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Kinetics of nucleation in the concentration gradient

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Abstract

The necessity of reconsidering the nucleation theory for the case of the initial stage of reactive diffusion is demonstrated. The existence of sharp concentration gradients and huge diffusion fluxes in the nucleation region changes both the thermodynamics and kinetics of nucleation as well as the very notions of critical nucleus and incubation time. In particular, the incubation period for intermediate phases depends on the diffusivity of the parent phase; nucleation behaviour for the 'total mixing mode' can be non-monotonic; the result of competition of different nucleation modes depends on the ratio of diffusivities in the new and parent phases.

1. Introduction

Recent developments in the field of nanotechnologies has produced a new wave of interest in the problem of nucleation of intermediate phases in binary and multicomponent alloys. Nucleation appears to be a controlling stage for producing multicomponent metallic glasses and bulk nanocrystalline materials [1–4]. Thermodynamics and kinetics of nucleation in such systems are now being intensively developed. Much less is known about nucleation in heterogeneous systems with sharp concentration gradients, for example, multilayers. Most important here is an initial stage of reactive diffusion, e.g. solid state reactions between two materials controlled by interdiffusion. First experimental evidence of the decisive role of nucleation was given by the solid state amorphizing reactions (SSARs), which take place only under condition of sufficient defect density in the diffusion zone (sufficient density of nucleation sites for metastable amorphous intermediate phase [5–7]). Usually the initial stage of reactive diffusion in binary diffusion couples (or thin films or multilayers) can proceed via different evolution paths, e.g. different sequences of phase formation. Evidently, the choice of evolution path is made first of all at the nucleation stage [7]. Moreover, for ternary and multicomponent diffusion couples an evolution path can be non-unique even at the late stages [8, 9]. In this case the choice of diffusion path should be determined by the hierarchy of incubation periods of intermediate phases at interfaces and in the two-phase regions.

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In all the above-mentioned processes the nucleation proceeds in the vicinity of initial interfaces, e.g. under conditions of sharp concentration gradient and huge diffusion fluxes across the newborn particles of intermediate phases. Recent investigations of solid state reactions in multilayers demonstrated that the nucleation stage can be observed directly as the first maximum of heat flux in DSC experiments [10–13]. Measurement of Avrami exponents for different parts of this nucleation maximum gives information about the rates of nucleation and lateral growth of intermediate phases. All this makes necessary the development of quantitative theory of nucleation kinetics in the concentration gradient.

So far we have a rigorous theory of the phase layer growth during reactive diffusion only for the case when each intermediate phase exists in the form of a continuous planar layer. At this stage a diffusion flux across each layer is determined by the gradient of chemical potential and by the rate of 'reactions' at the moving interfaces [14–16]. Yet, we still do not have any good recipe for calculation of the period of initial layer formation. In general, this time should include four terms: (a) time of 'concentration preparation', e.g. time for formation of the space region with compositions favourable for the intermediate phase; (b) time to reach the critical size by the growing nuclei (traditional incubation time); (c) time of diffusional suppression by neighbouring phases; (d) time of lateral growth until formation of continuous layers.

In this paper we will concentrate on the items (a) and (c). In section 2 we will present a sketch of a 'naive' theory of phase competition which takes into account the diffusional interaction between the critical nuclei of all intermediate phases in the diffusion zone. The above-mentioned theory is based on assumption of nonconstrained formation of critical nuclei. In section 3 we show that this assumption may be not valid in many cases, especially in the case of nucleation during SSAR. The presence of a concentration gradient changes the thermodynamics of nucleation, and this change is not reduced to Cahn–Hilliard gradient terms. The dependence of the Gibbs free energy of nucleus formation on the number of atoms in the newborn nucleus $\Delta G(N)$ appears to be determined by the value of concentration gradient at the nucleation place and by the 'mode of nucleation'. We consider three possible nucleation modes—polymorphic, transversal and total mixing modes. During the last decade the present authors and P Desre [17–23] calculated the dependences $\Delta G(N, \nabla C)$ for each mode. Here only the main results of these calculations are presented. Of course, different thermodynamics of nucleation causes different kinetics. In section 4 a modified Fokker–Planck (F–P) equation for nucleus size distribution $f(N, t)$ is solved for these modes in the case where they operate separately. Numeric solution of the F–P equation with a time-dependent driving force gives information about the incubation period as a function of ratio of diffusivities in the parent and daughter phases. In section 5 we try to take into account that several nucleation modes can, in principle, operate simultaneously. Thus, interference and competition of nucleation modes should take place.

We are not confident enough to pretend to creation of a new nucleation theory. The aim of this paper is to demonstrate that the basic notions of standard nucleation theory, (i) the notion of a critical nucleus, (ii) the physical sense of incubation period and (iii) the interrelation between thermodynamics and kinetics of nucleation, should be reconsidered in the case of reactive diffusion.

2. Naive theory of phase competition

2.1. 'Critical nucleus'—what does it mean for reactive diffusion?

The very notion of the critical nucleus loses its simple interpretation for the case of nucleation in the diffusion zone. Usually the two following alternative definitions of a critical nucleus

are considered as equivalent for nucleation during decomposition of an initially uniform supersaturated solid solution:

(a) maximum (saddle-point) of the Gibbs free energy dependence $\Delta G(N)$ on the size of the embryo/nucleus;
(b) particles for which probability of growth is equal to probability of dissolution so that

$$\Delta\nu(N_{cr}) \equiv \nu_+(N_{cr}) - \nu_-(N_{cr}) = 0 \tag{1}$$

where ν_+ is a frequency of joining one structure unit and ν_- is a frequency of 'departure' of this unit.

In the standard Fokker–Planck approach to nucleation one uses the relation

$$\Delta\nu = -\frac{\nu_+ + \nu_-}{2}\frac{1}{\Theta}\frac{\partial\Delta G}{\partial N}. \tag{2}$$

Therefore zero derivative $\partial\Delta G/\partial N$ means zero 'driving force' so that definitions (a) and (b) coincide.

The case of nucleation during reactive diffusion situation is not so simple.

Let us consider an A/B couple where phases 1 and 2 can be, in principle, formed.

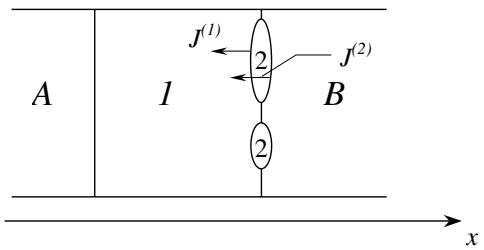

Figure 1. Attempt at phase 2 nucleation at 1/B interface.

Lets, say, phase 2 with average composition C_2 (C_2 is a molar fraction of component B) and narrow homogeneity range $\Delta C_2 \ll 1$ try to nucleate at the moving interface between the growing phase (phase 1) and material B (see figure 1). Even if the newborn particle of phase 2 is overcritical in the standard sense ($N > N_{cr}$, $\partial\Delta G/\partial N < 0$), this does not necessarily mean that phase 2 will succeed in growing.

Indeed, the particle of phase 2 from the very beginning appears in the fields of chemical potential gradients and of diffusion fluxes $J^{(i)}$. These fluxes change abruptly at the interfaces 1–2 and 2–B: $w^{(1)}J^{(1)} = -D_1\Delta C_1/\Delta x_1$, $w^{(2)}J^{(2)} = -D_2\Delta C_2/\Delta x_2$, $w^{(\beta)}J^{(\beta)} \approx 0$, where w is a volume per atom. Each sudden change of flux generates movement of the corresponding interface, with some velocity u according to the conservation law. If one neglects the change of molar volumes, then

$$\begin{aligned}(C_2 - C_1)u_{12} &= \frac{D_1\Delta C_1}{\Delta x_1} - \frac{D_2\Delta C_2}{\Delta x_2}\\ (1 - C_2)u_{2B} &= \frac{D_2\Delta C_2}{\Delta x_2} - 0\end{aligned} \tag{3}$$

(we consider solubility of A in B as negligible, so that $C_\beta \approx 1$, $J(\beta) \approx 0$; we consider interfaces 1–2 and 2–B as nearly planar, so that nucleus 2 is platelike, see [19, 20]).

Evidently, the phase 2 width should change with the following rate (if one neglects the random joining/departures):

$$\frac{\mathrm{d}\Delta x_2}{\mathrm{d}t} = u_{2B} - u_{12} = \frac{1}{C_2 - C_1}\left(-\frac{D_1\Delta C_1}{\Delta x_1} + \frac{1 - C_1}{1 - C_2}\frac{D_2\Delta C_2}{\Delta x_2}\right). \tag{4}$$

If phase 2 is a 'critical' nucleus with thickness $l_{cr}^{(2)}$, if diffusivity of phase 1 is much larger than that of phase 2, $D_1\Delta C_1 \gg D_2\Delta C_2$, and if the phase 1 layer is not too wide,

$$\Delta x < \Delta x_1^* = \frac{1-C_2}{1-C_1}\frac{D_1\Delta C_1}{D_2\Delta C_2}l_{cr}^{(2)} \tag{5}$$

then, according to equations (4) and (5), $(\mathrm{d}\Delta x_2/\mathrm{d}t)|_{l_{cr}} < 0$.

This means that under condition (5) the overcritical nuclei of phase 2 are not able to grow: they are 'consumed' by neighbouring 'shark phase' ('vampire phase') 1 with larger diffusivity.

Such unsuccessful attempts at phase 2 nucleation will be repeated during the 'incubation period'

$$\tau = \frac{C_1(1-C_1)}{2D_1\Delta C_1}(\Delta x_1^*)^2 = \frac{C_1(1-C_2)^2}{2(1-C_1)}\frac{D_1\Delta C_1}{(D_2\Delta C_2)^2}l_2^2. \tag{6}$$

(In this equation we have used the parabolic growth law for single phase 1 in the absence of a phase 2 layer.)

Thus, we have an alternative:

(1) overcritical nucleus size is not a guarantee of growth, or
(2) condition

$$\frac{\partial\Delta G}{\partial N} = 0 \tag{7}$$

is not a definition of the critical nucleus.

2.2. *Diffusional phase competition—kinetic constraints*

Here we consider the simplest model of unlimited nucleation of the intermediate phases [24, 25]. According to this model, from the very beginning of contact the critical nuclei of all intermediate phases appear due to heterophase fluctuations. In this model it makes no difference which of them appear first. We can imagine the layers of nuclei with critical width as an initial condition.

Then the competition begins. As was mentioned in the previous section, every nucleus appears between the neighbouring phases with different chemical potentials. Therefore the diffusion fluxes arise via the nuclei. These fluxes change abruptly at every interphase boundary generating its movement. Due to this movement some phase nuclei can grow and others decrease, becoming subcritical.

To obtain a criterion of growth/suppresion, consider simple binary diffusion couple A–B with two intermediate phases 1, 2.

To determine which of the phases will grow first, one should consider diffusional interaction between two initial layers of critical nuclei of both phases. One can easily check that in the approximation of constant fluxes [26]

$$\left.\frac{\mathrm{d}\Delta x_1}{\mathrm{d}t}\right|_{l_1} = \frac{1}{C_2-C_1}\left(\frac{C_2}{C_1}\frac{D_1\Delta C_1}{l_1} - \frac{D_2\Delta C_2}{l_2}\right) \tag{8}$$

$$\left.\frac{\mathrm{d}\Delta x_2}{\mathrm{d}t}\right|_{l_2} = \frac{1}{C_2-C_1}\left(-\frac{D_1\Delta C_1}{l_1} + \frac{1-C_1}{1-C_2}\frac{D_2\Delta C_2}{l_2}\right). \tag{9}$$

Here we have three possibilities (see figure 2) depending on the ratio

$$r = \frac{D_1\Delta C_1}{D_2\Delta C_2}\frac{l_2}{l_1} \tag{10}$$

(1) $r < C_1/C_2 \Rightarrow (\mathrm{d}\Delta x_1/\mathrm{d}t)|_{l_1} < 0$; $(\mathrm{d}\Delta x_2/\mathrm{d}t)|_{l_2} > 0$—phase 2 ('vampire') starts growing, 'eating' the nuclei of phase 1;
(2) $C_1/C_2 < r < (1 - C_1)/(1 - C_2) \Rightarrow (\mathrm{d}\Delta x_1/\mathrm{d}t)|_{l_1} > 0$; $(\mathrm{d}\Delta x_2/\mathrm{d}t)|_{l_2} > 0$—both phases grow from the moment of nucleation;
(3) $r > (1-C_1)/(1-C_2)$—phase 1 ('vampire') starts growing, 'eating' the nuclei of phase 2.

Such a simple approach is easily generalized to an arbitrary number of intermediate phases [24].

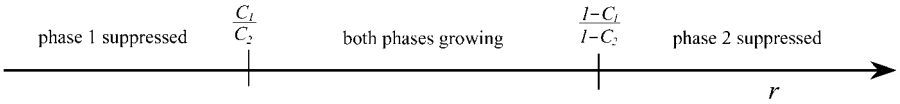

Figure 2. Suppression/growth criterion for two intermediate phases.

Obviously, the above-mentioned approach is too simplified since it does not take into account the influence of concentration gradients on the nucleation barrier, e.g. the thermodynamic constraints.

3. Thermodynamic constraints on nucleation

The nucleation barrier for intermediate phase formation in the diffusion zone should be calculated taking into account the redistribution of components outside the newly born nucleus. Strictly speaking, nucleation is a transition over the saddle-point of the Gibbs free energy surface in the multidimensional phase space including the nucleus size and values of concentration in each point (composition distribution). Sectioning of this surface by the hyperplane of constant composition distribution gives a dependence $\Delta G(R)$ with a maximum. The height of this maximum is different for different composition distributions. In many cases the diffusion process in the parent phases (decreasing of the concentration gradient) makes the height less and less. Thus, from a purely thermodynamic point of view, it is favourable for the system to wait for homogenization (when the barrier is lower) and only then to nucleate. The parent phase (or two adjacent phases) is metastable in relation to new phase formation, but simultaneously it is (they are) unstable in respect to further interdiffusion. Therefore, at fixed size and composition of the nucleus the optimal distribution for outside parent phase(s) will be reached only after full homogenization. Obviously, the nucleus will not 'wait' for this. This means that true minimisation of the Gibbs potential for nucleation during diffusion is impossible. Therefore the problem of nucleation in an inhomogeneous system should be solved under certain constraints, which are determined by kinetics of diffusion processes. Depending on the type of constraint one has different nucleation modes. We can point out at least three possible nucleation modes.

(a) Polymorphic mode [17, 19, 20, 23]. This is possible if the parent metastable phase (for example, amorphous) can exist in the concentration range advantageous for a new intermediate phase. (The role of parent phase can be played by the metastable solid solution or previously formed amorphous layer.) At first the interdiffusion forms a concentration profile in the parent phase overlapping the concentration interval where the new intermediate phase has lower Gibbs potential (figure 3). Then the polymorphic transformation in the limited region takes place forming the lattice of new phase at a frozen concentration gradient. The driving force is denoted as Δg_a. The less sharp is the concentration gradient (larger annealing time), the wider is the region profitable for the new

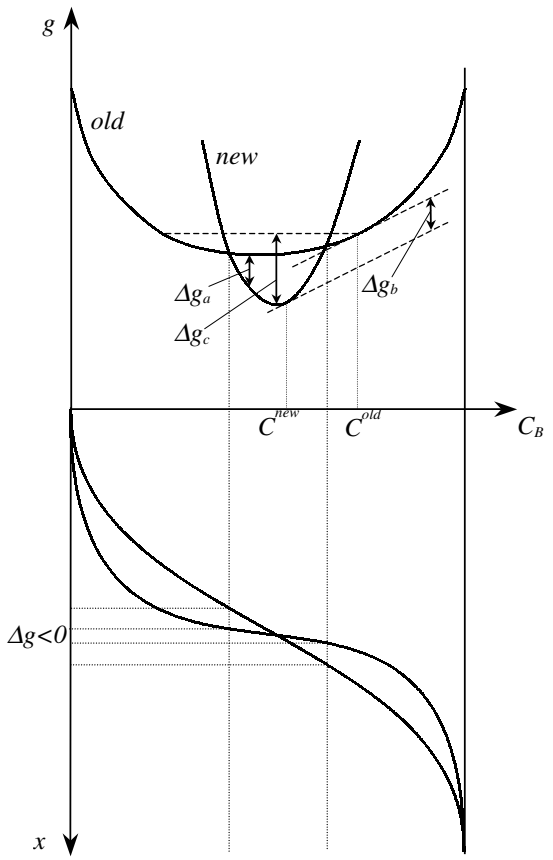

Figure 3. Dependences $g(C)$ and $C(x)$ in the case of full mutual solubility in the metastable state $\Delta g_{a,b,c}$—driving forces per atom of newborn nucleus for nucleation modes (a), (b) and (c).

phase—the more probable is nucleation. After nucleation the diffusion proceeds, and the newly born nucleus interacts with parent phase due to a steplike change of diffusion fluxes at its boundaries. In some cases (during solid state amorphizing reactions) amorphous phase can form at the very beginning due to easy nucleation at, for example, triple grain boundary junctions. Due to the comparatively big diffusivity in such a phase it can grow fast playing the role of a parent metastable phase [7].

(b) Transversal mode [18, 21, 23]. This mode is possible both for cases shown in figures 3 and 4. In the case shown in figure 4, interdiffusion before formation of an i-phase nucleus leads to 'metaquasiequilibrium' α–β with metastable concentration ranges $(C_\alpha, C_{\alpha'})$ and $(C_{\beta'}, C_\beta)$, unstable to decomposition into α + i and i + β. According to P Desre [18, 21], during the nucleus formation in the concentration gradient (in x-directions) each thin slice $(x, x+\mathrm{d}x)$ of this nucleus is formed via unlimited redistribution of components inside this slice independently of other slices. Optimal concentration $C^{new}(x)$ in this nucleus slice is determined by the concentration $C^{old}(x)$ in the surrounding phase (for the same slice) according to the rule of parallel tangents (not the joint tangent) (figure 3):

$$\frac{\partial g^{new}}{\partial C^{new}} = \frac{\partial g^{old}}{\partial C^{old}}.$$

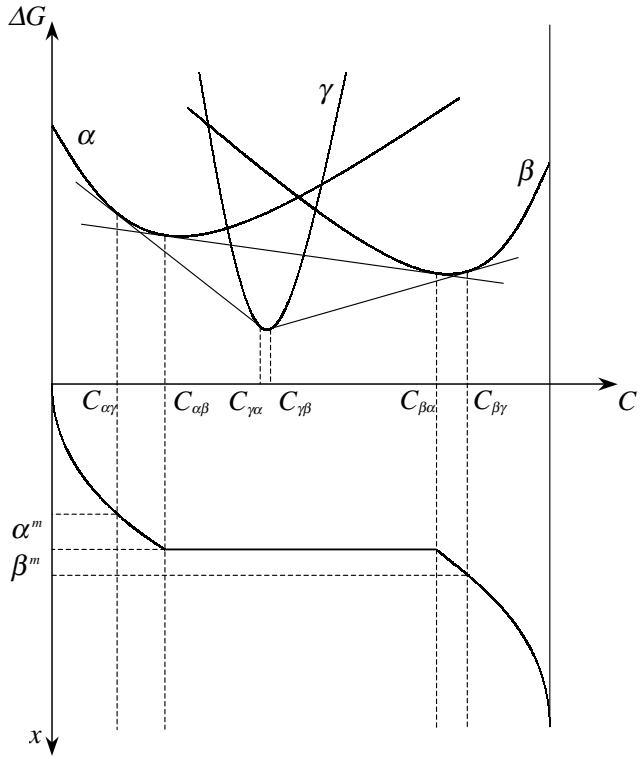

Figure 4. Dependences $g(C)$ and $C(x)$ in the case when solubility is limited even in the metastable state (g—Gibbs free energy per atom).

The driving force is denoted as Δg_b. To make the transversal mode real, diffusivity in the parent phase(s) should be much larger than in the new phase ($D_m \gg D_i$) since the transversal redistribution in a thin infinite slice should proceed faster than the nucleus growth.

(c) Total mixing (longitudinal) mode [22, 23]. This mode means nucleus formation only by the cost of redistribution in the transformed region of the parent phase, the concentration distribution outside nucleus being unchanged. The driving force is denoted as Δg_c. To make this mode real, diffusivity in the forming phase should be much more than in the parent phase ($D_i \gg D_m$) since the redistribution in the newly formed nucleus should proceed faster than the change of concentration gradient outside the nucleus.

Obviously, in the general case all these modes (and, maybe, some others) should operate simultaneously. It is a problem of kinetics.

The general expression for the change of Gibbs free energy caused by nucleation of particle with the arbitrary shape $y(x)$ of the figure of rotation around the direction of concentration gradient is as follows:

$$\Delta G = n\int_{x=-R_a}^{x=R_\beta} \Delta g(C_{old}(x) \to C_{new}(x))\pi y(x)^2 \mathrm{d}x + \int_{x=-R_\alpha}^{x=R_\beta} 2\sigma\pi y(x)\sqrt{1+\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2}\,\mathrm{d}x - \sigma_{\alpha\beta}S_{\alpha\beta} + \Delta G_{elastic}. \tag{11}$$

Here Δg is a bulk driving force per atom corresponding to transformation of parent phase with composition $C_{old}(x)$ into new phase with composition $C_{new}(x)$. These compositions coincide for the polymorphic mode; they are linked by the parallel tangent rule for the transversal mode; they are determined by conservation of the substance inside the nucleus for the total mixing mode. σ is a surface tension between new and parent phases, $\sigma_{\alpha\beta}$ is a surface tension between parent phases, $S_{\alpha\beta}$ is an initial contact area disappearing during nucleation, $R_\alpha + R_\beta$ is a longitudinal size of the nucleus and $\Delta G_{elastic}$ is an elastic energy due to misfit, calculated, for example, according to Nabarro's approximation. The elastic term will be neglected below—it was taken into account for the special case of spheroidal nuclei in [27]. ΔG is a function of nucleus volume and a functional of nucleus shape. It depends also on concentration gradient as a parameter. We determine the optimal shape for every fixed volume and concentration gradient. In the case of polymorphic mode this was done for arbitrary shape by solving the corresponding Euler–Lagrange equation that in our case is an integro-differential equation [20]. The dependence of ΔG on volume has the following form:

$$\Delta G(V) = \alpha V^{\frac{2}{3}} - \beta V^1 + \gamma(\nabla C)^2 V^{\frac{5}{3}}.$$

Coefficients α and β are the functionals of the shape function $y(x)$: they are constant for fixed shape. The factor γ in this expression is positive for polymorphic and transversal modes and negative for total mixing mode.

The gradient term was introduced first in the case of a spherical embryo in [17] and in the case of a cubic embryo in [18]. The detailed analysis of the first two modes, (a) and (b), was made in [17–21] and for the third mode in [22].

If one takes the nucleus to be a parallelepiped $2h \times 2h \times 2r$ ($2r$ is a longitudinal size), then the free energy change for the formation of the nucleus (embryo) is given by:

$$\Delta G = -n\Delta g V + 8(\sigma_1 h^2 + 2\sigma_2 hr) + \gamma(\nabla c)^2 h^2 r^3 \tag{12}$$

where n is a number of atoms per unit volume, Δg a maximal driving force of transformation per atom, σ_1, σ_2 the energies per unit surface for two directions and $V = 8h^2 r$. Coefficient γ depends on the nucleation mode [23]. If the free energy concentration dependences of the metastable (parent) and new intermediate phases are approximated by parabolas, then

$$\gamma^{(a)} = \frac{4}{3}n(\alpha' - \alpha) \qquad \gamma^{(b)} = \frac{4}{3}n\frac{\alpha}{\alpha'}(\alpha' - \alpha) \qquad \gamma^{(c)} = -\frac{4}{3}n\alpha. \tag{13}$$

Here α and α' are the second derivatives of Gibbs free energy per atom with concentration for the parent and new phases correspondently. Equation (12) is valid only if the nucleation proceeds due to only one nucleation mode. It is very important to note that $\gamma^{(c)}$ is negative. This means that, in contrast to the modes (a) and (b), when the increase of concentration gradient leads to bigger nucleation barriers and even to prohibition of nucleation at sufficiently sharp concentration gradient, the nucleation mode (c) corresponds to decrease of nucleation barrier at increasing concentration gradient. In the cases (a) and (b) the shape of the embryo becomes more and more pancake-like with growing volume. In contrast, in the case (c) the shape should become more and more needle-like with growing volume.

Evidently, all these nucleation modes (and at least one more—taking into account diffusion in the ∇c-direction outside the nucleus) should operate simultaneously in the real nucleation process.

4. Fokker–Planck approach

The above-mentioned thermodynamic approach does not take into account that the nucleation proceeds simultaneously with the evolution of concentration gradient in the parent phase.

A more appropriate way to simulate the initial stage of reactive diffusion is to solve the corresponding equation (in partial derivatives) for the distribution f of new phase particles in the size space:

$$\frac{\partial f(N,t)}{\partial t} = -\frac{\partial}{\partial N}(\Delta\nu\, f) + \frac{\partial^2}{\partial N^2}(\overline{\nu}\, f) = -\frac{\partial j}{\partial N}. \tag{14}$$

Here $f(N,t)$ is a number of new phase particles containing N atoms of species B (the number of A atoms is approximately determined by stoichiometry) at time t, $j(N,t)$ is the flux density in the size space and $\Delta\nu$ is determined by equation (2).

Since the process of nucleation proceeds in a sharp concentration gradient, an expression for $\Delta G(N)$ contains an additional gradient term, proportional to $(\nabla C)^2 N^{\frac{5}{3}}$. The value and the sign of the factor at this gradient term depend on the nucleation mode. We will investigate polymorphic and total mixing modes.

4.1. Kinetics of nucleation of polymorphic mode

In the case of the polymorphic mode the gradient term is positive (concentration gradient hinders the nucleation). Under assumption of spherical nucleus shape the dependence of Gibbs free energy on the number of atoms in the nucleus has the following form:

$$\Delta G(N) = \Delta g_m\, N + \left(\frac{3}{4\pi n}\right)^{\frac{2}{3}} \frac{g''}{10}(\nabla C)^2 N^{\frac{5}{3}} + \left(\frac{3}{4\pi n}\right)^{\frac{2}{3}} 4\pi\sigma N^{\frac{2}{3}}. \tag{15}$$

Here the nucleus is considered to be spherical, the nucleation mode to be polymorphic and g'' is the second derivative of Gibbs free energy per atom on concentration for the new phase. If the concentration gradient in the nucleation place changes according to a parabolic law

$$(\nabla C)^2 = \frac{1}{4\pi D_{parent} t} \tag{16}$$

then a drift term in the F–P equation explicitly depends on time, which physically means the lowering of the nucleation barrier due to interdiffusion in the parent phase(s).

It is convenient to use further the non-dimensional variables

$$\tau \equiv \overline{\nu} t \qquad \alpha \equiv \frac{\Delta g_m}{kT} < 0 \qquad \beta \equiv C_3 \frac{g''\overline{\nu}/kT}{24\pi D_{parent}} \qquad \gamma \equiv C_3 \frac{8}{3}\frac{\pi\sigma}{kT} \tag{17}$$

where $C_3 = (3/4\pi n)^{\frac{2}{3}}$.

Here $\overline{\nu}$ is treated as approximately constant. Then

$$\frac{\partial f(N,t)}{\partial \tau} = \frac{\partial^2 f}{\partial N^2} + \frac{\partial}{\partial N}\left(f\left(\alpha + \beta\frac{N^{\frac{2}{3}}}{\tau} + \frac{\gamma}{N^{\frac{1}{3}}}\right)\right). \tag{18}$$

Numeric solution of this last equation has been obtained for fixed total number of nucleation sites (heterogeneous nucleation):

$$\int f(N,t)\,\mathrm{d}N = \text{const}. \tag{19}$$

The evolution in time of the size distribution $f(N)$ corresponds to evolution of the potential field $\Delta G(N)$ but is shifted in time. For small annealing times, when the concentration gradient remains sharp enough, the dependence $\Delta G(N)$ is monotonically increasing so that nucleation is thermodynamically forbidden (figure 5).

In this period a distribution $f(N)$ remains monotonously decreasing. After a certain incubation thermodynamic 'time', when the concentration gradient in the parent phase becomes

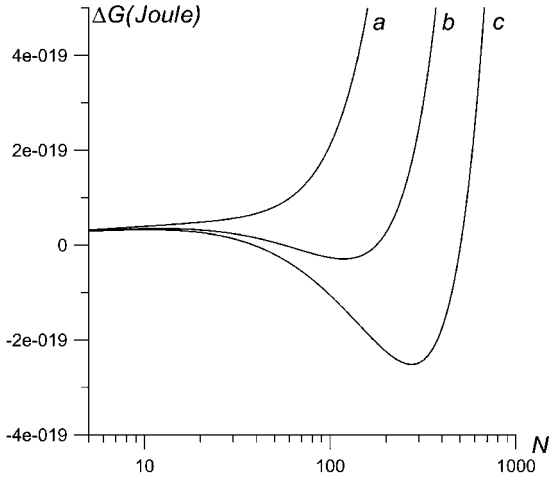

Figure 5. Dependence $\Delta G(N)$ for sharp ∇C (small annealing time) and low ∇C (longer annealing time). $\tau = 50$ (a), 100 (b), 150 (c). $D_{parent} = 10^{-20}$ m s^{-2}, $\Delta g_m = -7.48 \times 10^{-21}$ J, $g'' = \partial^2 g/\partial C^2 = 7.77 \times 10^{-19}$ J, $n = 10^{29}$ m^{-3}, $T = 600$ K, $\sigma = 0.15$ J m^{-2}. The same data were used for figures 7–9.

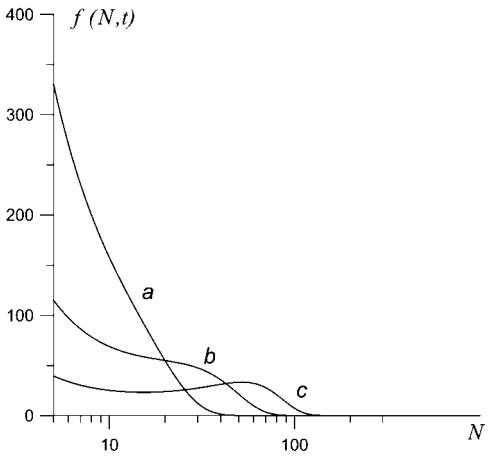

Figure 6. Evolution of size distribution for nuclei of intermediate phase. $\tau = 100$ (a), 200 (b), 300 (c). $D_{parent} = 10^{-20}$ m s^{-2}, $\Delta g_m = -7.48 \times 10^{-21}$ J, $g'' = \partial^2 g/\partial C^2 = 7.77 \times 10^{-19}$ J, $n = 10^{29}$ m^{-3}, $T = 600$ K, $\sigma = 0.15$ J m^{-2}.

less than the critical value, nucleation becomes thermodynamically possible ($\Delta G(N)$ non-monotonic with a maximum corresponding to the nucleation barrier). Yet, a distribution function $f(N)$ reveals a maximum not at once, but after a certain 'kinetic incubation period' (figure 6).

We define an incubation time as a period of peak formation for size distribution $f(N)$ (not counting an initial peak at $N = N_{min}$). Obviously, in dimensionless scale τ the incubation time (τ_{inc}) should depend on the ratio of two kinetic parameters: $\overline{\nu}$ and D_{parent}.

Dependences $\tau_{inc}(D_{parent}/\overline{\nu})$ for different surface tensions are shown in figure 7.

To evaluate the realistic range of the ratio $D/\overline{\nu}$ one should take into account that the frequency ν can be estimated as $\nu \sim N^{\frac{2}{3}} D_{boundary}/\lambda^2$, where $D_{boundary}$ is the diffusivity of

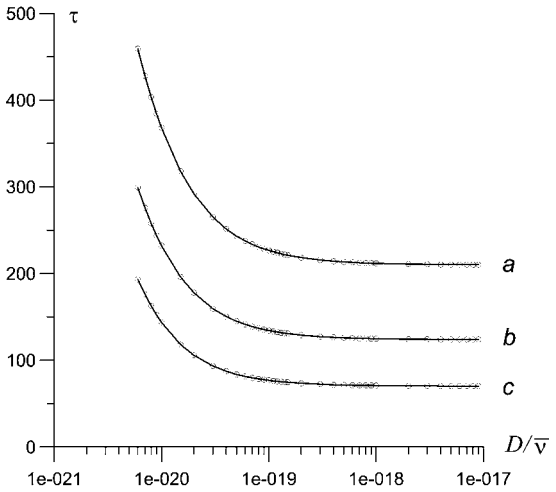

Figure 7. Dependence of dimensionless incubation time $\tau_{inc} = \overline{\nu} t_{inc}$ on the ratio $D/\overline{\nu}$ for different surface tensions: 0.09 (a), 0.10 (b) and 0.11(b) J m^{-2}.

the interface between new and old phases, and the number of atoms in the nucleus and λ is the characteristic length of random walk of an atom looking for a suitable place to join the new phase. It is reasonable to suppose that $D_{boundary} > D_{parent}$ and $\lambda > a$, where a is an atomic distance. If $N \sim 30$ and $\lambda \sim 10^{-10}$–10^{-8} m, then the ratio $D/\overline{\nu}$ belongs to the interval 10^{-17}–10^{-21} m^2.

One can see that with growing diffusivity of parent phase a dimensionless incubation time decreases to some asymptotic level.

It means that this level represents the time for nuclei growth even when gradient effect does not hinder the nucleation. Then we may consider the difference $\tau - \tau_{min}$ as a time of 'concentration preparation'.

Evidently, the transversal mode gives similar results since it corresponds to the same sign of the gradient term.

4.2. Kinetics of nucleation via total mixing mode

For total mixing mode the gradient term (factor γ) in equation (18) is negative—the concentration gradient ∇C helps the nucleation process. The results of calculation for the total mixing mode differ substantially from those for the polymorphic mode. First of all, nucleation is never suppressed. Moreover, nucleation behaviour may well be oscillatory—for a certain range of parameters the time evolution of new phase volume is non-monotonic (see figure 8). Similar non-monotonic behaviour is observed as well for the number of smallest embryos (in our case $N_{min} = 5$) for the same thermodynamic parameters except surface tension (figure 9).

Why are the embryos generated intensively at the very first stage and than partially dissolved? Our answer is the following: for the total mixing mode the gradient term helps nucleation. At first the gradient is large, making the nucleation barrier low and the nucleation process easy. With time the gradient decreases; the nucleation barrier and critical nucleus size increase. Therefore, particles which had been generated earlier as overcritical and which did not manage to reach the new critical size, find themselves to be subcritical and are dissolved. In other words, if the growth rate of particles is less than the rate of critical size growth (due to decreasing concentration gradient), these particles will be disintegrated.

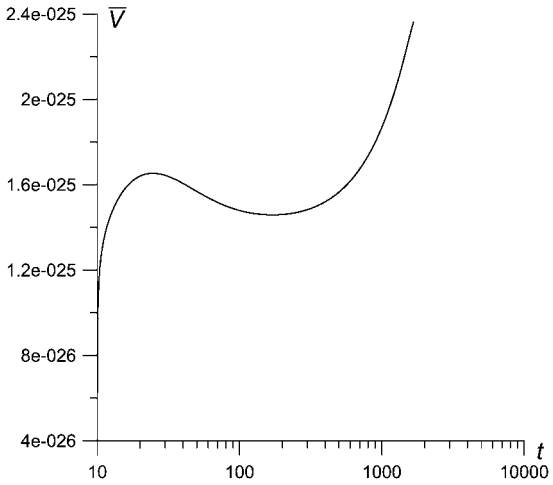

Figure 8. Time dependence of new phase volume in the case of the total mixing mode for $\sigma = 0.20$ J m^{-2}.

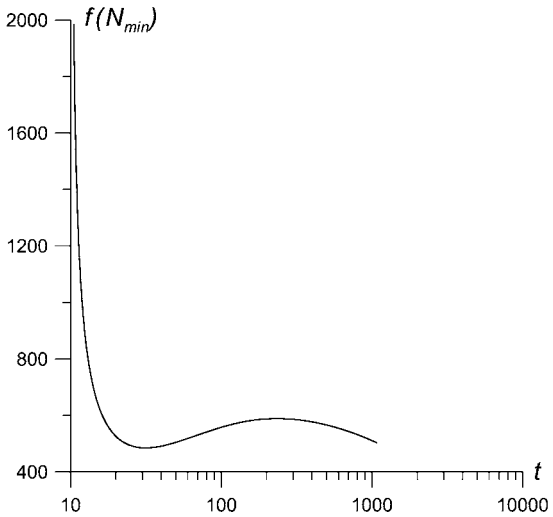

Figure 9. Time dependence of the number of smallest new phase embryos ($N_{min} = 5$) for heterogeneous nucleation via the total mixing mode for $\sigma = 0.15$ J m^{-2}.

We had observed the non-monotonic behaviour of new phase formation during interdiffusion by Monte Carlo simulations both for second-order and first-order phase transitions in the concentration gradient [28, 29].

5. Competition of intermediate phase nucleation modes in the concentration gradient

5.1. General remarks

As we have just seen, nucleation of intermediate phase during reactive diffusion can proceed via different 'modes', each being characterized by its own nucleation barrier, its own frequency factor and own shape/volume dependence. We restrict ourselves to a special shape, a

parallelepiped, leaving the only free shape parameter $\varphi = h/r$, where $2h$, $2r$ are the nucleus sizes in transversal and longitudinal directions.

Every mode has its own velocity determined by diffusivities and embryo shape. Since the embryo growth is a random process, generated by fluctuations, it should be described by the size distribution function $f(N, \varphi|t)$, where N is a number of atoms, say, of the B species in the embryo. Up to now we do not know for sure the mechanism of the smallest embryo formation, containing some small number of atoms, N_0. It can be formed, for example, by some kind of cooperative mechanism. Further growth of this embryo is supposed to proceed by a 'one by one' mechanism: atoms join the embryo one by one via the different kinds of diffusion process. Here we will consider in detail the interference of only two modes of this 'one by one' mechanism—(b) and (c).

We will suppose that at every stage of the embryo evolution of the shape is somehow optimized for every fixed N, so that $\varphi = \varphi(N)$, and $f(N, \varphi) = f(N, \varphi(N)) = f(N)$. The method of such optimisation, taking the kinetic factors into account, will be considered in section 5.3. The distribution function $f(N|t)$ is determined by the Fokker–Planck equation that is constructed and analysed in section 5.2. In this equation the 'jump frequency' in the size space is taken as a superposition of frequencies for two modes—(b) and (c). To obtain an effective nucleation barrier, one does not need to solve the F–P equation in the general case. It is enough to analyse the stationary case, $\partial f/\partial t = 0$. A minimum of the function $f(N)$ for this case (if it exists!) corresponds to the effective nucleation barrier and to the critical number N_{cr} of atoms A (and the corresponding critical volume V_{cr} of the intermediate phase). It depends on the concentration gradient and on the ratio of diffusivities in the new and parent phases. In section 5.4 the general scheme and numeric calculations for non-dimensional parameters are presented.

5.2. Fokker–Planck equation for the interfering nucleation modes

Further we neglect the (a) mode of nucleation. Then the time evolution of the size distribution function $f(N|t)$ is determined by the superposition of frequencies of the (b) (transversal) and (c) (total mixing) modes.

$$\frac{\partial f}{\partial t} = \nu_+(N-1)f(N-1) + \nu_-(N+1)f(N+1) - [\nu_+(N) + \nu_-(N)]f(N). \tag{20}$$

Here $\nu_{+/-}(N)$ is a frequency (probability per unit time) of one B atom joining (leaving) the embryo lattice (in combination with q A atoms needed to preserve the stoichiometry A_qB_1). In the case of two operating modes

$$\nu_{+/-}(N) = \nu^{(b)}_{+/-}(N) + \nu^{(c)}_{+/-}(N). \tag{21}$$

In fact, frequencies, as well as distribution function f, depend on shape as well. An equation for determining the dependence $\varphi(N)$ for most probable shapes will be obtained in section 5.3. An expansion of the function f into Taylor series around N transforms equation (20) into the usual Fokker–Planck equation (14) where the 'flux density' j in the size space consists of the drift term $(\nu_+ - \nu_-)f$ and the 'diffusional', purely stochastic term $-(\partial/\partial N))([(\nu_+ + \nu_-)/2]f)$, which makes the very process of nucleation possible.

Consider now the explicit form of $\nu^{(b)}_{+/-}$ and $\nu^{(-)}_{+/-}$. Each of the frequencies is a product of 'kinetic' (pre-exponential) and 'thermodynamic' (Boltzmann) factors. The Boltzmann factor is a probability of climbing on the potential barrier shown in figure 10. For the (c) mode (total mixing inside the newly formed nucleus) the pre-exponential factor is an inverse time τ^{-1} of the process of joining (leaving) the embryo by one B atom, multiplied by the number of atoms

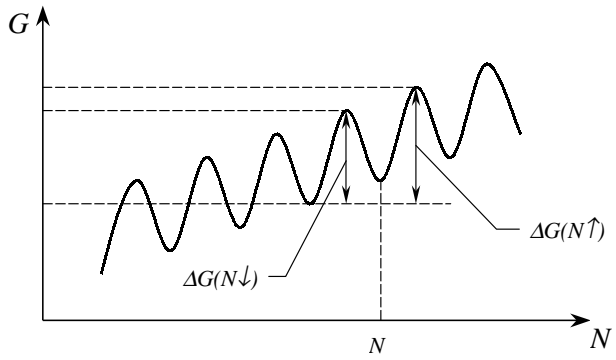

Figure 10. Schematic 'microscopic' dependence of the Gibbs free energy on the number of A atoms in the embryo of intermediate phase.

$(2h)^2/s_0$ which can try to fulfil the procedure of joining (s_0 is the area per atom). In the case when the B atoms are much faster than A atoms,

$$\tau = \tau_{m-i} + \frac{(2r)^2}{2D_i} + \tau_{i-m} \tag{22}$$

where $(2r)^2/2D_i$ is an average time of diffusion of the B atom through the embryo along the ∇C-direction, τ_{m-i} the time of transfer over the right interface (metastable parent phase/embryo) before diffusion and τ_{i-m} the time of reaction with A atoms at the left interface (embryo/metastable phase).

Therefore

$$\nu_+^{(c)} = \frac{(2h)^2}{s_0} \frac{1}{\tau_{m-i} + (2r)^2/2D_i + \tau_{i-m}} \exp\left\{-\frac{\Delta G^{(c)}(N\uparrow)}{\Theta}\right\} \tag{23}$$

$\Delta G^{(c)}(N\uparrow)$ is a potential barrier for joining one B atom (and q A atoms, necessary for stoichiometry A_qB_1) via the (c) mode and $\Theta = kT$. This potential barrier can be interpreted as a change of Gibbs free energy by one defect B and q defects A in the intermetallic before reaction between them.

Evidently, the times of reaction at the interfaces and of random walk in opposite direction are the same as for elementary joining process, so that ν_- differs from ν_+ only due to Boltzmann factors.

$$\nu_-^{(c)} = \frac{(2h)^2}{s_0} \frac{1}{\tau_{m-i} + (2r)^2/2D_i + \tau_{i-m}} \exp\left\{-\frac{\Delta G^{(c)}(N\downarrow)}{\Theta}\right\} \tag{24}$$

where $\Delta G^{(c)}(N\downarrow)$ is a potential barrier for departure of one B atom (and q A atoms) from the embryo (figure 10).

Evidently, the difference of the right and left barriers is equal to the change of the Gibbs free energy by joining one B atom:

$$\Delta G^{(c)}(N\uparrow) - \Delta G^{(c)}(N\downarrow) = G^{(c)}(N+1) - G^{(c)}(N) = \frac{\partial G^{(c)}}{\partial N}$$
$$= \Delta g\left\{-1 + \frac{4}{3}\left(\frac{\sigma_1}{n\Delta g}\varphi^{\frac{2}{3}} + \frac{2\sigma_2}{n\Delta g}\varphi^{-\frac{1}{3}}\right)V^{-\frac{1}{3}} + \frac{\gamma^{(c)}}{n\Delta g}(\nabla c)^2\frac{5}{96}\varphi^{-\frac{4}{3}}V^{\frac{2}{3}}\right\}. \tag{25}$$

First we will consider the 'interface reaction times' τ_{m-i}, τ_{i-m} to be negligibly small compared with the time of migration across the embryo. This can be a good approximation in

the case of coherent boundaries. In this case

$$\nu_{+/-}^{(c)} = \frac{2D_i}{s_0}\left(\frac{h}{r}\right)^2 \exp\left\{-\frac{\Delta G^{(c)}(N\uparrow/\downarrow)}{\Theta}\right\}. \tag{26}$$

The difference of frequencies is equal to

$$\Delta\nu^{(c)} = \nu_+^{(c)} - \nu_-^{(c)} = \frac{2D_i}{s_0}\left(\frac{h}{r}\right)^2 \exp\left\{-\frac{\Delta\overline{G}^{(c)}(N)}{\Theta}\right\} 2\sinh\left(-\frac{1}{2\Theta}\frac{\partial G^{(c)}}{\partial N}\right)$$

where $\Delta\overline{G}^{(c)}(N) = [\Delta G^{(c)}(N\uparrow) + \Delta G^{(c)}(N\downarrow)]/2$. Further we suppose $|\partial G^{(c)}/\partial N| \ll \Theta$. Then the explicit form of the driving force in the size space $\Delta\nu$ and average frequency $\nu^{(c)} = (\nu_+^{(c)} + \nu_-^{(c)})/2$ are

$$\Delta\nu^{(c)} = -\frac{1}{\Theta}\frac{\partial G^{(c)}}{\partial N}\nu^{(c)} \qquad \nu^{(c)} \approx \frac{2D_i}{s_0}\left(\frac{h}{r}\right)^2 \exp\left(-\frac{\Delta\overline{G}^{(c)}}{\Theta}\right). \tag{27}$$

For the transversal mode (b) the frequencies have a similar form differing from the mode (c) due to the diffusion time $h^2/2D_m$ instead of $(2r^2)/2D_i$; h is an average distance over which atoms must migrate in the transversal direction to join the embryo, where D_m is the interdiffusion coefficient in the metastable parent phase. The frequencies are approximately given by

$$\nu_{+/-}^{(b)} = \frac{4h^2}{s_0}\frac{2D_m}{h^2}\exp\left\{-\frac{\Delta G^{(b)}(N\uparrow/\downarrow)}{\Theta}\right\}. \tag{28}$$

The explicit form of the driving force in the size space $\Delta\nu^{(b)} = \nu_+^{(b)} - \nu_-^{(b)}$ and average frequency $\nu^{(b)} = (\nu_+^{(b)} + \nu_-^{(b)})/2$ under the assumption $|\partial G^{(b)}/\partial N| \ll \Theta$ are as follows:

$$\Delta\nu^{(b)} = -\frac{1}{\Theta}\frac{\partial G^{(b)}}{\partial N}\nu^{(b)} \tag{29}$$

$$\nu^{(b)} \approx \frac{16D_m}{s_0}\exp\left(-\frac{\Delta\overline{G}^{(b)}}{\Theta}\right). \tag{30}$$

To obtain the nucleation barrier, one should consider the equilibrium solution of the Fokker–Planck equation,

$$\Delta\nu f - \frac{\partial}{\partial N}(\nu f) = 0. \tag{31}$$

Really, in the case of only one operating nucleation mode, say, (b), the solution of equation (31) corresponds to the critical nucleus: $\partial G^{(b)}/\partial N = 0$. The general solution of equation (31) is as follows:

$$f(N) = \frac{\nu(N_0)f(N_0)}{\nu(N)}\exp\left\{\int_{N_0}^{N}\frac{\Delta\nu}{\nu}\mathrm{d}N'\right\}. \tag{32}$$

Then the expression for the equilibrium size distribution function has the following simple form:

$$f(N) = f(N_0)\mathrm{e}^{-\frac{1}{\sigma}\int_{N_0}^{N}\frac{\partial G^{(b)}}{\partial N}\mathrm{d}N'}. \tag{33}$$

Evidently, the minimum of this function is determined by the condition $\partial G^{(b)}/\partial N = 0$, that coincides with the well known expression from the classical nucleation theory.

Further we generalize the above-mentioned approach on the case of superposition of two modes. The critical nucleus corresponds to the minimum of the size distribution function

which is found from the expression (32), where $\Delta\nu$ and ν are found as the superposition of two modes.

In this case

$$\frac{\Delta\nu}{\nu} = -\frac{1}{\theta}\frac{(D_i/4r^2)(\partial G^{(c)}/\partial N)\exp(-\Delta\overline{G}^{(c)}/\Theta) + (D_m/h^2)(\partial G^{(b)}/\partial N)\exp(-\Delta\overline{G}^{(b)}/\Theta)}{(D_i/4r^2)\exp(-\Delta\overline{G}^{(c)}/\Theta) + (D_m/h^2)\exp(-\Delta\overline{G}^{(b)}/\Theta)}$$
$$= -\frac{1}{\Theta}\frac{\Lambda(\partial G^{(c)}/\partial N) + (r^2/h^2)(\partial G^{(b)}/\partial N)}{\Lambda + r^2/h^2}. \tag{34}$$

Here parameter $\Lambda = (D_i/4D_m)\exp(-(\Delta\overline{G}^{(c)} - \Delta\overline{G}^{(b)})/\Theta)$ plays a crucial role in the competition of nucleation modes. In this paper we will not discuss a thermodynamic part of this parameter and will concentrate on its dependence on the ratio of diffusivities of intermediate and parent phases.

Let the derivative $\partial \ln \nu/\partial N$ be negligibly small. Then the condition $f(N) = \min$ reduces to the equation

$$\frac{\Delta\nu}{\nu} = 0$$

e.g. (in fact, we treat this equation as a definition of critical point instead of $\Delta G = \max$)

$$-1 + \frac{4}{3}\left(\frac{\sigma_1}{n\Delta g}\varphi^{\frac{2}{3}} + \frac{2\sigma_2}{n\Delta g}\varphi^{-\frac{1}{3}}\right)V^{-\frac{1}{3}} + \frac{5(\nabla c)^2}{96}\frac{\varphi^{-\frac{4}{3}}V^{\frac{2}{3}}}{n\Delta g}\frac{\gamma^{(b)} + \gamma^{(c)}\Lambda\varphi^2}{1+\Lambda\varphi^2} = 0. \tag{35}$$

It is convenient to introduce the non-dimensional parameters

$$\tilde{V} = \frac{V}{V^*} \qquad \frac{\sigma_2}{\sigma_1} = s \qquad \tilde{\gamma}^{(b,c)} = \frac{\gamma^{(b,c)}}{n\Delta g} \qquad \tilde{\nabla}c = \nabla c\,(V^*)^{\frac{1}{3}},\ \text{where } V^* = \frac{64\sigma_1\sigma_2^2}{(n\Delta g)^3}.$$

Then equation (36) reduces to the following form:

$$-1 + \frac{1}{3}\left(\left(\frac{\varphi}{s}\right)^{\frac{2}{3}} + 2\left(\frac{\varphi}{s}\right)^{-\frac{1}{3}}\right)\tilde{V}^{-\frac{1}{3}} + \frac{5(\tilde{\nabla}c)^2}{96}\varphi^{-\frac{4}{3}}\tilde{V}^{\frac{2}{3}}\frac{\tilde{\gamma}^{(b)} + \tilde{\gamma}^{(c)}\Lambda\varphi^2}{1+\Lambda\varphi^2} = 0. \tag{36}$$

It is very important that the second, gradient term in equation (36) can have different signs for different D_i/D_m ratios. This means that there exists competition between two nucleation modes. To make this fact obvious consider two limiting cases.

1. $\Lambda \to 0$—only the transversal mode is operating. Then the last term in equation (36) is positive, and under a sufficiently sharp concentration gradient, this term together with the second (surface) term will be more than 1 at any volume. Therefore under sharp concentration gradients equation (36) has no solutions, there is no critical nucleus and the nucleation process is impossible. This result coincides with previous results [17–21].
2. $\Lambda \to \infty$—only the total mixing mode is operating. Then the last term in equation (36) is negative. In this case the solution of equation (36) exists (and nucleation is possible) at any concentration gradient.

Certainly, the shape factor depends on volume, and one should take this dependence into account when solving equation (36). The corresponding equation for the shape factor will be obtained and solved in the next section. Meanwhile let us analyse equation (36) regarding factor φ as a constant. In this case equation (36) reduces to the cubic equation

$$ax^2 - b + \frac{c}{x} = 0 \qquad x = \tilde{V}^{1/3}. \tag{37}$$

If $D_i/4D_m > (1-\alpha/\alpha')/\varphi^2$, this equation has a solution at any concentration gradient. If $D_i/4D_m < (1-\alpha/\alpha')/\varphi^2$ then it has solution under the condition

$$(\tilde{\nabla}c)^2 > \frac{1+\Lambda\varphi^2}{\tilde{\gamma}^{(b)}+\tilde{\gamma}^{(-)}\Lambda\varphi^2}\cdot\frac{64}{5((\varphi/s)^{2/3}+2(\varphi/s)^{-\frac{1}{3}})}. \tag{38}$$

Thus, under the assumption of constant shape factor the critical gradient exists only if the diffusivity of the new phase is substantially lower than that of the parent phase. Otherwise nucleation is possible at any gradient. This conclusion coincides qualitatively with the result obtained in [22] in the frame of thermodynamics. Nevertheless, strictly speaking, this conclusion is not correct as we will see below.

5.3. Calculation of shape factor

In the purely thermodynamic approach for every mode of nucleation the shape factor φ can be determined by minimization of the function $g(N,\varphi)$ at every fixed volume V. In the case of combined modes one cannot calculate φ according to this recipe. Obviously, there must be some distribution of shapes at every given volume V. It is obvious as well that such distribution must be non-monotonic, with a maximum. The main idea of this section is to find such a dependence $\varphi(V)$ (or $\varphi(N)$), which makes the magnitude of the function $f(N,\varphi)$ maximal at every fixed N. For this, according to equation (32) for the distribution function, the following functional derivative should be equal to 0:

$$\frac{\delta}{\delta\varphi}\int_{N_0}^{N}\frac{\Delta\nu(N',\varphi(N'))}{\nu(N',\varphi(N'))}\,\mathrm{d}N' = 0. \tag{39}$$

It is easy to show that this equation is equivalent to the differential equation

$$\frac{\partial}{\partial\varphi}\left(\frac{\Delta\nu}{\nu}\right) = 0 \tag{40}$$

e.g.

$$2\tilde{V}^{-\frac{1}{3}}s^{-\frac{1}{3}}(\varphi^{-\frac{1}{3}}-s\varphi^{-\frac{4}{3}}) - \frac{5(\tilde{\nabla}c)^2}{32}\frac{\tilde{V}^{\frac{2}{3}}\varphi^{-\frac{7}{3}}}{1+(D_i/4D_m)\varphi^2}\left\{-\frac{4}{3}(\tilde{\gamma}^{(b)}+\tilde{\gamma}^{(c)}\Lambda\varphi^2) - \frac{(\tilde{\gamma}^{(b)}+\tilde{\gamma}^{(c)})\,24}{1+\Lambda\varphi^2}\right\} = 0. \tag{41}$$

Thus, the calculation of critical parameters φ_c and $\tilde{V}_c$ for the intermediate phase nucleation in the concentration gradient is made on the basis of equations (36) and (41). The role of nucleation barrier is played by an integral in the exponential dependence (32) with the upper limit equal to critical particle number:

$$\Delta G^{cr} = \Theta\int_{N_0}^{N^{cr}}\frac{\Delta\nu(N',\varphi(N'))}{\nu(N',\varphi(N'))}\,\mathrm{d}N'. \tag{42}$$

An expression $f(N_0)\exp\{-\Delta G_{cr}/\Theta\}$ is a minimum of the size distribution function corresponding to the effective saddle point on the 'trajectory' of growing embryo. Here the shape factor φ at any subcritical value N' is calculated according to equation (41). It is easy to check that in the limiting cases of the only one operation mode (b) or (c) expression (42) is reduced to the classical nucleation barriers corresponding to the maximal values of the functions $\Delta G^{(b)}(N)$ and $\Delta G^{(c)}(N)$. Further we calculate the non-dimensional effective nucleation barrier $\Delta\tilde{G}_{cr} = \Delta G_{cr}/\Theta nV^* = \int_{\tilde{V}_0}^{\tilde{V}_{cr}}(\Delta\nu/\nu)\,\mathrm{d}\tilde{V}$.

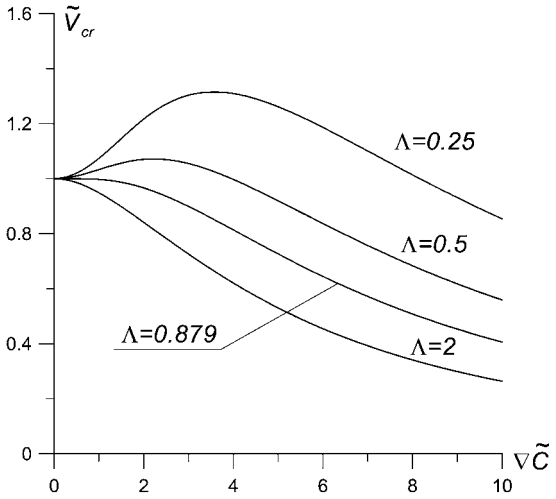

Figure 11. Dependence of the critical nucleus volume (non-dimensional) on the non-dimensional concentration gradient at different ratios of diffusivities in the new and parent phases.

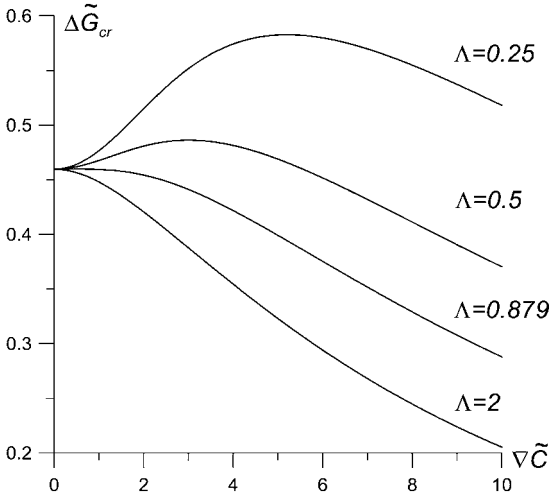

Figure 12. Dependence of the effective nucleation barrier (non-dimensional) on the non-dimensional concentration gradient at different ratios of diffusivities in the new and parent phases.

5.4. Results

The dependences $\tilde{V}_{cr}(\tilde{\nabla}c)$, $\Delta\tilde{G}_{cr}(\tilde{\nabla}c)$, $\varphi_{cr}(\tilde{\nabla}c)$ have been obtained for the case $s = 1$, $\tilde{\gamma}^{(b)} = 0.9$, $\tilde{\gamma}^{(c)} = -1$. Formally speaking, the critical nucleus exists at any concentration barrier and the critical volume can increase rather substantially, making the nucleation very difficult. The specific form of the functions $\tilde{V}_{cr}(\tilde{\nabla}c)$ and $\Delta\tilde{G}_{cr}(\tilde{\nabla}c)$ depends on the ratio $D_i/4D_m$. At $d \equiv D_i/4D_m < d^* = 3.58$ the functions $\tilde{V}_{cr}(\tilde{\nabla}c)$ and $\Delta\tilde{G}_{cr}(\tilde{\nabla}c)$ are non-monotonic with a maximum (figures 11 and 12) which shifts to the zero $\tilde{\nabla}c$ on increasing Λ to d^*. On decreasing d to zero this maximum ΔG_{cr}^{max} tends to infinity, figure 13 (the transversal mode is overwhelming). At $d > d^*$ the functions $\tilde{V}_{cr}(\tilde{\nabla}c)$ and $\Delta\tilde{G}_{cr}(\tilde{\nabla}c)$ are

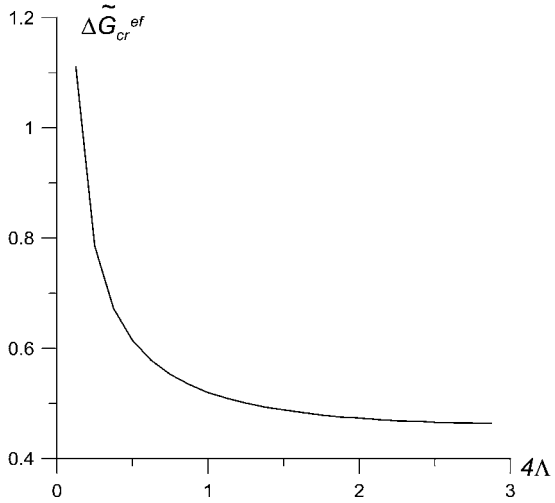

Figure 13. Dependence of maximal nucleation barrier (non-dimensional) on the ratio of diffusivities.

monotonous—the sharper is the concentration gradient, the lower is the nucleation barrier (the total mixing mode is overwhelming). Thus, strictly speaking, there is no critical gradient in the general case, and nucleation of intermediate phase is possible at any gradient due to the possibility of the total mixing mode. Instead of a critical gradient beyond which nucleation would be impossible the characteristic gradient exists at which the probability of nucleation is the smallest. In the process of the interdiffusion in the parent phase the concentration gradient decreases and the nucleation barrier increases at first. This means that the nuclei of the new phase born at the very beginning can become subcritical at the later stage (if they had no time for growth). Therefore the oscillatory regime of intermediate phase formation can be possible. Figure 14 shows that critical φ ($\varphi(\tilde{V}_{cr})$) decreases when D_i/D_m increases.

Here and below calculations are made for the following parameter values: $\tilde{\gamma}_b = 0.9$, $\tilde{\gamma}_c = -1$.

The main result is that the kinetic constraints and the interference of different nucleation modes lead to the effective nucleation barriers depending on the ratio of diffusivities as well as on usual thermodynamic factors.

6. Summary

(1) The choice of the phase formation sequence is determined at the nucleation stage.

(2) Intermediate phase formation can be suppressed by kinetic and/or by thermodynamic factors.

(3) Kinetic suppression means 'sucking out' of the critical nuclei by the growing competing neighbouring phases with larger diffusivities. It leads to the kinetic part of the incubation period.

(4) The thermodynamic factor is connected with the concentration gradient influencing the nucleus shape and the nucleation barrier. The type of influence depends on the mode of nucleation.

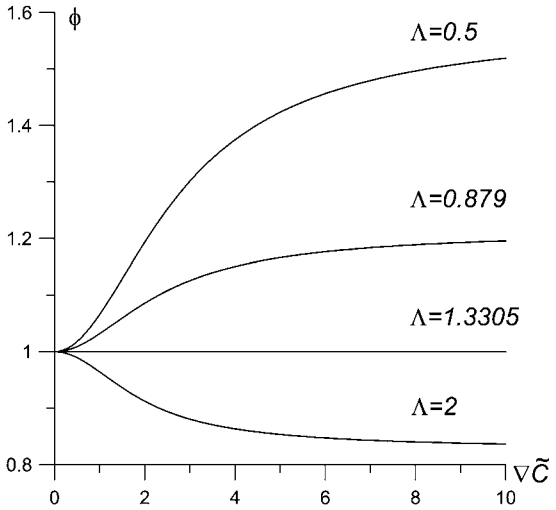

Figure 14. Dependence of the shape factor for the critical nucleus on the non-dimensional concentration gradient at different ratios of diffusivities in the new and parent phases.

(5) For polymorphic and transversal modes a sharp ∇C leads to large ΔG^* and 'pancake' shape. $\nabla C > \nabla C^{crit}$ prohibits the nucleation completely.
(6) In the case of the pure polymorphic nucleation mode the incubation period of intermediate phase decreases with increasing diffusivity of the parent phase to some asymptotic level τ_{min}. The difference $\tau - \tau_{min}$ can be treated as a time of 'concentration preparation', necessary for decreasing the concentration gradient below a certain critical value.
(7) In the case of total mixing nucleation mode the time behaviour of new phase volume and of number of minimal clusters can be non-monotonic. This means that if the growth rate of 'primary' critical clusters is less than the rate of critical size growth (due to decreasing concentration gradient), these particles will be disintegrated.
(8) Nucleation modes operate simultaneously with different rates. This leads to a dependence of the nucleation barrier on the ratio of kinetic parameters—the larger the diffusivity of the new phase, the lower is the effective nucleation barrier.
(9) Oscillatory nucleation is possible due to simultaneous competitive contributions of different nucleation modes—overcritical nuclei may find themselves subcritical with lowering of the concentration gradient.

Acknowledgments

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