The microscopical theory of homogeneous nucleation in alloys: I. General relations

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Abstract. The earlier-described generalized Gibbs distribution approach to the theoretical description of non-equilibrium alloys is used to develop the microscopical theory of homogeneous nucleation in metastable alloys. Some exact and approximate relations for the free energy of a non-uniform alloy $F\{c_i\}$ depending on the local concentrations c_i are presented. These relations are used to microscopically describe the alloy state with the critical embryo. This state is supposed to correspond to the saddle point of the generalized grand canonical potential in the c_i-space, while the variations of the size and the position of the embryo correspond to certain fluctuative modes at this saddle point. These notions are used to derive the microscopical expressions for all of the parameters of the phenomenological theory of nucleation—in particular, for the nucleation barrier and the prefactor in the Zeldovich–Volmer equation for the nucleation rate.

1. Introduction

There are two main kinetic forms of phase transformation for an initially homogeneous phase-separating system quenched into the two-phase equilibrium region: nucleation and spinodal decomposition. For definiteness we discuss the disordered binary alloy $A_c B_{1-c}$ where $c = c_A$ is the A-component concentration. Then the kinetic evolution type is mainly determined by the position of the initial quenched state in the concentration–temperature plane c, T. There are two important curves in this plane that delineate the regions of different kinetic behaviour: the two-phase equilibrium curve, or the binodal $T_b(c)$, and the stability limit of the uniform state, or the spinodal $T_s(c)$. The first curve is determined by the phase equilibrium equations, and the second one is determined by the equation $(\partial^2 F/\partial c^2)_T = 0$ where $F = F(c, T)$ is the extrapolated or calculated expression for the free energy of the uniform alloy. According to classical ideas [1–5], in the metastability region $T_s(c) < T < T_b(c)$ the homogeneous phase separation is realized via nucleation, i.e. formation of critical and supercritical embryos of the new phase within the original metastable one, while at $T < T_s(c)$ the main kinetic mechanism is the spinodal decomposition via the development of unstable concentration waves with growing amplitudes [4]. Even though the borderline between these two evolution types in the c, T plane can be not entirely sharp [6], the transition region between them in the available experimental studies for both solid alloys [7] and liquid mixtures [8] was found to be quite narrow: $\Delta T/T_s \lesssim 10^{-3}$–$10^{-2}$.

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In this work we discuss the nucleation problem. When the number of embryos of the new phase is small and their interaction is negligible (which is the case, in particular, when the initial c, T point is close to the binodal), the nucleation rate J, i.e. the number of supercritical nuclei being formed in unit volume per unit time, is given by the Zeldovich–Volmer relation derived by Zeldovich in his phenomenological theory [5]:

$$J = J_0 \exp(-\beta \, \Delta\Omega_c). \tag{1}$$

Here $\beta = 1/T$ is the reciprocal temperature, and $\Delta\Omega_c$ is the activation barrier for the formation of the critical embryo, while the prefactor J_0 is determined by some kinetic characteristics.

The theory [5] includes a number of phenomenological parameters: the size of the critical embryo $a = a_c$, the nucleation barrier $\Delta\Omega_c$, and the kinetic factors entering the prefactor J_0. The nucleation barrier $\Delta\Omega_c$ is the minimal work required to create the critical embryo [2]; when the nucleation process occurs at constant chemical potential (which corresponds to usual experimental conditions for the first stages of nucleation under consideration) this work is equal to the grand canonical potential difference $\Omega(a_c) - \Omega_0$ where $\Omega(a)$ corresponds to the state with the embryo of size a, and Ω_0 corresponds to the initial uniform metastable state. The potential Ω is related to the free energy F and the total number of atoms N as: $\Omega = F - \mu N$. The critical size a_c corresponds to the borderline between the unstable undercritical embryos with $a < a_c$, and the growing supercritical embryos with $a > a_c$. For the undercritical embryo, its vanishing is thermodynamically more favourable than growth: the derivative $d\Omega/da$ for these small embryos is positive, as the free-energy loss due to the formation of interfaces with the exterior phase exceeds the volume gain in Ω due to the presence of the more stable phase within the embryo. For the supercritical embryos the situation reverses: for them $d\Omega/da < 0$, so they can grow spontaneously. The critical size $a = a_c$ corresponds to the $\Omega(a)$ maximum point: $d\Omega/da = 0$; thus the critical embryo is in unstable equilibrium with the exterior phase. The prefactor J_0 is expressed via several parameters that characterize the probability flow through the $\Omega(a)$ maximum point $a = a_c$ in the embryo size a-space [5]. Analogous phenomenological parameters are used in more recent approaches treating more complex problems of nucleation in multi-component systems [9, 10].

The classical theory [5] (like earlier approaches [1, 2]) treats the critical embryo as a macroscopic homogeneous droplet with the sharp boundary and the definite radius a. However, the microscopical estimates given in references [3] and [11] show that such notions are adequate only when the initial metastable state is quite close to the two-phase equilibrium limit. For alloys it corresponds to very small values of supersaturation $|c - c_b(T)| \lesssim 10^{-2}$, where $c_b(T)$ is the concentration value at the binodal. At higher supersaturations the embryo becomes rather non-uniform while its interface with the exterior phase gets diffuse. Therefore, to treat cases of not very small supersaturation (that are of the most practical interest for alloys), the theory [5] should be made specific and generalized.

The microscopical approach to the calculations of the nucleation barrier $\Delta\Omega_c$ has been proposed by Cahn and Hilliard [3]. These authors used the Ginzburg–Landau-type gradient expansion for the free energy F treated as a functional of the local concentrations $c(\boldsymbol{r})$. The $c(\boldsymbol{r})$ distribution for the critical embryo was found as the saddle point configuration for this functional. Employing both phenomenological arguments and the mean-field approximation (MFA) to treat the functional $F\{c(\boldsymbol{r})\}$, Cahn and Hilliard found that the critical embryo has a number of features that are absent in the classical approach [1, 2]. In particular, with increasing supersaturation the embryo becomes significantly non-uniform and its interface with the exterior phase gets rather diffuse (even though the embryo can still include many

atoms), while the nucleation barrier $\Delta\Omega_c$ lowers and tends to zero when the initial c, T point approaches the spinodal. However, Cahn and Hilliard discussed only the thermodynamics and not the kinetics of nucleation; thus no discussion of the prefactor J_0 in (1) has been given. Possible errors of the mean-field and gradient expansion approximations employed for F were not discussed in reference [3] either, while, for example, the fluctuative effects neglected in the MFA can be rather important for this problem [11].

A microscopical model of nucleation has been discussed by Langer [12]. He considered a set of non-specified 'microscopical coordinates' η_i and supposed the critical embryo to correspond to the saddle point of the energy $E\{\eta_i\}$ in the η_i-space. Langer has shown that the critical normal coordinate u, for which the curvature $\partial^2 E/\partial u^2$ at the saddle point is negative, can be treated as an analogue of the embryo size a in the Zeldovich theory [5] (though this theory was not mentioned in reference [12]), while the critical size $a = a_c$ corresponds to the saddle point value $u = u_c$. Unfortunately, applications of these results to physical problems are prevented by a number of unclear points of the model [12]: why statistical fluctuations of microscopical variables η_i in the system with significant interactions are supposed to be Gaussian; why the critical embryo corresponds to the saddle point of the energy $E\{\eta_i\}$ rather than that of the free energy F (as defined in [12]), and thus what the physical meaning of this saddle point is; whether the assumption of [12] that the microscopical kinetic coefficients do not depend on the dynamical variables η_i can correspond to physical situations; etc.

Recently we proposed the 'generalized Gibbs distribution' approach to treat the configurational kinetics of alloys at arbitrary degree of non-equilibrium [13, 14]. Applications of this approach to concrete problems yielded a number of new results [13, 15–18]. In the present work we apply this approach to develop a fully microscopical theory of nucleation in alloys.

We adopt the main ideas and assumptions of the classical theory [5], and aim to derive the microscopical expressions for all of its phenomenological parameters, including J_0 and $\Delta\Omega_c$ in equation (1). In accordance with the Zeldovich approach [5], the problem of finding the nucleation rate is divided into two. First we determine the size distribution function for the undercritical embryos. This is done using certain relations for the free energy of a non-uniform alloy which are discussed in section 2. Secondly, we investigate the kinetics of the probability flow through the critical point $a = a_c$ in the embryo size a-space. This is done using the microscopical approach to the alloy kinetics described in references [13, 14].

In section 2 we discuss some general relations for the free energy of a non-uniform alloy which are used below. In section 3 we discuss the microscopical description of the alloy state with the critical embryo. In section 4 we find the above-mentioned embryo size distribution function. In section 5 we consider growth of the embryo and derive the explicit microscopical expressions for the nucleation barrier $\Delta\Omega_c$ and the prefactor J_0 in equation (1). In the following paper [11] (to be referred to as II) these expressions are used to calculate the nucleation rate for various alloy models. Our main conclusions are summarized in section 6.

2. Exact and approximate relations for the free energy of a non-uniform alloy

In this section we discuss some general relations for the free energy of a non-uniform alloy. These relations will be used below to treat the thermodynamics of nucleation, but they can also be applied to other problems of the physics of non-uniform systems.

For simplicity we consider the binary alloy A–B. The alloy configurational states, i.e. the distributions of A and B atoms over lattice sites i, are described as usual, using the occupation number operator n_i which is equal to unity when an atom A is at the site i

and zero otherwise. The configurational Hamiltonian H has the form

$$H = \sum_i \varphi_i n_i + \sum_{i>j} v_{ij} n_i n_j + \sum_{i>j>k} v_{ijk} n_i n_j n_k + \cdots \tag{2}$$

where v_{ij} and v_{ijk} are the configurational interactions, while the external potentials φ_i may correspond to lattice defects, impurities, etc. Such inhomogeneities can be important for heterogeneous nucleation when they can become centres for embryo formation. However, in this work we consider only the homogeneous nucleation in a defectless alloy; thus in the following sections we put $\varphi_i = 0$.

The free energy of a non-uniform alloy was discussed in references [14, 18] in terms of the probability distribution $P\{n_i\}$ of various alloy configurations $\{n_i\}$. For the states in which short-range equilibrium has been achieved (only such states are considered in this work) the distribution has the form [18]

$$P\{n_i\} = \exp\left[\beta\left(\Omega + \sum_i \lambda_i n_i - H\right)\right]. \tag{3}$$

Here the λ_i are the parameters of the distribution, the grand canonical potential $\Omega = \Omega\{\lambda_i\}$ is determined by the normalization condition

$$\Omega = -T \ln \mathrm{Tr} \exp\left[\beta\left(\sum_i \lambda_i n_i - H\right)\right] \tag{4}$$

and the symbol Tr means summation over all configurations $\{n_i\}$. The free energy $F = F\{c_i\}$ is determined by the relation

$$F = \Omega + \sum_i \lambda_i c_i \tag{5}$$

where $c_i = \langle n_i \rangle = \mathrm{Tr}(n_i P)$ is the mean occupation number, or the local concentration. Equations (4)–(6) imply the relations

$$c_i = -\partial\Omega/\partial\lambda_i \qquad \lambda_i = \partial F/\partial c_i. \tag{6}$$

For the stationary state the free energy obeys the equilibrium equations [14]

$$\partial F/\partial c_i = \mu = \text{constant} \tag{7}$$

where μ is the chemical potential.

The occupation fluctuation correlator $K_{ij} = \langle(n_i - c_i)(n_j - c_j)\rangle$ for the distribution (4) is related to $F\{c_i\}$ by the matrix equation

$$(K^{-1})_{ij} = \beta\, \partial^2 F/\partial c_i\, \partial c_j \tag{8}$$

which follows from the relation $K_{ij} = -T\, \partial^2\Omega/\partial\lambda_i\, \partial\lambda_i$ and equations (6).

When the interactions are pairwise, i.e. Hamiltonian (2) includes only the first two terms, one can derive an exact relation between K_{ij} and $F\{c_i\}$ which is important for what follows. Let us consider a set of systems with interactions gv_{ij} scaled by a 'charge' variable g; the real case corresponds to $g = 1$. Then the quantities $F\{c_i, g\}$ and $K_{ij}\{c_k, g\}$ obey the equation

$$F\{c_i, g\} = T \sum_i (c_i \ln c_i + c_i' \ln c_i') + \frac{1}{2} g \sum_{ij} v_{ij} c_i c_j + \frac{1}{2} \sum_{ij} v_{ij} \int_0^g \mathrm{d}g'\ K_{ij}\{c_k, g'\}. \tag{9}$$

Here $c_i' = 1 - c_i$; the first sum is the free energy $F\{c_i, 0\}$ of the non-interacting lattice gas, and keeping in mind the application in section 4 we include in the sums over i and j the terms with $i = j$, i.e. we consider in the Hamiltonian (2) also the 'charge-dependent

potentials' $\varphi_i(g) = g v_{ii}/2$. To derive equation (9) we can differentiate over g the expression $\Omega\{\lambda_i, g\}$ given by equation (4) with $v_{ij}(g) = g v_{ij}$. According to equations (5), (6), the partial derivative $(\partial\Omega/\partial g)_{\lambda_i}$ at fixed λ_i is equal to the derivative $(\partial F/\partial g)_{c_i}$ at fixed c_i. Integrating the resulting relation over g from $g = 0$, we obtain equation (9).

Equations (8) and (9) can be viewed as an exact and explicit set of equations for the function $F\{c_i\}$. Similar relations for uniform systems have been discussed by a number of authors; see e.g. [19]. However, for the non-uniform systems under consideration, this relation appears to be more useful; see below.

For actual calculations of $F\{c_i\}$ one can use various approximate methods of statistical physics, such as the MFA or cluster expansions [20, 21], as well as the approximations based on equation (9). Below we discuss several such approximate forms of $F\{c_i\}$ which will be used in our calculations.

The simplest approximation is the MFA that neglects all statistical fluctuations and their correlations, i.e. corresponds to neglecting the last term in equation (9). Omitting this term and putting $g = 1$, we obtain the MFA expression for $F\{c_i\}$, to be denoted as F_{MFA}.

The MFA is formally applicable, i.e. fluctuative corrections to the zero-order MFA results are small, when the interaction range of potentials v_{ij} includes a sufficiently large number of sites, N_{int}. Then, a certain perturbation theory for finding such fluctuative corrections has been developed for uniform systems [22], with the formal expansion parameter $1/N_{int}$. Equation (9) is suitable for generalizing this perturbative approach to the non-uniform case. In the MFA applicability region, the last, fluctuative term of (9) is small. Thus to find the correlator $K_{ij}\{c_i, g\}$ in this term we can use in the rhs of equation (8) the zero-order expression $F^{(0)} = F_{MFA}\{c_i, g\}$. Taking the integral over g' and putting $g = 1$, we obtain the 'mean-field-with-fluctuations' expression F_{MFf}, that includes the first-order fluctuative correction F_{1f} to the zero-order MFA result:

$$F_{MFf}\{c_i\} = F_{MFA} + F_{1f} \tag{10}$$

$$F_{1f}\{c_i\} = T \frac{1}{2} \mathrm{Tr} \ln(1 + \hat{z}\beta\hat{v}\hat{z}^{-1}) \tag{11}$$

where the matrix elements of the operators $\hat{z}$ and $\hat{v}$ are: $(\hat{z})_{ij} = \delta_{ij}/c_i c'_i$ and $(\hat{v})_{ij} = v_{ij}$. For the uniform case, the operator $\hat{z}$ becomes the scalar $1/cc'$, the operator $v_{ij} = v(\mathbf{r}_i - \mathbf{r}_j)$ can be diagonalized by the Fourier transformation: $v_{\mathbf{k},\mathbf{k}'} = \delta_{\mathbf{k},\mathbf{k}'} v(\mathbf{k})$ with $v(\mathbf{k}) = \sum_{\mathbf{r}} v(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})$, and the fluctuative correction (11) takes the well-known form given, e.g., in [22].

The higher-order fluctuative corrections not included in equation (10) are formally proportional to $1/N_{int}^2$, and thus they may be supposed to be small. However, calculations for uniform systems [22] have shown that the convergence of such expansions in $1/N_{int}$ is usually slow, and the first-order correction (11) usually overestimates the fluctuative contribution, particularly in the critical region which in alloys corresponds to the vicinity of spinodals.

To more accurately describe the thermodynamics of alloys, more refined, cluster-type approaches have been elaborated, such as the well known cluster-variation method (CVM)—see e.g. [23]—and also its simplified version—the cluster-field method (CFM) [20, 21]. These approaches consider the interactions and fluctuations within each cluster with no approximations, but the interactions of clusters with their surroundings are treated approximately, with the use of some self-consistent fields. The great wealth of experience with cluster calculations for both model and real systems shows that these approaches usually have sufficient accuracy, particularly when sufficiently large clusters are employed.

Until now the cluster methods have been used mainly for uniform systems or for specific non-uniform problems of high symmetry, such as that of planar antiphase boundaries [24, 25]. However, the CFM is easily generalized to the case of arbitrary non-uniform systems. In particular, in the simplest, pair-cluster approximation (PCA) the general expressions for the free energy $F = F_{PCA}\{c_i\}$ and its second derivative can be explicitly written out using the results of [20, 21]:

$$\beta F_{PCA}\{c_i\} = \sum_i (c_i \ln c_i + c'_i \ln c'_i) + \sum_{i>j}[2c_i \ln(1 - c_j g_{ij}) - \ln(1 - c_i c_j g_{ij})] \tag{12}$$

$$\beta\, \partial^2 F_{PCA}/\partial c_i\, \partial c_j = (\hat{K}_{PCA}^{-1})_{ij} = \delta_{ij} a_{ii} - f_{ij}/R_{ij}. \tag{13}$$

Here g_{ij} and R_{ij} are expressed via the Mayer function $f_{ij} = \exp(-\beta v_{ij}) - 1$ as follows:

$$g_{ij} = 2f_{ij}/[R_{ij} + 1 + f_{ij}(c_i + c_j)] \qquad R_{ij} = [1 + 2f_{ij}(c_i c'_j + c'_i c_j) + f_{ij}^2(c_i - c_j)^2]^{1/2} \tag{14}$$

while $a_{ii} = \beta\, \partial^2 F/\partial c_i^2$ is

$$a_{ii} = \frac{1}{c_i c'_i} + \sum_j \frac{4 f_{ij}^2 c_j c'_j}{R_{ij}[(R_{ij} + 1)^2 - f_{ij}^2(c_i - c_j)^2]}. \tag{15}$$

Equations (12)–(15) show, in particular, that the effects of the interactions v_{ij} are described in the cluster approximations using the Mayer functions f_{ij} rather than using the parameters βv_{ij} characteristic of the MFA relations (10), (11). Therefore, when the βv_{ij}-values are not small (for example, when strong competing interactions are present [20, 21]), the cluster approaches can significantly refine the MFA, while at $\beta v_{ij} \ll 1$, the PCA results (12)–(15) reduce to those of the MFA.

The cluster approaches take into consideration only the part of the correlative contributions that corresponds to the intra-cluster correlations. In particular, the PCA takes into account only the pair correlations and neglects the many-site ones. Thus one may expect that if one puts in equation (9) the PCA result for the correlator K_{ij}, the resulting F will also include some part of the 'inter-site' correlations, and thus it can be more accurate than both F_{MFA} and F_{MFf} in equation (10). The result of such a substitution will be referred to as the 'pair-cluster-with-fluctuations' approximation F_{PCf}:

$$F_{PCf}\{c_i\} = T \sum_i (c_i \ln c_i + c'_i \ln c'_i) + \sum_{i>j} v_{ij} c_i c_j + \sum_{i>j} v_{ij} \int_0^1 dg\ (\hat{K}_{PCA})_{ij}\{c_i, g\}. \tag{16}$$

The above-discussed expressions F_{MFA}, F_{MFf}, F_{PCA}, and F_{PCf} can be viewed as a series of successive approximations for $F\{c_i\}$ in which fluctuative effects are treated at various levels of sophistication. However, the accuracy of each of such treatments is generally not clear, and applying them to concrete problems may help us to assess this accuracy. The applications to the nucleation problem described in II seem to show that in the cases for which the fluctuative effects are important—and, in particular, when the degree of inhomogeneity of the system is high—the accuracy of the above-discussed approximations usually rises in the sequence MFf, MFA, PCA, and PCf, while employing the simple MFA can lead to significant differences from the more accurate PCA-based approaches.

3. Microscopical description of the critical embryo

In what follows we consider the uniform disordered alloy $A_c B_{1-c}$ quenched into the metastability region $T_s(c) < T < T_b(c)$. For definiteness we suppose the value of the

concentration c to be lower than that at the critical point (c_c, T_c); thus $c > c_b(T)$. The supersaturation of the metastable state can be conveniently characterized with its reduced value s defined as

$$s = \frac{c - c_b(T)}{c_s(T) - c_b(T)} \tag{17}$$

where $c_s(T)$ is the concentration value at the spinodal. As c varies between the binodal and the spinodal, the value of s varies between zero and unity.

We shall investigate the evolution of the near-critical embryos, neglecting their interaction with each other. This entails assuming that their density is low, which corresponds to low values of the supersaturation s. The validity region for the approach used will be discussed in more detail in II. The number of sites N_e within the embryo is assumed to be large; the quantitative estimates given in II show that the relation $N_e \gg 1$ usually holds for all values of c, T of physical interest. We also suppose the total amount of the new, A-rich phase within the metastable one to be small, i.e. we consider only the initial stage of the nucleation process.

The kinetic aspects of nucleation will be discussed using the master equation approach to the alloy kinetics described in reference [14]. In particular, the time evolution of local concentrations will be described using the kinetic equation that corresponds to the mean-field or the cluster-field approximation of this approach:

$$\frac{dc_i}{dt} = 2 \sum_j M_{ij} \sinh\left[\frac{\beta}{2}\left(\frac{\partial F}{\partial c_j} - \frac{\partial F}{\partial c_i}\right)\right] \tag{18}$$

where M_{ij} is the generalized mobility for which explicit expressions are presented in II.

Following the ideas of classical theory [5], we consider the state with the critical embryo as the non-uniform alloy state for which the occupations c_i obey the local equilibrium conditions (7); thus the rhs of equation (18) vanishes for this state. However, the equilibrium is unstable with respect to growth of the embryo, i.e. with respect to variations of a certain variable $a = a\{c_i\}$ that characterizes its size.

In the microscopical approach, the stationarity equations (7) imply that the state with the critical embryo corresponds to the extremum point $c_i = c_i^s$ in the c_i-space for the function $\Omega\{c_i\} = F\{c_i\} - \mu N$: $(\partial\Omega/\partial c_i)_\mu = 0$, where $N = \sum_i c_i$. Near this point, $\Omega\{c_i\}$ varies quadratically with the differences $\delta c_i = c_i - c_i^s$:

$$\Delta\Omega = \Omega\{c_i\} - \Omega\{c_i^s\} = \frac{1}{2} \sum_{ij} F_{ij} \, \delta c_i \, \delta c_j \tag{19}$$

where $F_{ij} = \partial^2 F/\partial c_i \, \partial c_j$.

Making the linear transformation

$$\delta c_i = \sum_k A_{ik} \, \delta u_k \qquad \delta u_k = \sum_i A_{ik} \, \delta c_i \tag{20}$$

with the real coefficients A_{ik} obeying the unitarity condition

$$\sum_i A_{ik} A_{il} = \delta_{kl} \tag{21}$$

we reduce (19) to the diagonal form

$$\Delta\Omega = \frac{1}{2} \sum_k \gamma_k (\delta u_k)^2 \tag{22}$$

where γ_k are the eigenvalues of the matrix F_{ij}. The instability of the critical embryo with respect to its growth implies that the lowest eigenvalue γ_0 in (22) is negative, i.e. the

extremum of $\Omega\{c_i\}$ at $c_i = c_i^s$ is the saddle point [3]. The 'critical' variable δu_0 evidently describes the size of the embryo. Therefore, this variable provides the microscopical generalization for the 'embryo radius variation' $a - a_c$ of the classical theory [5], while the saddle point value $u_0 = u_0^s$ corresponds to the critical size a_c.

As was mentioned by Langer [12], the transformation (20) should also include the 'translational' variables $\delta u_1, \delta u_2, \delta u_3$ (denoted below as $\delta\boldsymbol{u}$) describing the position of the embryo—e.g. that of its centre $\boldsymbol{R} = (R_1, R_2, R_3)$. Under the full translational invariance, for example, for liquids or vapours, the relevant eigenvalues γ_α in (22) with α equal to 1, 2 or 3 should vanish. For the crystal alloy these γ_α are generally non-zero and depend on the position $\boldsymbol{R}$ in the crystal elementary cell. However, for the large embryos under consideration, the values of γ_α are quite low; our calculations described in II yield $|\beta\gamma_{1,2,3}| \lesssim 10^{-4}\text{--}10^{-3}$. Thus both for alloys and for liquids or vapours one can put $\gamma_{1,2,3} = 0$ and treat the translational motion of the embryo as barrierless diffusion.

Therefore, the embryo is characterized by its size $a = u_0$ and its position $\boldsymbol{R} = \boldsymbol{R}(\boldsymbol{u})$. The rest variables u_k with $k \geqslant 4$ in the state with the embryo are supposed to have the saddle point values $u_k = u_k^s$—that is, $\delta u_k = 0$, which corresponds to the local equilibrium conditions (7).

4. The size distribution function for embryos

Following the work described in [5], to find the nucleation rate J in equation (1) we should first find the probability of forming the state with the critical embryo due to statistical fluctuations in the metastable state treated as the equilibrium one (i.e. neglecting its actual non-stationarity). This is done in the present section. The second problem, the embryo growth kinetics, will be considered in the next section.

The probability $\mathrm{d}w(a, \boldsymbol{R})$ of finding the system within the group of microscopical states under consideration, i.e. the states in which an embryo of size a with its centre located within the volume d^3R near the point $\boldsymbol{R}$ is present, is proportional to the sum of the Gibbs probabilities taken under the condition that each of microscopical variables $\hat{u}_\alpha = \sum_i A_{i\alpha} n_i$ with α equal to 0, 1, 2 or 3 has the fixed value u_α. If we define the distribution function $f_0(a, \boldsymbol{R})$ by the standard relation

$$\mathrm{d}w(a, \boldsymbol{R}) = f_0(a, \boldsymbol{R})\,\mathrm{d}a\,\mathrm{d}^3R \tag{23}$$

then we should also pass from the above-mentioned variables $\boldsymbol{u}(\boldsymbol{R})$ to the coordinate $\boldsymbol{R}$ using the Jacobian

$$D_R(\boldsymbol{u}) = \frac{D(u_1, u_2, u_3)}{D(R_1, R_2, R_3)}. \tag{24}$$

Therefore, the microscopical expression for the distribution function $f_0(a, \boldsymbol{R})$ is

$$f_0(a, \boldsymbol{R}) = \sum_{\{n_i\}} \exp\left[\beta\left(\Omega + \mu\sum_i n_i - H\right)\right] \prod_{\alpha=0}^{3} \delta\left(u_\alpha - \sum_i A_{i\alpha} n_i\right) D_R(\boldsymbol{u}) \tag{25}$$

where $u_\alpha = \sum_i A_{i\alpha} c_i$. To perform the summation over states $\{n_i\}$ in equation (25), it is convenient to write each δ-function as a Gaussian:

$$\delta(\hat{u}_\alpha - u_\alpha) = \lim_{\xi_\alpha \to 0} (\pi\xi_\alpha)^{-1/2} \exp[-(\hat{u}_\alpha - u_\alpha)^2/\xi_\alpha]. \tag{26}$$

After substitution of (26) into equation (25) we obtain

$$f_0(a, \boldsymbol{R}) = \prod_\alpha (\pi\xi_\alpha)^{-1/2} \exp\left(\beta\Omega - \sum_\alpha u_\alpha^2/\xi_\alpha\right) D_R(\boldsymbol{u}) Z_\xi. \tag{27}$$

The sums and products over α here and below include terms with α varying from 0 to 3, while the factor Z_ξ has the form of a statistical sum:

$$Z_\xi = \sum_{\{n_i\}} \exp\left[\beta \sum_i \lambda_i^\xi n_i - \frac{1}{2}\beta \sum_{ij}(v_{ij} + v_{ij}^\xi)n_i n_j\right] \qquad (28)$$

with the 'potentials' λ_i^ξ and the 'additional interactions' v_{ij}^ξ of the form

$$\lambda_i^\xi = \mu + 2T \sum_\alpha u_\alpha A_{i\alpha}/\xi_\alpha \qquad v_{ij}^\xi = 2T \sum_\alpha A_{i\alpha} A_{j\alpha}/\xi_\alpha. \qquad (29)$$

To get an idea of the character of the interactions v_{ij}^ξ in (29), we note that according to the physical meaning of equations (20) for $k = 0, 1, 2, 3$ (illustrated by our calculations in II), the quantities $A_{i\alpha}$ vary rather smoothly with the position of the site i, having broad maxima near the boundaries of the embryo and vanishing outside of it. As the embryo includes the great number of sites N_e, equation (21) implies that the values $A_{i\alpha} \sim N_e^{-1/2}$ are small, while the number of sites N_ξ within the interaction range of the potential v_{ij}^ξ is large: $N_\xi \sim N_e \gg 1$. Therefore, if we take the auxiliary small parameters ξ_α in (27) to be, say, of the order of $N_e^{-\delta}$ with $0 < \delta < 1$, interaction (29) obeys the conditions for the applicability of the perturbative self-consistent-field method [22] whose zeroth approximation is the MFA: $|\beta v_{ij}^\xi| \ll 1$, $N_\xi \gg 1$.

The MFA corresponds to neglecting the interaction of fluctuations $v_{ij}^\xi(n_i - c_i)(n_j - c_j)$ in the 'Hamiltonian' of equation (28) (see e.g. [22]):

$$\sum_{ij} v_{ij}^\xi n_i n_j \simeq \sum_{ij} v_{ij}^\xi (n_i c_j + c_i n_j - c_i c_j). \qquad (30)$$

In accordance with equations (30), (9), the zero-order MFA contribution of the terms with v^ξ to the free energy

$$F_\xi = \Omega_\xi + \sum_i \lambda_i^\xi c_i \qquad (31)$$

(where $\Omega_\xi = -T \ln Z_\xi$) has the form

$$F_\xi\{c_i\} = F\{c_i\} + \sum_\alpha \sum_{ij} A_{i\alpha} A_{j\alpha} c_i c_j/\xi_\alpha. \qquad (32)$$

Here $F\{c_i\}$ is the true free energy that corresponds to the interaction v_{ij}.

However, in the exponent in equation (27) these MFA terms combine with the other terms proportional to $1/\xi_\alpha$ to form the expressions $(u_\alpha - \sum_i A_{i\alpha} c_i)^2/\xi_\alpha$ that vanish according to the definition of u_α in equation (25). The finite contribution arises only from the first fluctuative correction in v_{ij}^ξ (that has formally the next order in $1/N_e$), i.e. from the relevant contribution to the last term of equation (9):

$$F_\xi^f = \frac{1}{2} \int_0^1 dg \sum_{ij}(v_{ij} + v_{ij}^\xi)K_{ji}^\xi(g). \qquad (33)$$

The correlator K_{ij}^ξ in this first-order correction can be found using equation (8) with the zero-order expression (32) for the free energy F_ξ:

$$\{[K^\xi(g)]^{-1}\}_{ij} = \beta F_{ij}(g) + 2g \sum_\alpha A_{i\alpha} A_{j\alpha}/\xi_\alpha \qquad (34)$$

where $F_{ij}(g)$ is $\partial^2 F(g)/\partial c_i \, \partial c_j$ with $F(g)$ found for the interaction $g v_{ij}$.

The rhs of equation (33) has the form of a matrix product trace that can be conveniently calculated in the representation of eigenmodes u_k defined by equation (20). Solving equation

(34) for the correlator K_{ij}^{ξ} in the small-ξ_{α} limit and substituting the result into equation (33), we can write F_{ξ}^{f} as

$$F_{\xi}^{f} = F_{r}^{f} + \sum_{\alpha} I_{\alpha} \tag{35}$$

Here F_{r}^{f} is the 'reduced' fluctuative term that does not include the contributions of the fluctuations of variables u_0 and $\boldsymbol{u}$:

$$F_{r}^{f} = \frac{1}{2} \int_{0}^{1} \mathrm{d}g \sum_{m \geqslant 4} v_{mm}(g) \frac{1}{\beta \gamma_{m}(g)} \tag{36}$$

where $\gamma_{m}(g)$ are the eigenvalues of the matrix $\hat{F}^{\mathrm{p}}(g)$, the projection of the matrix $\hat{F}(g)$ in (34) onto the subspace of variables u_k, u_l with $k, l \geqslant 4$:

$$F_{kl}^{\mathrm{p}}(g) = \sum_{ij} A_{ik} F_{ij}(g) A_{jl} \tag{37}$$

while $v_{mm}(g)$ is the diagonal element of the interaction matrix $\hat{v}$ over the eigenvectors corresponding to the eigenvalue $\gamma_{m}(g)$.

The terms I_{α} in (35) include the matrix

$$F_{\alpha\beta}(g) = \sum_{ij} A_{i\alpha} F_{ij}(g) A_{\beta j} \tag{38}$$

with $0 \leqslant \alpha, \beta \leqslant 3$. Let us for simplicity suppose this matrix to be diagonal (which is the case for crystal lattices of a high symmetry such as the FCC or BCC ones discussed in II): $F_{\alpha\beta}(g) = F_{\alpha\alpha}(g) \delta_{\alpha\beta}$. Then I_{α} can be written as

$$I_{\alpha} = \int_{0}^{1} \mathrm{d}g \, \frac{1}{\xi_{\alpha} \beta F_{\alpha\alpha}(g) + 2g}. \tag{39}$$

For the small ξ_{α} under consideration, only the small-g limit of the function $F_{\alpha\alpha}(g)$ is significant in the integral (39). Denoting for brevity the matrix $\beta F_{ij}(0) = \delta_{ij}/c_i c_i'$ as z_{ij}, we obtain

$$I_{\alpha} = \frac{1}{2} \ln \frac{2}{\xi_{\alpha} z_{\alpha\alpha}} \tag{40}$$

where

$$z_{\alpha\alpha} = \sum_{ij} A_{i\alpha} z_{ij} A_{j\alpha} = \sum_{i} A_{i\alpha}^2 / c_i c_i'. \tag{41}$$

Using equations (29), (31), (32), (35) and (40), we see that the auxiliary factors ξ_{α} in equation (27) cancel, and the final expression for the distribution function f_0 is

$$f_0(a, \boldsymbol{R}) = \mathcal{N} \exp(-\beta \, \Delta\Omega) D_{\boldsymbol{R}}(\boldsymbol{u}). \tag{42}$$

Here $\mathcal{N}$ is an analogue of the normalizing constant of the conventional thermodynamic fluctuation theory (see section 110 of [2]):

$$\mathcal{N} = \prod_{\alpha=0}^{3} \left(\frac{z_{\alpha\alpha}}{2\pi} \right)^{1/2} \tag{43}$$

$\Delta\Omega = \Delta\Omega\{c_i\}$ in (42) is the grand canonical potential difference

$$\Delta\Omega\{c_i\} = \Omega\{c_i\} - \Omega(c) = \frac{1}{2} \gamma_0 (a - a_c)^2 + F_r\{c_i\} - F(c) - \mu(c) \sum_{i} (c_i - c). \tag{44}$$

$F_r\{c_i\}$ is the 'reduced' free energy that does not include the contributions of fluctuations of the size a and the position $\boldsymbol{R}$ of the embryo, and has the form

$$F_r\{c_i\} = F_{\mathrm{MFA}}\{c_i\} + F_r^f. \tag{45}$$

$F_{\mathrm{MFA}}\{c_i\}$ is the MFA expression

$$F_{\mathrm{MFA}}\{c_i\} = T \sum_i (c_i \ln c_i + c_i' \ln c_i') + \frac{1}{2} \sum_{ij} v_{ij} c_i c_j \tag{46}$$

and the fluctuative contribution F_r^f is given by equation (36). $F(c)$ is the free energy of the initial metastable state which is given by the general expression (9) with all c_i equal to the initial concentration c, while $\mu(c)$ is the chemical potential of this metastable state, equal to the derivative $N_s^{-1} \partial F(c)/\partial c$ where N_s is the total number of lattice sites.

When the matrix $F_{\alpha\beta}(g)$ in equation (38) is non-diagonal (which can occur for low-symmetry crystal lattices, such as the monoclinic ones), the product of four $z_{\alpha\alpha}$ in equation (43) is replaced by the determinant of the matrix $\beta F_{\alpha\beta}(0) = z_{\alpha\beta}$, where

$$z_{\alpha\beta} = \sum_i A_{i\alpha} A_{i\beta} / c_i c_i'. \tag{47}$$

5. The microscopical expression for the nucleation rate

Now we have to consider the kinetics of growth, i.e. the temporal evolution of the embryo sizes a. Zeldovich [5] treated the problem using the phenomenological kinetic equation for the size distribution function $f(a, t)$. In the microscopical approach, it is convenient to consider the probability $\rho\{c_i, t\}$ of finding the set of local concentrations $\{c_i\}$ in the alloy state under consideration. Note that if the state is described by the probability distribution (4) with a definite set $\{\lambda_i\}$, the set $c_i = c_i\{\lambda_j\}$ would be determined uniquely:

$$\rho\{c_i\} = \text{constant} \times \prod_i \delta[c_i - c_i\{\lambda_j\}].$$

However, the non-equilibrium alloy states can usually be characterized only in much less detail, via some small number of mesoscopic characteristics $\{q_\alpha\}$, such as the embryo size and position in our problem. Therefore, for an actual non-equilibrium alloy the probability distribution $\rho\{c_i\}$ is smooth and non-singular.

The function ρ should obey the probability conservation equation

$$\frac{\partial \rho}{\partial t} + \sum_i \frac{\partial J_i}{\partial c_i} = 0 \tag{48}$$

where $J_i = J_i\{c_j\}$ is the probability flow in the c_i-space. Let us discuss the expression for J_i. It should include the convective part $J_i^c = \rho \dot{c}_i$ that describes the 'drift' probability flow, and the diffusional term J_i^d that corresponds to the relaxation of the inhomogeneities of $\rho\{c_i\}$ in the c_i-space, and thus should be proportional to the derivatives $\partial \rho/\partial c_i$, $\partial^2 \rho/\partial c_i \partial c_j$, etc. Physically, the diffusion is realized via the atomic jumps between neighbouring lattice sites. The alloy states under consideration are characterized by the mesoscopic variables $q_\alpha\{c_i\}$ which are additive in c_i. As relative changes of such additive variables under each jump are small, one can retain in J_i^d just the first-order derivatives $\partial \rho/\partial c_i \sim (\partial \rho/\partial q_\alpha)(\partial q_\alpha/\partial c_i)$ and neglect the higher-order ones. Then the probability flow J_i takes a 'Focker–Planck' form similar to that used in [5]:

$$J_i = \rho \dot{c}_i - \sum_j D_{ij} \partial \rho/\partial c_j \tag{49}$$

where D_{ij} is the diffusivity in the c_i-space.

For the time derivative $\dot{c}_i$ in (49), we use the kinetic equation (18) which appears to be sufficient for most applications of interest [14]. When the difference $\partial F/\partial c_i - \partial F/\partial c_s$ in equation (18) is small—in particular, for alloy states close to the locally equilibrium one described by equations (7)—the kinetic equation becomes linear in $\partial F/\partial c_j$:

$$\dot{c}_i = \sum_j \left[M_{ij} - \delta_{ij} \sum_k M_{ik} \right] \beta \, \partial F/\partial c_j. \tag{50}$$

The diffusivity D_{ij} in equation (49) can be related to the mobilities M_{ij} in equation (50) via a generalized Einstein relation similar to that used by Zeldovich [5]. To derive it, we consider the probability distribution ρ that corresponds to the full statistical equilibrium. In this case the function $\rho = \rho_0\{c_i\}$ does not change over time, and the probability flow J_i (49) should vanish:

$$\rho_0 \dot{c}_i - \sum_j D_{ij} \, \partial \rho_0/\partial c_j = 0. \tag{51}$$

Let us apply equation (51) to the non-equilibrium state characterized by some set of mesoscopic variables $q_\alpha\{c_i\}$. Using the same arguments as in the derivation of equation (42) we again obtain for $\rho_0\{c_i\}$ the expression

$$\rho_0\{c_i\} = A \exp[-\beta\Omega\{c_i\}] \tag{52}$$

where the prefactor A varies under variations of q_α much more slowly than the exponent as the latter, unlike the prefactor, is additive in the variables c_i. Thus in finding the derivatives $\partial \rho_0\{q_\alpha\}/\partial c_j$ in equation (51), the c_i-dependence of A can be neglected. Taking into account that for the constant-chemical-potential case under consideration the derivatives $\partial F/\partial c_j$ differ from $\partial\Omega/\partial c_j$ only by the constant μ which cancels in equation (50), we obtain from equations (50)–(52) the generalized Einstein relation between D_{ij} and M_{ij}:

$$D_{ij} = \delta_{ij} \sum_k M_{ik} - M_{ij}. \tag{53}$$

In the further derivation we can closely follow the Zeldovich arguments [5]. The equilibrium function (25) correctly describes the size distribution only for undercritical embryos whose sizes a are not close to the critical one a_c. For the near-critical embryos, the distribution should be found with the use of the kinetic equation (48). The early stages of nucleation under consideration correspond to the constant-probability flow J through the saddle point $a = a_c$ in the c_i-space, while the function ρ in equation (49) can be supposed not to change over time and to depend only on the embryo size $a = u_0$ defined by equation (20) with $k = 0$. So one can obtain the equation for the distribution function $f(a)$ by substituting $\rho = f(a)$ in equation (49) for $J = J_a = \sum_i A_{i0} J_i$. Using also the arguments regarding the vanishing of the ratio $f(a)/f_0(a)$ at large a [5], we get the following relation for $f(a)$:

$$\frac{f(a)}{f_0(a)} = J \int_a^\infty \frac{\mathrm{d}a'}{D_{aa} f_0(a')}. \tag{54}$$

Here $D_{aa} = D_{00}$ is the tensor D_{ij}-component that describes the diffusion along the $u_0 = a$ direction in the c_i-space:

$$D_{aa} = \sum_{ij} A_{i0} \left(\delta_{ij} \sum_k M_{ik} - M_{ij} \right) A_{j0} \tag{55}$$

where we have used equation (53) to express D_{ij} in terms of the mobilities M_{ij}.

At small sizes a the ratio f/f_0 should approach unity [5], so the flow J can be expressed via the full integral over a' in equation (54). Taking into consideration the fact that the main contribution to the integral is made by the a'-values in the vicinity of the critical size a_c [5], we obtain the Zeldovich–Volmer expression (1) for the nucleation rate J. The nucleation barrier $\Delta\Omega_c$ in that relation is given by the expression (44) for the saddle point values $c_i = c_i^s$ that correspond to the critical embryo:

$$\Delta\Omega_c = \Delta\Omega\{c_i^s\} \tag{56}$$

and the prefactor J_0 is

$$J_0 = \left(\frac{\beta|\gamma_0|}{2\pi}\right)^{1/2} D_{aa}\mathcal{N}D_R(\boldsymbol{u}). \tag{57}$$

Here γ_0 is the same as in equation (22), while D_{aa}, $\mathcal{N}$, and $D_R(\boldsymbol{u})$ are given by equations (55), (43), and (24) for $c_i = c_i^s$.

Let us make a remark on the accuracy of the expressions (56) and (57) for the parameters $\Delta\Omega_c$ and J_0 in equation (1). In the calculations of the exponent $\Delta\Omega_c$ we employed the standard methods of statistical physics, neglecting terms of the order of unity as compared to the additive contributions proportional to N_e. Therefore, expression (57) for the prefactor J_0 holds true, strictly speaking, only up to the factor of the order of unity. However, this expression includes all of the physically significant factors of the problem, and describes properly their dependence on the supersaturation and the temperature.

Equations (56) and (57) provide the microscopical expression for the Zeldovich–Volmer relation (1). Using for the free energy $F\{c_i\}$ and the mobility M_{ij} in these equations the approximate expressions described in section 2 and in reference [14], we can calculate the nucleation rate for various alloy models. Such calculations and their physical implications are discussed in II.

6. Conclusions

Let us summarize the main results of this work. The earlier-developed master equation approach to the configurational kinetics of non-equilibrium alloys [14] is used to obtain the microscopical expression for the nucleation rate at the first stages of homogeneous nucleation in metastable alloys. To this end we present some exact and approximate relations for the free energy of a non-uniform alloy $F\{c_i\}$ that can also be applied to other non-uniform problems. In the treatment of nucleation we adopt the main ideas and assumptions of the phenomenological theory given in [5] and derive the microscopical expressions for all of the parameters that enter this theory. The alloy state with the critical embryo corresponds to the saddle point of the function $\Omega\{c_i\}$, equation (19), in the multi-dimensional space of local concentrations c_i. The concentrational modes corresponding to variations of the size a and the position $\boldsymbol{R}$ of the embryo are described in terms of the eigenvectors of the matrix $F_{ij} = \partial^2 F/\partial c_i\,\partial c_j$ at the saddle point. These ideas are used to derive the explicit expression (42) for the embryo size distribution function $f_0(a, \boldsymbol{R})$ in the metastable state treated as the equilibrium one. The other parameter of the phenomenological theory [5], the diffusivity D_{aa} in the embryo size space, is obtained with the use of the earlier-suggested kinetic equation for local concentrations [14], as well as the generalized Einstein relation (53) between the mobility M_{ij} entering the kinetic equation and the diffusivity D_{ij} in the c_i-space. The final equations (56) and (57) provide the microscopical expressions for the nucleation barrier $\Delta\Omega_c$ and the prefactor J_0 in the phenomenological Zeldovich–Volmer

relation (1) for the nucleation rate J. Applications of these results to calculations of J for various alloy models are described in the following paper [11].

Acknowledgments

References

 [1] Gibbs J W 1948 *Collected Works* vol 1 (New Haven, CT: Yale University Press) pp 105–15, 252–8
 [2] Landau L D and Lifshitz E M 1976 *Statistical Physics* (Moscow: Nauka) §162
 [3] Cahn J W and Hilliard J E 1959 *J. Chem. Phys.* **31** 688
 [4] Cahn J W 1961 *Acta Metall.* **9** 795
 [5] Zeldovich Ya B 1942 *Zh. Eksp. Teor. Fiz.* **12** 525
      Lifshitz E M and Pitaevsky L P 1979 *Physical Kinetics* (Moscow: Nauka) §99
 [6] Gunton J D, San Miguel M and Sahni P 1983 *Phase Transitions and Critical Phenomena* vol 8, ed C Domb
      and J L Lebowitz (London: Academic) pp 269–466
 [7] Oki K, Sagane H and Eguchi T 1977 *J. Physique Coll.* **38** C7 414
 [8] Tanaka H, Yokokawa T, Abe H, Hayashi H and Nishi T 1990 *Phys. Rev. Lett.* **65** 3136
 [9] Trinkaus H 1983 *Phys. Rev.* B **27** 7372
[10] Shi G and Seinfield J H 1990 *J. Chem. Phys.* **93** 9033
[11] Dobretsov V Yu and Vaks V G 1998 *J. Phys.: Condens. Matter* **10** 2275
[12] Langer J S 1969 *Ann. Phys., NY* **54** 228
[13] Vaks V G, Beiden S V and Dobretsov V Yu 1995 *Pis. Zh. Eksp. Teor. Fiz.* **61** 65 (Engl. Transl. 1995 *JETP
      Lett.* **61** 68)
[14] Vaks V G 1996 *Pis. Zh. Eksp. Teor. Fiz.* **63** 447 (Engl. Transl. *JETP Lett.* **63** 471)
[15] Dobretsov V Yu, Martin G, Soisson F and Vaks V G 1995 *Europhys. Lett.* **31** 417
[16] Dobretsov V Yu, Vaks V G and Martin G 1996 *Phys. Rev.* B **54** 3227
[17] Belashchenko K D and Vaks V G 1996 *Phys. Lett.* **222A** 345
[18] Belashchenko K D and Vaks V G 1997 *Zh. Eksp. Teor. Fiz.* **112** 714
[19] Abrikosov A A, Gor'kov L P and Dzyaloshinsky I E 1962 *Methods of Quantum Field Theory in Statistical
      Physics* (Moscow: Nauka) §10
[20] Vaks V G and Orlov V G 1986 *Fiz. Tverd. Tela* **28** 3627
[21] Vaks V G, Zein N E and Kamyshenko V V 1988 *J. Phys. F: Met. Phys.* **18** 1641
[22] Vaks V G, Larkin A I and Pikin S A 1966 *Zh. Eksp. Teor. Fiz.* **51** 361
[23] Sanchez J M, Ducastelle F and Gratias D 1984 *Physica* A **128** 334
[24] Cahn J W and Kikuchi R 1966 *J. Phys. Chem. Solids* **27** 1305
[25] Finel A, Mazauric V and Ducastelle F 1990 *Phys. Rev. Lett.* **65** 1016