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Stochastic description of phase separation near the spinodal curve in alloys

V. Yu. Dobretsov, I. R. Pankratov, V. G. Vaks[1)]

Russian Research Centre "Kurchatov Institute", 123182 Moscow, Russia

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The earlier-developed statistical methods for non-equilibrium alloys are applied to stochastically describe phase separation near the spinodal curve. An important parameter of the theory is the size of locally equilibrium regions which is estimated using simulations for the different values of this parameter. The simulations based on this approach reveal significant changes in the type of evolution from nucleation to spinodal decomposition under variation of concentration and temperature across the spinodal curve. The scale of these changes seems to be mainly determined by the difference of the properly defined supersaturation parameters.

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Studies of microstructural evolution in phase-separating alloys attract interest from both fundamental and applied points of view [1, 2]. Many detailed experimental [2 – 6] and theoretical [1] studies of these problems are available. However, up to now the theoretical approaches seem to provide few information about the microscopical details of evolution [2]. There are two main kinetic forms of phase separation for an initially homogeneous system quenched into the two-phase equilibrium region: nucleation and spinodal decomposition. For definiteness we consider the disordered binary alloy $\mathrm{A}_c\mathrm{B}_{1-c}$. There are two important curves in the concentration-temperature plane c, T: 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 the classical ideas [7, 8], in the metastability region $T_s(c) < T < T_b(c)$ the homogeneous phase separation is realized via nucleation and growth (NG) of isolated precipitates of the new phase, while at $T < T_s(c)$ the main kinetic mechanism is the spinodal decomposition (SD) via the development of unstable concentration waves with growing amplitudes. Taking into account the fluctuative effects (neglected in the classical theories) should result in some smearing of the borderline between these two evolution types in the c, T plane [1], though in the available experiments [3, 5] the transition region was found to be rather narrow. There are some detailed studies of NG at low supersaturation, i.e. near $T_b(c)$ [9, 10], as well as those for SD at high supersaturation, i.e. well below $T_c(c)$ [11, 12]. However, there seems to be "no theoretical approach to describe the behavior in the transition region from SD to NG" [1]. One can also mention the phenomenological treatments of this problem using the "stochastic phase-field equations", e.g., [13], but both the applicability region and the methods of calculations of fluctuative terms in these treatments seem to be unclear and arbitrary.

Recently, the microscopic generalized Gibbs distribution approach (GGDA) [14] has been suggested to study the diffusional kinetics of non-equilibrium alloys. Below we use this approach to describe phase separation near the spinodal curve.

Let us first present the main equations of GGDA disregarding the fluctuative effects. Various distributions of atoms are described by the occupation numbers $\{n_i\}$ where n_i is 1 when the site i is occupied by atom A and 0 otherwise. GGDA is based on the master equation for the probability P to find the number set $\{n_i\} = \xi$,

$$dP(\xi)/dt = \sum_\eta [W(\xi,\eta)P(\eta) - W(\eta,\xi)P(\xi)], \qquad (1)$$

where $W(\xi,\eta)$ is the $\eta \to \xi$ transition probability per unit time for which we use the conventional thermally activated atomic exchange model [14]. As discussed in detail in [14], for the usual conditions of phase transformations the probability P in (1) can be written in the following "quasi-equilibrium" form:

$$P\{n_i\} = \exp\,[\,\beta\,(\Omega + \sum_i \lambda_i n_i - \sum_{i>j} v_{ij} n_i n_j)\,]. \qquad (2)$$

Here β is $1/T$; the parameters λ_i (being, generally, both time- and space-dependent) can be called the "site

[1)]e-mail: vaks@mbslab.kiae.ru

chemical potentials"; quantities v_{ij} describe interatomic interaction supposed to be pairwise; and the constant $\Omega = \Omega\{\lambda_i\}$ is determined by the normalization.

Multiplying equation (1) by the operator n_i and summing over all configurational states, we obtain the "quasi-equilibrium" kinetic equation [14]:

$$dc_i/dt = \sum_j M_{ij}\, 2\sinh[\beta(\lambda_j - \lambda_i)/2]. \qquad (3)$$

Here the mean site occupation c_i corresponds to the averaging of the operator n_i over the distribution (2):

$$c_i = \langle n_i \rangle = \sum_{\{n_j\}} n_i\, P\{n_j\} \qquad (4)$$

and the "generalized mobility" M_{ij} is a similar average of some other function of occupation numbers. To explicitly find the functions $\lambda_i\{c_j\}$ and $M_{ij}\{c_k\}$ in Eqs. (3), (4) we should use some approximate method of calculations. For example, in the simplest, "kinetic mean-field" approximation (KMFA) we obtain [14]:

$$\lambda_i = T\ln(c_i/c_i') + \sum_j v_{ij}c_j; \qquad (5)$$

$$M_{ij} = \gamma_{ij}[c_i c_i' c_j c_j' \exp(\beta u_i + \beta u_j)]^{1/2}, \qquad (6)$$

where c_i' is $(1 - c_i)$, the factor γ_{ij} determines the probability of an inter-site atomic exchange, and u_i is the "asymmetrical potential" supposed below to be zero.

For simplicity we consider disordered cubic alloys at sufficiently high temperatures T not far from the critical temperature T_c, say, $T \gtrsim 0.9\,T_c$. Then the space and time variations of the local concentration $c_i = c(\mathbf{R}_i, t)$ under phase separation are very smooth [8, 10], and Eqs. (3)–(6) can be rewritten in the continuous form [12]:

$$dc/dt = \operatorname{div}[M(c)\beta\nabla\lambda(c)]; \qquad (7)$$

$$\lambda(c) = T\ln(c/c') - 4T_c\left[c + (r_0^2/6)\nabla^2 c\right], \qquad (8)$$

where $M(c)$ is $\gamma cc'$; γ is $\frac{1}{6}\sum_j \gamma_{ij} r_{ij}^2$ with $r_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$; $T_c = (-\sum_j v_{ij}/4)$ is the critical temperature in the MFA used, and $r_0^2 = \sum_j v_{ij} r_{ij}^2 / \sum_j v_{ij}$ is the mean interaction radius squared. If to calculate $\lambda_i\{c_j\}$ and $M_{ij}\{c_k\}$ in Eqs. (3), (4) we use a more refined method than KMFA (e. g., kinetic cluster methods [14]), the basic equation (7) retains its form but functions $\lambda(c)$ and $M(c)$ are given by some more complex expressions. This difference is unessential for what follows.

Let us go over to a discrete description dividing the lattice into the cubic cells of size L (L-cells). To this end we (i) sum Eq. (7) over all sites j within the cell centered at $\mathbf{R}_i$ ("cell i") obtaining in the left-hand side $d\bar{N}_i/dt$ where $\bar{N}_i$ is $\sum_j c_j$; (ii) transform the right-hand side (rhs) of (7) into surface integrals over six facets s of cell i; and (iii) integrate the result over a small time interval δt. Then (7) takes the "finite difference" form:

$$\delta\bar{N}_i = \sum_{s=1}^{6} (L^2/v_a)\, \mathbf{n}_s\, \beta(M\nabla\lambda)_s\, \delta t. \qquad (9)$$

Here v_a is the volume per site; $\mathbf{n}_s$ is the unit vector normal to the facet s directed off the cell i; and the gradient term $\nabla\lambda$ is written as the appropriate finite difference. The mesh size L in (9) should be lower than the smallest inhomogeneity length which in our problem is the interphase boundary width, while employing the larger L is convenient for computations. In our simulations we used $L \gtrsim a$ where a is the face-centred cubic (FCC) lattice constant.

Let us now discuss the relation between the quantities c_i or $\bar{N}_i$ in (4) or (9) and the concentration distribution $c_{\rm obs}(\mathbf{R}, t)$ observed experimentally. Note that the GGDA, being a statistical approach based on "ensemble averages" $c_i = \langle n_i \rangle$, is physically informative and complete only for the "macroscopically" non-equilibrium system ([7], § 7) that can be divided into some locally equilibrated subsystems with the size $l_{\rm le}$ much exceeding the interatomic distance a. Within each subsystem the site chemical potential λ_i in (2) is approximately constant, and its fluctuations have a relative scale $(a/l_{\rm le})^{3/2} \ll 1$. Therefore, the summation over alloy states in Eq. (4) should include not all distributions $\{n_i\}$ but only those with the limited inhomogeneity lengths $l < l_{\rm le}$, while the long-wave fluctuations with $l \gtrsim l_{\rm le}$ remain to be fixed in the macroscopically non-equilibrium state under consideration. Therefore, the "diffusive" term in the rhs of Eqs. (7) or (9) corresponds just to a "coarse-grained" averaging in (4) performed at the fixed distribution of these long-wave fluctuations, and the terms allowing for their dynamics should also be considered to describe $c_{\rm obs}(\mathbf{R}, t)$. These fluctuative terms were neglected in the previous GGDA-based treatments of phase transformations [14] as usually they have little effect on evolution. However, for the phase separation above and near the spinodal curve the presence of such terms is crucial.

We describe these fluctuative terms using the stochastic Langevin-type approach. To this end we proceed from the average $\bar{N}_i = \sum_j c_j$ in Eq. (9) to an "individual phase trajectory", that is to the actual atom number $N_i(t) = \sum_j n_j$ within each L-cell. It differs from the average $\bar{N}_i(t)$ due to the fluctuations of the atomic transfer δN_{fs} across each facet s for the time interval δt. Therefore, instead of Eq. (9) we have:

$$\delta N_i \equiv N_i(t + \delta t) - N_i(t) = \delta N_{di}\{c_j\} + \delta N_{fi}, \qquad (10)$$

where the diffusive term δN_{di} is given by the rhs of Eq. (9) and the fluctuative term δN_{fi} is $\sum_s \delta N_{fs}$.

Following the Langevin's idea [15] we treat each fluctuative transfer δN_{fs} as a random quantity with the Gaussian probability distribution $W(\delta N_{fs})$:

$$W(\delta N_{fs}) = A_s \exp(-\delta N_{fs}^2/2D_s), \qquad (11)$$

where A_s is the normalization constant and the dispersion D_s is the same as that for the actual fluctuative transfer δN_{fs}. For example, for the nearest-neighbor atomic exchange model with γ_{ij} in (6) equal to γ_{nn}, the KMFA calculation of D_s yields:

$$D_s = \langle \delta N_{fs}^2 \rangle = \gamma_{nn} \delta t\, N_b\, 2c_s(1-c_s) \qquad (12)$$

where N_b is the total number of bonds crossed by each facet s. For the FCC lattice, N_b is $8L^2/a^2$, while the number of sites N_L within an L-cell is $4L^3/a^3$.

Let us now discuss which quantities c_j should be used as the arguments for the local chemical potential $\lambda\{c_j\}$ and the mobility $M\{c_j\}$ in the "diffusive" term δN_{di} in (10). The most "natural" (but naive) prescription seems to be just to put $c_j = N_j/N_L$, that is, to treat the fluctuations of both the atom number N_i and the chemical potential $\lambda_i = \lambda_i\{c_j\}$ within each L-cell on the same footing, which is declared, for example, in the "stochastic phase-field" treatments [13]. However, the numerical realization of this "direct" receipt for the reasonable L values mentioned above leads to the physically unacceptable results, namely, to the totally chaotic evolution with no hints of a tendency to the thermodynamic equilibrium of any kind at any T and c.

If one arbitrarily decreases the fluctuation scale D_s in Eqs. (10)–(12) by one-two orders of magnitude, the evolution becomes to look more plausible. However, there seem to be no arguments for such drastic reducing of fluctuations within this "direct" approach.

The physical origin for the failure of such "direct" approach is the fundamental difference between the fluctuations of the "mechanistic" quantities N_i having a direct and measurable meaning, and the fluctuations of the "thermodynamic" quantities λ_i describing the locally equilibrium subsystems. As mentioned, the expression (9) for the diffusive term is obtained by the statistical averaging over all fluctuations of occupations $\{n_j\}$ except for those with the large wavelengths l exceeding the length $l_{\rm le}$ of a local equilibrium. Thus it makes no sense to include again the short-wave fluctuations in the diffusive term δN_{di} that has been already averaged over these fluctuations. The fluctuation of the parameter λ_i in (2) can have a physical meaning only if it takes an approximately same value for the whole volume $V_{\rm le} \sim l_{\rm le}^3$, that is, if it has a wavelength $l \gtrsim l_{\rm le} \gg L \sim a$. In other words, the total fluctuative transfer N_{fs} across each facet s described by Eqs. (11), (12) is by no means small. However, the main, short-wave contribution of these fluctuations to the microstructural evolution is self-averaging and is described by the diffusional term δN_{di}. Only the long-wave fluctuations with $l \gtrsim l_{\rm le}$ remain to be meaningful for this term and should be taken into account in the calculations.

To describe this physical picture we suggest the following model. Instead of the full stochastic quantities $N_i(t)$ and δN_{fi} in Eq. (10) we consider only their long-wave parts, $N_i^c(t)$ and δN_{fi}^c, which are determined by a "coarse-grained" version of Eq. (10):

$$N_i^c(t+\delta t) = N_i^c(t) + \delta N_{di}\{c_j\} + \delta N_{fi}^c. \qquad (13)$$

Here the local concentration c_j in the diffusional term δN_{di} is $N_j^c(t)/N_L$ while the last term is the sum of coarse-grained fluctuative transfers δN_{fs}^c across all facets s: $\delta N_{fi}^c = \sum_s \delta N_{fs}^c$. This transfer δN_{fs}^c is obtained from the full stochastic distribution δN_{fs} determined by Eqs. (11) and (12) by a "filtration of noise" procedure, that is, by introducing a proper cut-off factor $F_c(\mathbf{k})$ in the Fourier-component $\delta N_{f\alpha}(\mathbf{k})$ of the full function $\delta N_{fs} = \delta N_{f\alpha}(\mathbf{R}_{s\alpha})$ where $\mathbf{R}_{s\alpha}$ stands for the center of facet s normal to the main crystal axis α:

$$\delta N_{f\alpha}^c(\mathbf{R}_{s\alpha}) = \sum_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{R}_{s\alpha})\, \delta N_{f\alpha}(\mathbf{k})\, F_c(\mathbf{k}), \qquad (14)$$

$$\delta N_{f\alpha}(\mathbf{k}) = \frac{1}{N_{tot}} \sum_{\mathbf{R}_{s\alpha}} \exp(i\mathbf{k}\mathbf{R}_{s\alpha})\, \delta N_{f\alpha}(\mathbf{R}_{s\alpha}), \qquad (15)$$

and N_{tot} is the total number of L-cells. The cut-off factor $F_c(\mathbf{k})$ is taken in a Gaussian-type form characterized by the cut-off length l_c or by the parameter $g_c = l_c/L$:

$$F_c(\mathbf{k}) = \exp\Big[-2g_c^2 \sum_\alpha \sin^2(k_\alpha L/2) \Big]. \qquad (16)$$

Here we took into account that the set of arguments $\mathbf{R}_{s\alpha}$ of the function $\delta N_{f\alpha}^c(\mathbf{R}_{s\alpha})$ forms a cubic crystal of L-cells, and so the Fourier-component $\delta N_{f\alpha}^c(\mathbf{k})$ should obey the relations: $\delta N_{f\alpha}^c(k_\beta + 2\pi/L) = \delta N_{f\alpha}^c(k_\beta)$. For the large $g_c^2 \gg 1$ used below the cut-off function (16) is effectively reduced to a Gaussian $\exp(-k^2 l_c^2/2)$.

The cut-off length l_c for our problem should evidently have the order of a characteristic length of a local equilibrium, $l_{\rm le}$, as the phase separation process can take place only when a sufficient thermodynamic driving force (i. e. supersaturation) is present, which implies a certain extent of the local thermodynamic equilibrium within a subsystem. At the same time, all fluctuations with the larger wavelengths $l \gtrsim l_{\rm le}$ can initiate this process and thus should be taken into account. The length $l_{\rm le}$ should, generally, depend on the concentration c, temperature T, and the interaction radius r_0 in (8). To estimate the $l_{\rm le}$ value, we made computer simulations of phase separation based on Eqs. (13)–(16) for a number of values c, T, r_0 varying the parameter $g_c = l_c/L$ in Eq. (16). In accordance with the considerations above, the decreasing of l_c from the values $l_c > l_{\rm le}$ to $l_c < l_{\rm le}$ should correspond to the loss of the local equilibrium assumed in Eqs. (2)–(6) and thus to sharp violations of the basic condition $\lambda_i \simeq$ constant within subsystems. The scale of these violations can be characterized, for example, by the "degree of non-equilibrium" $I_m(l_c)$ defined as the maximum value of the reduced gradient $\beta\, a\, |\nabla\lambda|_{\rm max}$ over the whole system for some characteristic time interval Δt_c. Then decreasing l_c across $l_{\rm le}$ should result in a sharp rise of $I_m(l_c)$. It is illustrated by Fig.1, and similar variations have been found for all other models

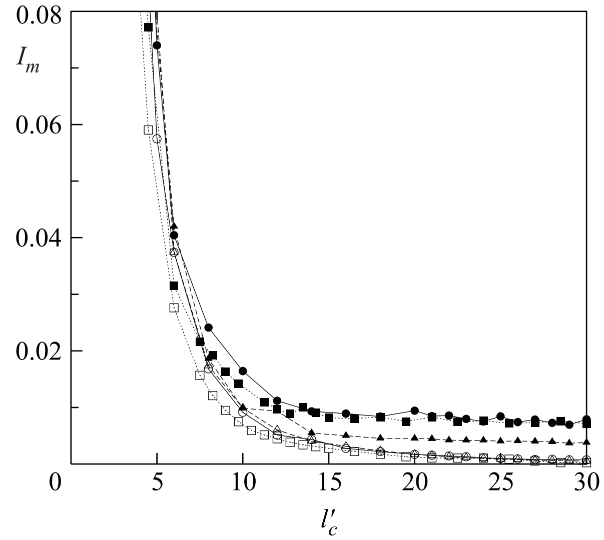

Fig.1. The inhomogeneity parameter I_m described in the text versus the reduced cut-off length $l'_c = l_c/a$ at $L = 2a$, $\Delta t'_c = 5$ and $c = 0.4$. Blacked and open symbols correspond to the reduced temperature $T' = 0.94$ and $T' = 0.98$, while circles, triangles and squares, to $r_0 = a$, $r_0 = 2a$ and $r_0 = 0.71\, a$, respectively

considered. The point $l_{\rm sr}$ where this sharp rise starts can be defined, for example, as the maximum curvature point for the function $I_m(l_c)$. The local equilibrium length $l_{\rm le}$ should evidently somewhat exceed the $l_{\rm sr}$ value. The experience of our simulations seems to show that employing $l_c = l_{\rm le} \simeq 2\, l_{\rm sr}$ provides usually an appropriate description of evolution, while varying l_c, say, between $2\, l_{\rm sr}$ and $1.5\, l_{\rm sr}$ results mainly in some re-scaling of time and only slight changes of microstructure; it is illustrated by comparison of frames (b) and (e) to (g) and (h) in Fig.3 below.

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Fig.2. Temporal evolution of $c_i = c(\mathbf{R}_i)$ for the alloy model described in the text at $L = 2a$, $c = 0.4$, $r_0 = a$, $T' = 0.98$, $l'_c = 26$, and the following $t' = t\gamma_{nn}10^{-4}$: (a) 2, (b) 5, (c) 10, and (d) 25. The grey level linearly varies with c_i between $c_{\rm min} = 0.3$ and $c_{\rm max} = 0.65$ from completely bright to completely dark

We used equations (11)–(16) with the above-described choice of l_c in (16) to simulate phase separation for a number of alloy models with the different c, T and r_0 values. Some our results are presented in Figs.2 and 3. They correspond to 2D simulation on the FCC lattice with 256×256 L-cells and periodic boundary conditions. The concentration c is 0.4, while the reduced temperatures $T' = T/T_c$ are chosen near the spinodal temperature for this c, $(T'_s)_{\rm MFA} = 0.96$. These c and T'_s values are close to those used in experiments [5] where the NG-SD transition was studied for some highly viscous liquid mixture, and so our results can be directly compared to this experiment. All simulations included a "pre-annealing" stage at $T'_{an} = 1.2$ for the interval $\Delta t'_{an} = 0.05$ where $t' = t\gamma_{nn}10^{-4}$ is the reduced time, while symbol t' in captions to figures shows the time after a rapid quench $T'_{an} \to T'$.

The patterns presented in Figs.2 and 3 reveal all main features of phase separation of the NG and the SD type, respectively, as mentioned, e. g., by Tanaka et al. [5]. Discussing their observations these authors note: "in NG the nuclei ... are born and grow almost independently. The density of droplets in NG is much lower than in SD. In SD the spatial concentration fluctuations grow in both amplitude and size, and form droplets, being first gray, become darker with time, and become larger and larger mainly by coalescence mechanism". All these features are seen in Figs.2 and 3.

The simulations reveal also a number of other microstructural details. In particular, for the NG-type evolution shown in Fig.2: (i) some rare coalescence events

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Fig.3. Frames (a)–(f): same as in Fig.2 but at $T' = 0.94$, $c_{\min} = 0.25$, $c_{\max} = 0.75$, and the following t': (a) 0.5, (b) 1, (c) 2, (d) 5, (e) 10, and (f) 20. Frames (g) and (h): same as in frames (a)–(f) but at $l'_c = 20$ and the following t': (g) 0.7, and (h) 7

are present, too; (ii) the precipitate shape is often nonspherical; and (iii) a concentration-depleted "bright" halo is typically adjacent to the precipitates. All that is seen in experiments [5, 4]. For the SD-type evolution in Fig.3 we observe: (i) peculiar initial "roe-like" arrays of droplets which later on often coalesce forming elongated tongue-like structures; and (ii) many coalescence events via a "bridge" mechanism noted in [12] when the diffusion fluxes first connect the adjacent precipitates by a thin and grey "bridge" that later on starts to sharply grow and thicken with the formation of a pear-like or a dumbbell-like precipitate. It again agrees with experiments [5, 6].

In our simulations for the transition region between NG and SD, in particular, for $c = 0.4, T' = 0.96$ just at the spinodal curve, we obtain a "mixed" type of evolution, first an NG-type pattern of a small number of wrong-shaped droplets, which later on form roe-like and tongue-like structures characteristic of SD. It seems to agree with the observations described in [5].

Finally, we comment on the smallness of the temperature width for the NG-SD transition illustrated by Figs.2 and 3: $\Delta T' \simeq 0.04$. It can be explained by the significant difference in the reduced supersaturation parameter for the alloy states c, T considered. This parameter characterizes a tendency to the NG or the SD-type evolution and can be defined as [10]:

$$s = [c - c_b(T)]/[c_b(T) - c_s(T)] \tag{17}$$

where $c_b(T)$ and $c_s(T)$ is the concentration at the binodal and the spinodal, respectively. For the two states considered, this parameter takes quite different values, $s_1 = 0.42$ and $s_2 = 1.27$, even though the temperature difference is small. It is due to the flatness of the binodal and the spinodal curves, $T_b(c)$ and $T_s(c)$, in the vicinity of the critical point being considered in this simulation. It can be still more so for experiments [5] where the curves $T_b(c)$ and $T_s(c)$ seem to be still more flat than in our MFA model; it can explain a rather small value of the NG-SD transition width, $\Delta T' \simeq 0.015$, found in [5].

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