

MEAN-FIELD EQUATIONS FOR CONFIGURATIONAL KINETICS OF ALLOYS AT ARBITRARY DEGREE OF NONEQUILIBRIUM

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We apply the mean-field approximation to the master equation describing the time evolution of alloy states to obtain kinetic equations for concentrations at an arbitrary degree of nonequilibrium. We discuss applications of these equations to several problems of phase transformations.

Problems of structural evolution of nonequilibrium alloy states attract much attention. Theoretically, they are studied using either approximate kinetic equations [1-7] (AKE) for the local concentration or mean occupation number $c_i = c(\mathbf{r}_i, t)$ at lattice site i (say, for A-atoms in the binary A-B alloy), or direct simulation, e.g. Monte-Carlo (MC) methods [8-11]. AKE seem to be more transparent and universal than simulation methods, and many new qualitative results in this field [1-4] were obtained using AKE. However, the currently used phenomenological forms of AKE are based on Onsager-type linear relations [12] between time derivatives dc_i/dt and thermodynamic driving forces $\partial F/\partial c_j$ (where F is the free energy of an inhomogeneous alloy), which hold only for near-equilibrium states. Thus application of these AKE to states far from equilibrium, such as those obtained by deep quenching, transient states at spinodal decomposition (SD), etc, can hardly be justified, while kinetic phenomena just in these states seem to attract most interest [3,4,13].

To more consistently investigate these phenomena, in this work we use the fundamental master equation determining the probability $P\{n_i, t\}$ to find the occupation number set $\{n_i\}$ (where $n_i = 1$ if atom A is at site i and $n_i = 0$ otherwise) in terms of microscopic probabilities for intersite atomic jumps [7]. To treat this equation we apply the mean-field approximation (MFA) which was earlier developed for description of steady states in irradiated alloys [7]. We suppose that interatomic potentials v_{ij} obey conditions for the applicability of MFA, i.e. their interaction range includes a sufficiently large number of sites $N_0 \gg 1$, which for actual alloys can be true even quantitatively [4].

Following to [7], we multiply master equation by operators $n_i, n_i n_j$ etc, and average these relations. For inhomogeneous alloys under consideration such averaging, e.g. that for $\langle n_i \rangle = c_i = c(\mathbf{r}_i, t)$, has a clear meaning only if characteristic lengths l for space variations of c_i exceed the intersite distance a . Since l is usually not lower than the interaction radius r_0 being supposed to be large, the above condition in our case is satisfied. Resulting equations for $\langle n_i \rangle$ and correlators of fluctuations $K_{i\dots j} = \langle (n_i - c_i) \dots (n_j - c_j) \rangle$ in the main approximation in $1/N_0$ decouple [7] and can be written explicitly. Accepting for thermally activated intersite jumps a "direct-jump" model described in [5,7] we

obtain the mean-field kinetic equation for the A-B alloy:

$$dc_i/dt = \sum_s \gamma_{is} \left(c'_s c_s e^{\varphi_s^A} + \varphi_s^B - c'_s c_s e^{\varphi_s^A} + \varphi_s^B \right) \quad (1)$$

Here $\gamma_{is} = \gamma_{si}$ is the c_i -independent part of the jump probability, $c'_i = 1 - c_i$, $\varphi_i^p = \beta(v^p c)_i$, $\beta = 1/T$ is the reciprocal temperature, $(v^p c)_i = \sum_j v_{ij}^p c_j$ is the MFA potential acting on a p-species atom at site i , and v_{ij}^A and v_{ij}^B are related to the configurational potential $v = V^{AA} + V^{BB} - 2V^{AB}$ and the "asymmetric" one $u = V^{AA} - V^{BB}$ as: $v^A = \frac{1}{2}(u + v)$, $v^B = \frac{1}{2}(u - v)$.

Writing the reduced MFA free energy $f = \beta F$ for an inhomogeneous alloy as

$$f = \sum_i (c_i \ln c_i + c'_i \ln c'_i) + \frac{1}{2} \sum_{ij} \beta v_{ij} c_i c_j \quad (2)$$

we can rewrite eq. (1) in the form

$$dc_i/dt = \sum_s A_{is} [\exp(\partial f / \partial c_s) - \exp(\partial f / \partial c_i)] \quad (3)$$

where $A_{is} = A_{si} > 0$. For fully equilibrium states all derivatives $f_i = \partial f / \partial c_i$ are equal to the chemical potential μ , so rhs of (3) vanishes. For near-equilibrium states we can expand this rhs in powers of $f_s - f_i$, which converts it into Onsager form $\sum_s L_{is} f_s$ used in [3,4]. We see that this linearized equation neglects not only higher powers of $f_s - f_i$ but also the c_i -dependence of kinetic coefficients L_{ij} . For states far from equilibrium, e.g. at deep quenching or at late stages of SD (when factors c_i or c'_i in (1) become close to zero), the latter can lead to significant errors.

Multiplying eq. (1) by f_i , summing over i and denoting $\exp(f_i)$ as ξ_i , we obtain an analog of H -theorem for alloys (earlier discussed by Penrose [6]):

$$df/dt = \frac{1}{2} \sum_{is} A_{is} (\xi_s - \xi_i) \ln(\xi_i / \xi_s) \leq 0 \quad (4)$$

Relations (1)-(4) are immediately generalized to many-component alloys. In particular, eqs. (1) and (2) for them take the form

$$dc_{pi}/dt = \sum_{qs} \gamma_{is}^{pq} [\exp(f_{ps} + f_{qi}) - \exp(f_{pi} + f_{qs})] \quad (5)$$

$$f = \sum_{pi} c_{pi} \ln c_{pi} + \frac{1}{2} \sum_{pi,qj} \beta v_{ij}^{pq} c_{pi} c_{qj} \quad (6)$$

Here $c_{pi} = \langle n_{pi} \rangle$ is the mean occupation number of site i by a p-species atom, and f_{pi} is the formal partial derivative $\partial f / \partial c_{pi}$ of function (6), disregarding the normalizing condition $\sum_p c_{pi} = 1$. Eq. (5) can be applied, in particular, to the alloy A-B with vacancies (ABv-alloy) being treated as a 3-component alloy. Since actually intersite jumps in alloys are mainly realized via vacancies, eqs. (5) enable us to find expressions for effective "direct jump probabilities" γ in (1) in terms of microscopic vacancy-atom jump probabilities, see below.

Intersite jumps in eqs. (1), (5) occur mainly between nearest or next-nearest sites i and s . For disordered alloys the relevant values of c_i and c_s in our case, as mentioned, are supposed to be close to each other. Expanding differences $c_s - c_i$ in powers of $r_{si} \nabla c$ where $r_{si} = r_s - r_i$, we obtain a continuous version of eq. (1):

$$\partial c_i / \partial t = \text{div} \{ M(c) [\nabla c / c c' + \nabla (\beta v c)_i] \} \quad (7)$$

Here $c = c_i$, $M(c) = \gamma c c' e^{\beta(u c)_i}$ is the c_i -dependent mobility, and tensor γ is $\frac{1}{2} \sum_s \gamma_{is} r_{is} r_{is}$ (becoming a scalar for cubic lattices). If we suppose the characteristic length l for space variations of c_i to exceed not only a but also the interaction radius r_0 , we can approximate the last term of (7) as $(v c)_i \simeq v_0 c + \epsilon \Delta c$ where $v_0 = \sum_j v_{ij} = -4T_0$ determines the critical temperature T_0 for SD, and ϵ is $\frac{1}{6} r_0^2 v_0$ (for cubic lattices). Then linearizing (7) in deviations $c_i - c_0$ from the initial constant value c_0 , we obtain the Cahn-Hilliard (CH) equation [1] describing early stages of SD, with the Martin's expression [6] for mobility $M_{CH} = M(c_0)$. At later stages of SD concentrations c_i approach their "liquid" or "gas" values at the binodal curve, while interface widths l decrease and become $\sim r_0$. Therefore, to describe these stages of SD (as well as effects of long-ranged elastic interactions for which inequality $l \gg r_0$ is violated [4]) we should employ the full equation (7).

Generalizing (7) for the m -component alloy, we obtain an analogous set of equations for $m-1$ independent concentrations c_{pi} . For the AB ν -alloy, we can take into account that c_{vi} is quite small and thus its time variations adiabatically fast follow to those of c_{Ai} , so c_{vi} is determined by eq. (5) with $p=v$ and $\dot{c}_{vi} = 0$. Then resulting equation for $c_i = c_{Ai}$ differs from eq. (7) only by a factor $\tilde{\gamma}^{AB} / \gamma$ before rhs, where $\tilde{\gamma}^{AB} \propto c_{vi}$ is determined by the "series connection" relation for mobilities

$$\tilde{\gamma}^{AB} c c' e^{\beta(u c)_i} = (1/M_{Av} + 1/M_{Bv})^{-1} \quad (8)$$

Here $M_{pq} = \gamma^{pq} c_p c_q e^{\varphi_p + \varphi_q}$, $c_p = c_{pi}$, $\varphi_p = \beta \sum_{qj} v_{ij}^{pq} c_{qj}$, and γ^{pq} is defined analogously to γ after eq. (7) substituting γ_{is} by γ_{is}^{pq} . However, the compact eq. (7) with substitution of M by eq. (8) can be used only in the linear approximation in ∇c , since $\tilde{\gamma}^{AB}$ in (8) depends on c_i .

For the ordered alloy with ν different sublattices α , averages $\langle n_{pi}^\alpha \rangle = c_{pi}^\alpha$ are taken for each sublattice separately. Thus site numbers i, j in eqs. (1)-(6) are replaced by pairs of indices: $i \rightarrow i\alpha$, $v_{ij}^{pq} \rightarrow v_{ij}^{pq, \alpha\beta}$, etc, where i or j now number different ν -atomic cells. Writing eqs. (5) in terms of mean cell concentrations c_{pi} and $\nu-1$ order parameters η_{pi}^λ we obtain a generalization of the Allen-Cahn equation [2] for kinetics of alloy ordering, which will be discussed elsewhere.

Eqs. (1)-(8) can be applied to most different problems of nonlinear kinetics of alloys. Below we discuss several examples.

1. *Nonlinear concentration waves at first stage of SD.* According to the linearized CH equation [1], after a quench of an alloy below the spinodal curve (SC) a wave-like distribution of concentrations $c(r, t)$ develops, having a characteristic wavelength $2\pi/k_{CH}$ and amplitudes increasing with a characteristic time $t_{CH} \sim k_{CH}^{-2}$, where k_{CH} is the CH wavenumber (that decreases when the initial concentration c_0 approaches SC). However, it was argued that non-linear effects neglected in the CH theory may suppress development of the pronounced CH waves [12]. From the other side, MC simulations using short-range potentials obtain for first stages of SD rather random cluster than wave-like patterns [8,9]. It was also shown [10] that with increasing of interaction range r_0 some MC results near SC converge to those of

MFA. However, even for long-range potentials importance of the above-mentioned non-linear effects seems to remain non-clear [11].

To investigate this and other problems of SD we performed two-dimensional (2D) simulations based on eq. (7). We approximated sums $(vc)_i$ by integrals and took $v(r)$ to be gaussian: $v(r) = -A \exp(-r^2/2\sigma^2)$ supposing $\sigma \gg a$, while constant A is proportional to the MFA critical temperature T_0 . The asymmetric potential u was supposed to be less long-ranged than v , thus we put $(uc)_i \simeq u_0 c_i$. Simulations were made at a square lattice $40\sigma \times 40\sigma$ with periodic boundary conditions, using the dimensionless time variable $t' = t\gamma\sigma^{-2}$. The as-quenched distribution $c(r, 0)$ was characterized by its mean value c_0 and small random fluctuations. Eqs. (7) were solved using the Runge-Kutta method.

For all states c_0, T within SC after times $t_1 \sim k_{CH}^{-2}$ we observed a pronounced wave-like structure with $\lambda \sim 2\pi/k_{CH}$. It retained its features well within the non-linear region, up to the next, coarsening stage of SD begins. It is illustrated by Fig. 1, while Fig. 3b shows the next stage. Thus non-linear effects don't destroy qualitative features of the CH picture for the first stage of SD, anyway for the long-range interactions considered.

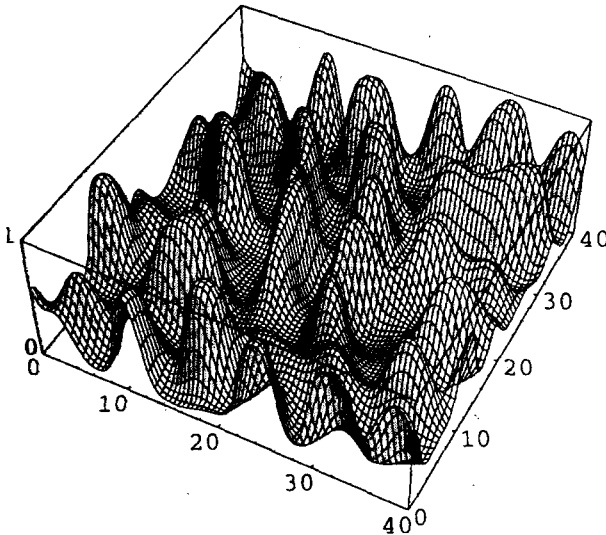


Fig. 1. Profile of concentration $c(r)$ at spinodal decomposition in the 2D model described in text for following parameter values: $c_0 = 0.35$, $T = 0.4T_0$, $u = 0$ and $t' = 10$

2. "Bridge" mechanism for droplet coalescence. Until recently only two coarsening mechanisms were discussed for droplet phase separation (i) Lifshits-Slyozov (LS) evaporation-condensation mechanism for separated droplets in which bigger droplets grow at the expense of evaporation of smaller ones [14], and (ii) Binder and Stauffer mechanism [9,11] for droplets coalescence caused by their thermal diffusion without any interaction. Recently Tanaka [13] observed peculiar effects of inter-droplet interaction under their coalescence during SD in a 2D fluid mixture which he attributed to features of droplet diffusion in liquids.

In our simulations we observe similar effects for the solid alloy model, where we see no diffusion of droplets as whole, but rather a strong dynamic coupling of diffusion fluxes around droplets. This new mechanism of coalescence (to be called the "bridge" mechanism) is illustrated in Fig. 2. It dominates the first

stage of coarsening of droplet pattern at intermediate c_0 values (for example, for $t' = 20 - 500$ at $c_0 = 0.35$, $u = 0$), before the LS mechanism becomes effective.

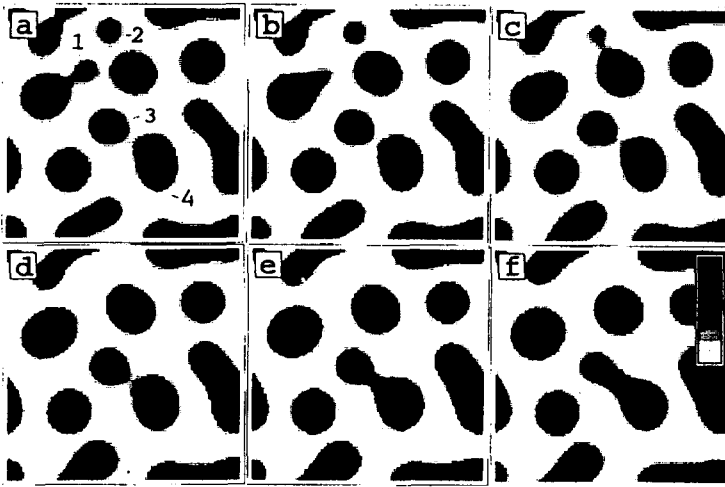


Fig. 2. Temporal evolution of concentration $c(r)$ for the 2D model described in text at $c_0 = 0.35$, $T = 0.4T_0$, $u = 0$ and following t' : (a) 120, (b) 130, (c) 140, (d) 160, (e) 180, and (f) 200. Insert in Fig. 2(f) shows relation between darkness and c values varying between 0 and 1 from bottom to top

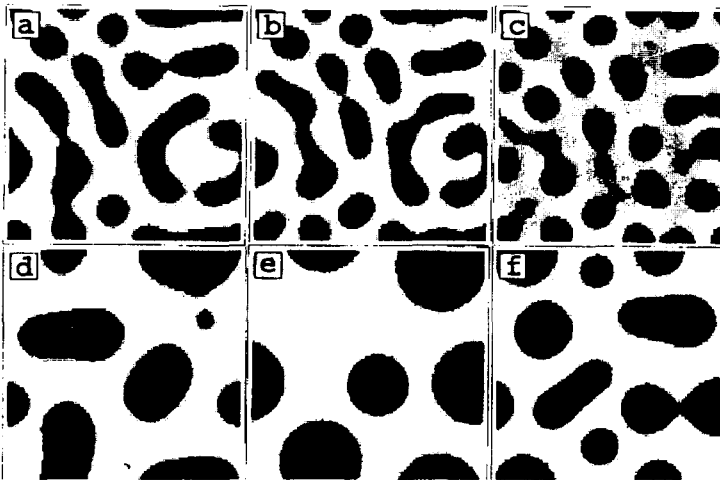


Fig. 3. Same as in Fig. 2 at $c_0 = 0.35$, $T = 0.4T_0$, and the following values (u_0 , t'): (a) $-2T_0$, 200; (b) 0, 20; (c) $2T_0$, 2.4; (d) $-2T_0$, 1230; (e) 0, 5000; and (f) $2T_0$, 16.5

Figs. 2a-2f illustrate two main versions of the bridge mechanism: (i) that for droplets 1 and 2 when a smaller droplet is consumed by its bigger neighbor(s) that pulls it over the bridge formed by diffusion fluxes, and (ii) that for droplets 3 and 4 of similar size when the "bridge" can occur for considerable time (e.g. $\Delta t' \sim 100$ for droplets 3 and 4) before its density begins to sharply rise and

droplets coalesce. These effects seem to be rather similar to those shown by Tanaka [13] in his Figs. 1 and 4.

3. *Effect of A-B asymmetry of mobilities in the A-B alloy on SD.* Such asymmetry is always present in real alloys but is usually disregarded in theoretical treatments. In our model it is described by the MFA value u_0 of the asymmetric potential u . Presence of factor $\exp(\beta u_0 c)$ in mobility results, firstly, in a c -dependent change of the time scale, i.e. slowing down kinetics at $u < 0$ and speeding it up at $u > 0$. Secondly, this factor changes a relative importance of the LS and droplet coagulation mechanisms of coarsening. Since coagulation proceeds via bridge mechanism corresponding to noticeable values $c \sim 0.1 - 0.2$ in the bridge region, negative u lead to suppression of this mechanism with respect to the LS one, as the latter is determined by diffusion over "gas" region $c \ll 1$ where the suppression is small. At positive u the situation reverses. For example, at $c_0 = 0.35$, $t = 0.4T_0$, $u_0 = -2T_0$ coarsening proceeds via evaporation of 5 and coalescence of 2 (of total 11) droplets during $t' = 250 - 2500$; at $u_0 = 0$, 7 droplets of 13 coalesce and 2 evaporate during $t' = 50 - 5000$; and at $u_0 = 2T_0$, 13 of 18 droplets coagulate and none evaporates during $t' = 3 - 35$. Figs. 3a-3c illustrate effect of u on the formation of droplet pattern, Figs. 3d and 3f show typical coarsening mechanisms for $u_0 = -2T_0$ and $u_0 = 2T_0$, respectively, and Fig. 3(e) shows an advanced stage of coarsening when the LS mechanism dominates.

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