \tag{51}$$

may be transformed easily into

$$\boldsymbol{j}_i = -D_i^{(0)} \operatorname{grad} \varphi_i \tag{52}$$

Thus the only modification which must be introduced into the relations for the description of nucleation and growth for perfect solutions, derived by Slezov [8], consists in the replacement $c_i \to \varphi_i$.

Taking into account that for the case of kinetic limited growth, the concentrations (or activities) in the immediate vicinity of the evolving cluster or equal to the average concentrations c_i (average activities φ_i) in the matrix, from Equations 37, 39 and 49 we have, for kinetic limited growth

$$w_{n,n+1} = \frac{3D^* n^{2/3}}{a_m^2} \left(\frac{\omega_s}{\omega_m}\right)^{2/3} \tag{53a}$$

$$\frac{1}{D^*} = \sum_i \frac{\nu_i^2}{\alpha_i D_i^{(0)} \varphi_i} \tag{53b}$$

By the method outlined elsewhere [7], we obtain for the general case

$$w_{n,n+1} = \left(\frac{4\pi R}{\omega_m}\right) \frac{D^* D^{**}}{[D^* + D^{**}(a_m/R)]} \tag{54a}$$

$$\frac{1}{D^*} = \sum_i \frac{\nu_i^2}{\alpha_i D_i^{(0)} \tilde{\varphi}_i} \tag{54b}$$

$$\frac{1}{D^{**}} = \sum_i \frac{\nu_i^2}{D_i^{(0)} \tilde{\varphi}_i} \tag{54c}$$

In this general case, the chemical activities at the boundary of the aggregate $\tilde{\varphi}_i$ have to be expressed through the average (φ_i) and equilibrium (for a cluster of size n, (φ_{ni}) chemical via Equations 21, 33 and 52 resulting in [8]

$$\tilde{\varphi}_i = \varphi_i(a_m/\alpha_i R) + \varphi_{ni}(c_{ni}) \Bigg/ \left[1 + \left(\frac{a_m}{\alpha_i R}\right)\right] \tag{55}$$

For diffusion limited growth, prevailing for large values of the cluster size R, Equation 54 is reduced to

$$w_{n,n+1} = \frac{4\pi R D^{**}}{\omega_m} = \frac{3D^{**} n^{1/3}}{a_m^2} \left(\frac{\omega_s}{\omega_m}\right)^{1/3} \tag{56}$$

In all considered cases, the rate of deterministic growth of a cluster of size n may be determined from the expressions for $w_{n,n+1}$ via an equation of the form of Equation 41, where, however, $\varphi_i(\tilde{c}_i) = \tilde{\varphi}_i$ has to be replaced by $\varphi_i(c_i)$, i.e. by

$$\frac{dn}{dt} = w_{n,n+1} \ln\left(\frac{\prod_i [\varphi_i(c_i)]^{\nu_i}}{K_n}\right) \tag{57}$$

In this way, the determination of the kinetic coefficients $w_{n,n+1}$ and the deterministic growth rates is finally accomplished.

6. The boundary conditions for the cluster size distribution function: the steady-state nucleation rate

In order to solve the kinetic equation for the determination of the evolution of the cluster size distribution, the boundary conditions for $n \to 0$ and $n \to \infty$ have to be specified. If we express $f(n, t)$ in the form

$$f(n) = \Psi(n) \exp\left(-\frac{\Delta\Phi(n)}{k_B T}\right) \tag{58}$$

the physically reasonable boundary condition for large values of n is (compare [8])

$$\lim_{n \to \infty} \Psi(n) = 0 \tag{59}$$

while for $n \to 0$ and non-interacting solute particles

$$\lim_{n \to 0} \Psi(n) = \frac{N}{zV} \prod_i c_i^{\nu_i} \tag{60}$$

was shown to hold. z is the number of lattice places in the matrix occupied by the particles forming one structural element, N and V, as mentioned, are the total number of lattice sites (N) in the volume V.

While the boundary condition, Equation 59, remains unchanged, Equation 60 has to be modified accounting for the change of the number of possible configurations (the change of entropy) due to the interactions between the solute components. Instead of Equation 60 we then obtain

$$\lim_{n\to 0} \Psi(n) = \frac{N}{zV} \prod_i c_i^{\nu_i} \exp\left(\frac{\Delta S^{(\mathrm{int})}}{k_{\mathrm{B}}}\right) \tag{61}$$

The entropy difference $\Delta S^{(\mathrm{int})}$ can be expressed through the work (with a minus sign) required in a reversible process to transfer the different particles containing a structural element of the new phase into the pre-transition state or, equivalently, through the differences in the chemical potentials as

$$T\Delta S^{(\mathrm{int})} = -\sum_i \nu_i [\mu_i^{(\mathrm{inter\,face})} - \mu_i] \tag{62}$$

In Equation 62, $\mu_i^{(\mathrm{inter\,face})}$ denotes the values of the chemical potentials of the different interacting solute components in a group of molecules in the interfacial region capable of being incorporated into the aggregate of the newly evolving phase, while μ_i, as introduced with Equation 9, refers to the respective values in the bulk of the matrix.

Denoting the energy of interactions of the group of molecules in the pre-transition state by ε, which differs, in general, from the value $\sum_{ik} \nu_i \beta_{ik} c_k$ for a random distribution of the same solute components in the bulk, Equation 62 may be rewritten in the form

$$T\Delta S^{(\mathrm{int})} = -\left(\varepsilon - \sum_{ik} \nu_i \beta_{ik} c_k\right) \tag{63}$$

A substitution of Equation 63 into Equation 61 yields

$$\lim_{n\to 0} \Psi(n) = \frac{N}{zV} \prod_i c_i^{\nu_i} \exp\left(-\frac{\varepsilon - \sum_{ik} \nu_i \beta_{ik} c_k}{k_{\mathrm{B}}T}\right) \tag{64}$$

and with Equations 7 and 9

$$\lim_{n\to 0} \Psi(n) = \frac{N}{zV} \exp\left(-\frac{\varepsilon}{k_{\mathrm{B}}T}\right) \times \prod_i c_i^{\nu_i} \prod_i \left[\exp\left(-\frac{\sum_k \beta_{ik} c_k}{k_{\mathrm{B}}T}\right)\right]^{\nu_i} \tag{65}$$

or (cf. Equation 11)

$$\lim_{n\to 0} \Psi(n) = \frac{N}{zV} \exp\left(-\frac{\varepsilon}{k_{\mathrm{B}}T}\right) \prod_i \varphi_i^{\nu_i} \tag{66}$$

is obtained.

Once the kinetic coefficients $w_{n,n+1}$ and the boundary conditions are known the Fokker–Planck equation can be solved and the steady-state nucleation rate I can be determined (for the details see [8]). Taking into account the interactions of the solute components, we obtain

$$I = \frac{N}{zV} \exp\left(-\frac{\varepsilon}{k_{\mathrm{B}}T}\right) w_{n,n+1}(n_{\mathrm{c}}) \prod_i \varphi_i^{\nu_i} \exp\left(-\frac{\Delta\Phi(n_{\mathrm{c}})}{k_{\mathrm{B}}T}\right) \times \left\{\frac{1}{2\pi k_B T} \left| \left[\frac{\partial^2 \Delta\Phi(n)}{\partial n^2}\right]_{n=n_{\mathrm{c}}} \right| \right\}^{1/2} \tag{67}$$

By a substitution of the respective values for the kinetic coefficient $w_{n,n+1}$ for $n = n_{\mathrm{c}}$ (denoted by $w_{n,n+1}(n_{\mathrm{c}})$) and the expressions for the derivatives of the thermodynamic potential with respect to n, we obtain

$$I = \left(\frac{N}{zV}\right) \exp\left(-\frac{\varepsilon}{k_{\mathrm{B}}T}\right) \prod_i \varphi_i^{\nu_i} \left(\frac{2D^* a_{\mathrm{s}}}{a_{\mathrm{m}}^2}\right) \left(\frac{\omega_{\mathrm{s}}}{\omega_{\mathrm{m}}}\right)^{2/3} \times \left(\frac{\sigma}{k_{\mathrm{B}}T}\right)^{1/2} \exp\left[-\frac{4\pi}{3}\left(\frac{\sigma}{k_{\mathrm{B}}T}\right)\left(\frac{3\omega_{\mathrm{s}}}{4\pi}\right)^{2/3} n_{\mathrm{c}}^{2/3}\right] \tag{68}$$

for kinetic limited growth

$$I = \left(\frac{N}{zV}\right) \exp\left(-\frac{\varepsilon}{k_{\mathrm{B}}T}\right) \prod_i \varphi_i^{\nu_i} \left(\frac{2D^{**} a_{\mathrm{s}}}{a_{\mathrm{m}}^2 n_{\mathrm{c}}^{1/3}}\right) \left(\frac{\omega_{\mathrm{s}}}{\omega_{\mathrm{m}}}\right)^{1/3} \times \left(\frac{\sigma}{k_{\mathrm{B}}T}\right)^{1/2} \exp\left[-\frac{4\pi}{3}\left(\frac{\sigma}{k_{\mathrm{B}}T}\right)\left(\frac{3\omega_{\mathrm{s}}}{4\pi}\right)^{2/3} n_{\mathrm{c}}^{2/3}\right] \tag{69}$$

for diffusion-limited growth. Taking into account Equation 54 for nucleation processes in solid solutions, usually Equation 68 should be applied.

The time required for the establishment of the steady-state nucleation rate may be approximated, again, by

$$\Delta t \simeq \frac{(\Delta n)^2}{w_{n,n+1}(n_{\mathrm{c}})} \tag{70}$$

while the condition where a constant nucleation rate is found may be written as

$$\frac{(\Delta n)^2}{w_{n,n+1}} \leqslant \frac{\Delta n}{\dot{n}_{\mathrm{c}}} \tag{71}$$

Δn characterizes the region in the space of structural elements near the critical cluster size n_{c} where the growth of the aggregates proceeds mainly by diffusion-like processes. This interval is given by (cf. [8])

$$\Delta n = \left\{\frac{1}{2k_{\mathrm{B}}T} \left| \left[\frac{\partial^2 \Delta\Phi(n)}{\partial n^2}\right]_{n=n_{\mathrm{c}}} \right| \right\}^{-1/2} = \left(\frac{3n_{\mathrm{c}}^{2/3}}{2a_{\mathrm{s}}}\right)\left(\frac{k_{\mathrm{B}}T}{\pi\sigma}\right)^{1/2} \tag{72}$$

Δt in Equation 70 is at the same time equal to the mean passage time of an aggregate from subcritical ($n = n_{\mathrm{c}} - \Delta n$) to supercritical ($n = n_{\mathrm{c}} + \Delta n$) values of the number of structural elements by diffusional motion in cluster size space. Equation 71 implies that during such a time interval, the change of the critical cluster size is sufficiently small.

7. Determination of the interaction parameters

The incorporation of solute–solute interactions into the description of segregation processes allows, in addition to the extension of the region of applicability of the theory, also a determination of the interaction parameters for a given solid solution by investigations of the course of segregation processes in it. In the simplest approach, the quantities β_{ik} may be considered as parameters which have to be determined in such a way as to allow the best fit of the experimental results.

It is possible, however, to obtain some additional information by varying the concentrations, c_i, of the different components. Considering the process of segregation, e.g. of only the ith component, one obtains from Equation 9 for a weak solution and an equilibrium coexistence of the pure ith phase with the matrix

$$\psi_i = \mu_i^{(s)} - k_B T \ln c_i^{(\infty)} \tag{73}$$

allowing determination of ψ_i and $\mu_i^{(s)}$ from a set of measurements by varying the temperature. Similarly, additional parameters may also be determined by varying the number of components and their concentration in the system.

8. Influence of interaction of the solute components on coarsening processes

In the case where the opposite to Equation 71, inequality, holds, the segregation process goes over into the late stages which have been studied extensively (cf. [8, 9]). In the late stage of segregation, the activities (or concentrations) of the different components in the matrix remain nearly constant and, although the parameters in the kinetic coefficients (the deterministic growth equations) are complicated functions of the composition, the kinetic equations governing the evolution of the cluster size distribution function are of the same form as for the case of a perfect solution. Here the same situation is found as for the case of segregation of only one component in the matrix (see [9]).

Introducing the reduced variables

$$u = \left(\frac{n}{n_c}\right) \tag{74a}$$

$$\tau = \ln\left(\frac{n_c}{n_{c_0}}\right) \tag{74b}$$

and the cluster size distribution function $\phi(u, \tau)$ in reduced variables [9]

$$\phi(u, \tau) = f(n, t) n_c \tag{75}$$

the Fokker–Planck equation may be written for kinetic limited growth, again in the form (for the details see [9, 20])

$$\frac{\partial \phi}{\partial \tau} + \frac{\partial}{\partial u}\{[\gamma_0(\tau) u^{1/3}(u^{1/3} - 1) - u]\phi\} - \left(\frac{\gamma_0(\tau)}{n_c^{2/3}\alpha}\right)\frac{\partial}{\partial u}\left[u^{2/3}\frac{\partial \phi}{\partial u}\right] = J_c, \tag{76}$$

$$J_c = \frac{n_c}{\tau_e}\frac{1}{2}\int_0^u \phi(u - u' \tau)\Omega(u - u', u')\phi(u', \tau) \times du' - \phi(u, \tau)\int_0^\infty \Omega(u, u')\phi(u', \tau)\, du' \tag{77a}$$

where $\tau_e \sim 1$, $\Omega(u, u') \sim u + u'$, and

$$\gamma_0(\tau) = \frac{\alpha}{\tau_0}\frac{n_c^{1/3}}{\dot{n}_c} \tag{77b}$$

$$\alpha = \frac{8\pi}{3}\left(\frac{\sigma}{k_B T}\right)\left(\frac{3\omega_s}{4\pi}\right)^{2/3} \tag{77c}$$

$$\frac{1}{\tau_0} = \frac{3D^*}{a_m^2}\left(\frac{\omega_s}{\omega_m}\right)^{2/3} \tag{77d}$$

For the case here considered of kinetic limited growth, the critical cluster radius behaves for large times as $R_c \propto t^{1/2}$. It turns out that in intermediate stages of the process (in the initial stages of coarsening), diffusion processes in cluster size space (stochastic effects, thermal noise) are of significance for the kinetics of coarsening, including the shape of the cluster size distribution function (cf. also [15, 17]). With time such effects become less important. However, processes of touching and merging of aggregates gain importance for sufficiently large volume fractions of the segregating phase in the transition from nucleation to coarsening and may influence the shape of the cluster size distribution function significantly (cf. also [16]).

For diffusion-limited growth, the collision integral retains the same form as for kinetic limited growth. The Fokker–Planck equation now reads,

$$\frac{\partial \phi}{\partial \tau} + \frac{\partial}{\partial u}\{[\gamma_1(\tau)(u^{1/3} - 1) - u]\phi\} - \left(\frac{\gamma_1(\tau)}{n_c^{2/3}\alpha}\right)\frac{\partial}{\partial u}\left[u^{1/3}\frac{\partial \phi}{\partial u}\right] = J_c, \tag{78}$$

$$\gamma_1(\tau) = \frac{\alpha}{\tau_1 \dot{n}_c} \tag{79a}$$

$$\alpha = \frac{8\pi}{3}\left(\frac{\sigma}{k_B T}\right)\left(\frac{3\omega_s}{4\pi}\right)^{2/3} \tag{79b}$$

$$\frac{1}{\tau_1} = \frac{3D^{**}}{a_m^2}\left(\frac{\omega_s}{\omega_m}\right)^{1/3} \tag{79c}$$

The conclusions remain qualitatively the same as for kinetic limited growth.

9. Discussion

In the present work, the influence of interactions between solute particles in multi-component solid solutions on processes of formation and growth of phases with a given stoichiometric composition was investigated. The analysis was carried out based on a newly developed general method of treating nucleation and a particular (but rather general) good enough approximation for the description of the interactions of the solute components.

It turns out that the basic kinetic equations remain of the same form as for the case of weak (perfect) solutions. However, the kinetic and thermodynamic parameters are complicated functions of the composition of the system and the interaction parameters. In this way, the outlined theory gives, for the first time, the possibility of an adequate quantitative interpretation of experimental results on segregation processes in concentrated multi-component solutions.

The outlined approach also allows a straightforward extension to cases when elastic effects, the influence of radiation on phase formation or other external factors, have to be taken into account. Moreover, it also provides the basis for a treatment of the general problem of phase formation under the condition that the monomeric building units of the evolving phase interact with each other in nucleation and growth. Such possible generalizations will be discussed in a forthcoming paper.

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