Microscopical derivation of Ginzburg-Landau-type functionals for alloys and their application to studies of antiphase and interphase boundaries

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The earlier-described cluster methods are used to generalize the Ginzburg-Landau gradient expansion for the free energy of an inhomogeneous alloy to the case of not small values of order parameters and variations of composition. The results obtained reveal a number of important differences with the expressions used in the phenomenological phase-field approach. Differential equations relating the local values of concentration and order parameters within the antiphase or interphase boundary (APB or IPB) are derived. These equations are applied to study the segregation at APBs near the phase transition lines; the structure of APBs and IPBs near tricritical points; wetting APBs in phases with single and several order parameters; and also some effects of anisotropy of APBs under L10 and L12-type orderings.

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Studies of inhomogeneous alloys attract interest from both fundamental and applied points of view, in particular, in connection with microstructure evolution under phase transformations [1–12]. Typical inhomogeneities in such problems are antiphase or interphase boundaries (APBs or IPBs) which separate differently ordered domains or different phases. Both experimental and theoretical studies show that in situations of practical interest the APB or IPB width usually much exceeds the interatomic distance [5–12]. Therefore, Ginzburg-Landau (GL) type gradient expansions can be used to describe the free energy of such states even though the order parameters and concentration variations here are typically not small, contrary to assumptions of the standard GL theory. Employing such generalized GL functionals (suggested first by Cahn and Hilliard [1]) is now referred to as the phase-field method, and it is widely used for most different systems, see e.g. [6–8]. However, a number of simplifying assumptions are usually employed in this phenomenological approach, and so its relation to more consistent theoretical treatments remains unclear. Recently microscopical cluster methods have been developed for inhomogeneous alloys [9–13]. Below I use these methods to derive the GL functionals and then apply them for studies of APBs and IPBs.

To be definite, I consider a binary alloy A1−cBc at c ≤ 1/2. Various distributions of atoms over lattice sites i are described by the mean occupations ci = ⟨ni⟩ where ni is unity when the site i is occupied by atom A and zero otherwise, while averaging is taken, generally, over the space- and time-dependent distribution function [1]. The free energy F{ci} in the cluster description can be written as a series [13]:

$$F = \sum_i f^i = \sum_i \left( F_i^1 + \sum_j F_{ij}^2 + \cdots + \sum_{j,...k} F_{ijkl}^m \right).$$ (1)

Here f^i is the free energy per site i; F_i^1 = T[c_i ln c_i + (1 − c_i) ln(1 − c_i)] is the mixing entropy contribution; F_{ijkl} = F_i(c_j,...,c_k) is the contribution of interactions within l-site cluster of sites i,...,k; and m is the maximum cluster size considered. The simplest mean-field approximation (MFA) and the pair-cluster one (PCA) correspond to neglecting many-site contributions F_{m>2} in (1), while in a more refined, tetrahedron cluster approximation – TCA (that should be used, in particular, to adequately describe the L12 and L10-type orderings [13]) Eq. (1) includes also 4-site terms F_{ijkl}^4 [13].

For the homogeneous ordered structure, the mean occupation cj = c(rj) at site j with the lattice vector rj can be written as a superposition of concentration waves with some superstructure vectors k_s [8–12]:

$$c_j = c + \sum_s \eta_s \exp(i k_s r_j) \equiv \sum_p \eta_p \exp(i k_p r_j).$$ (2)

Here amplitudes \eta_s can be considered as order parameters; the last expression includes also term with \eta_p = c and k_p = 0; and for simplicity both parameters \eta_s and factors \exp(i k_s r_j) are supposed to be real which is the case, in particular, for the B2, L10 and L12-type order. For weakly inhomogeneous states, amplitudes \eta_p in (2)

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are not constants but smooth functions of coordinates \( r_i \). Thus functions \( f^i(c_j) \) in \( (3) \) can be expanded in powers of differences \( \delta c = \sum_p \delta \eta_p \exp(\text{i} k_p r_j) \) where

\[
\delta \eta_p = \eta_p^j - \eta_p^i = r_j \nabla \eta_p + \frac{1}{2} \sum_r r^a_j r^b_j \nabla_{\alpha \beta} \eta_p. \tag{3}
\]

Here \( \nabla \eta_p = \partial \eta_p / \partial r^n \), \( \nabla_{\alpha \beta} \eta_p = \partial^2 \eta_p / \partial r^n \partial r^\beta \), \( r_j = (r_j - r_i) \), and the summation over repeated Cartesian indices \( \alpha, \beta = 1, 2, 3 \) is implied. After substitution of these expressions into Eq. \( (2) \) one can proceed from summation over \( i \) to integration over continuous variable \( r = r_i \). Making also standard manipulations with part-by-part integration of terms with \( \nabla_{\alpha \beta} \eta_p \) one obtains for the GL functional:

\[
F = \frac{1}{v_\alpha} \int d^3 r \sum_{p, q} g_{pq}^{\alpha \beta} \nabla_{\alpha \beta} \eta_p \nabla_{\alpha \beta} \eta_q + \{ f \{ \eta_p \} \}. \tag{4}
\]

Here \( v_\alpha \) is volume per atom; \( f \{ \eta_p \} \) is function \( f^i(c_j) \) in \( (3) \) averaged over all sublattices with \( c_i \) given by Eq. \( (2) \); and \( g_{pq}^{\alpha \beta} \) is given by the expression:

\[
g_{pq}^{\alpha \beta} = \frac{1}{2} \sum r_{ij}^{\alpha} r_{ij}^{\beta} S_{ij}^{\alpha \beta} \exp[i (k_p r_j - k_p r_i)] + \frac{1}{2} \sum_{k, j, k \neq j} r_{ki}^{\alpha} (r_{jk}^{\alpha} - r_{kj}^{\beta}) S_{ij}^{\alpha \beta} \exp[i (k_p r_j - k_p r_i)] \tag{5}
\]

where \( S_{ij}^{\alpha \beta} = \partial^2 f^i / \partial c_i \partial c_j \). Note that the last term of \( (5) \) is nonzero only when all three sites \( i, j, k \) are different, and so it is present only when the non-pairwise contributions \( F_{MFA}^{ijkl} \) in \( (3) \) are taken into account, such as the TCA terms \( F_{TCA}^{ijkl} \).

For the Ll2 and Ll1_2 phases in FCC alloys, Eq. \( (6) \) includes waves with three vectors \( k_\alpha \): \( k_1 = (100)2\pi/a \), \( k_2 = (010)2\pi/a \), and \( k_3 = (001)2\pi/a \) where \( a \) is the lattice constant [8–15]. The local order within APBs in these phases can be described by the distribution of amplitudes of these waves \( \{ \eta_1, \eta_2, \eta_3 \} \) of the type \( (\cdot, \eta, \eta) \) and corresponds to the tetragonal symmetry \( \{ \eta_1 \} \) \cite{1}. To illustrate the form of terms \( g_{pq}^{\alpha \beta} \) in \( (5) \), we present their MFA and PCA expressions for this type local order. Tensors \( g_{pq}^{\alpha \beta} \) here can be described in terms of their “transverse” and “anisotropic” components, \( g_{pq}^{\alpha \beta} = g_{pq}^{T} + g_{pq}^{A} \). Using for simplicity the 2-neighbor-interaction model: \( v_{n>2} = 0 \), one obtains in the MFA:

\[
g_{pq}^{\alpha \beta} = g_{pq}^{T}(\eta) + g_{pq}^{A}(\eta) \]

\[
\begin{align*}
g_{cc}^{\alpha \beta} &= \frac{1}{4} a^2 v_2; \quad g_{\zeta \zeta, \eta \eta}^{\alpha \beta} = \eta_\eta; \\
g_{cc}^{\alpha \beta} &= \frac{1}{4} a^2 v_1 + v_2; \quad g_{cc}^{\zeta \zeta} = g_{cc}^{\zeta \zeta} = 0,
\end{align*}
\]

while the PCA expressions for \( g_{pq}^{\alpha \beta} \) and \( g_{pq}^{\alpha \beta} \) are:

\[
g_{pq}^{\alpha \beta} = \frac{1}{4} a^2 (\psi_\eta^+ - \psi_\zeta^+ - \psi_\zeta^+ + \psi_\eta^d); \quad g_{cc}^{\alpha \beta} = \frac{1}{4} a^2 \eta_\eta.
\]

Here plus or minus in (\pm) corresponds to the first or the second pair of lower indices in the left-hand-side of Eqs. \( (7)-(9) \):

\[
\begin{align*}
\varphi_\zeta^{\pm} &= - T f_n / R_{n}^{\zeta}; \quad \varphi_\eta^{\pm} = \frac{1}{2} (\varphi_\eta^{\pm} + \varphi_\zeta^{\pm}); \\
\psi_\eta^{\pm} &= \frac{1}{2} (\varphi_\eta^{\pm} + \varphi_\zeta^{\pm}); \quad \chi_\eta^{\pm} = \frac{1}{2} (\varphi_\eta^{\pm} + \varphi_\zeta^{\pm}); \\
R_{n}^{\zeta} &= [1 + 2 f_n (c_i + c_j - 2 c_k c_j) + f_{n}^{2} (c_i - c_j)^{2}]^{1/2}; \quad f_n = \exp(-v_n / T) - 1 \text{ is the Mayer function; and indices } i \text{ and } j \text{ equal to } a, b \text{ or } d \text{ corresponds to the mean occupation } c_i \text{ or } c_j \text{ of one of three different sublattices: } c_a = c + \zeta + 2 \eta; \quad c_b = c + \zeta - 2 \eta; \quad c_d = c - \zeta. \tag{9}
\end{align*}
\]

If the TCA is used, the nearest-neighbor contributions \( \varphi_\zeta^{ij} \) in Eqs. \( (7)-(9) \) are replaced by the relevant tetrahedron contributions \( S_{ij}^{\alpha \beta} \) presented in Ref. \( (13) \). For the B2 order, there is only one order parameter \( \eta_\eta = \eta_\zeta \); terms \( g_{pq}^{\alpha \beta} \) have a cubic symmetry: \( g_{pq}^{\alpha \beta} = \delta_{\alpha \beta} g_{pq} \); and the MFA and PCA expressions for \( g_{pq}^{\alpha \beta} \) are similar to those for \( g_{pq}^{\alpha \beta} \) in Eqs. \( (7)-(9) \).

In the phase field method, terms \( g_{pq}^{\alpha \beta} \) are assumed to not depend on local parameters \( \eta_\eta \), and so to be zero at \( p \neq q \) “on considerations of symmetry” [6–8]. Eqs. \( (7)-(9) \) show that it may correspond only to the simplest MFA, while in more accurate approaches, such as PCA and TCA, the dependences \( g_{pq}^{\alpha \beta}(\eta_\eta) \) can be significant.

Let us now consider the case of a plane APB (or IPB) when parameters \( \eta_\eta \) in \( (7) \) depend only on the distance \( \xi = r_{mn} \) where \( r_{n0} = (\cos \alpha, \sin \alpha \cos \varphi, \sin \alpha \sin \varphi) \) is normal to the APB plane. To find the equilibrium structure, one should minimize the functional \( (7) \) over functions \( \eta_\eta(\xi) \) at the fixed total number of atoms \( \xi \). Let us first consider the APB between two B2-ordered domains. Then variational equations for the order parameter \( \eta(\xi) \) and the concentration \( c(\xi) \) have the form:

\[
\begin{align*}
g_{nn}^{\eta \eta} + g_{nc}^{\eta \eta} + \frac{1}{2} g_{nn}^{\eta \eta} \psi_\eta^d + g_{nn}^{\eta \eta} \psi_\eta^d + (g_{nc}^{\eta \eta} - \frac{1}{2} g_{nn}^{\eta \eta}) (\psi_\eta^d)^2 &= \frac{1}{2} f_n; \\
g_{nc}^{\eta \eta} + g_{cc}^{\eta \eta} + (g_{nc}^{\eta \eta} - \frac{1}{2} g_{nn}^{\eta \eta}) \psi_\eta^d + g_{cc}^{\eta \eta} \psi_\eta^d + \frac{1}{2} g_{cc}^{\eta \eta} &= \frac{1}{2} (f_c - \mu), \tag{10}
\end{align*}
\]
Here prime means taking derivative over $\xi$; the lower index $\eta$ or $c$ means taking derivative over $\eta$ or $c$; and $\mu$ is the chemical potential. At $\xi \to \infty$ functions $c$ and $\eta$ tend to their equilibrium values, $c_0$ and $\eta_0(c_0)$.

Multiplying first and second Eq. (16) by $\eta'$ and $c'$, respectively, summing them, and integrating the result, one obtains the first integral of this system of equations:

$$g_{\eta\eta}(\eta')^2 + 2g_{\eta c}\eta'c' + g_{cc}(c')^2 = \Omega(\eta, c)$$  (11)

where $\Omega$ is the non-gradient part of the local excess grand canonical potential per atom:

$$\Omega = f(\eta, c) - f_0 - \mu(c - c_0),$$  (12)

and index zero at the function means its value at $\eta = \eta_0$ and $c = c_0$.

For what follows it is convenient to consider the order parameter $\eta$ as an independent variable, while $c$ and $\Omega$, as its functions determined by Eqs. (10)–(12). Then the dependence $\eta'(\eta)$ is determined by Eq. (4):

$$\eta' = d\eta/\xi = (\Omega/G)^{1/2}$$  (13)

where $G$ is $(g_{\eta\eta} + 2g_{\eta c} + g_{cc}c^2)$, and $\dot{c}$ is $dc/d\eta$. Using Eq. (13) one can exclude $\eta'$ from the system of equations (10) and obtain the differential equation for $c(\eta)$ to be called the composition-order equation (COE):

$$[\dot{c}(g_{\eta\eta} - g_{cc}c) + \Phi] 2 \Omega / G = (\mu - f_0)(g_{\eta\eta} + g_{\eta c} + f_\eta g_{\eta c} + f_{cc}g_{\eta c})$$  (14)

where $\Phi$ is a linear function of derivatives $g_{pq}^c$: $g_{pq}^c = (g_{pq} + c\dot{c})\left[\frac{1}{2}\frac{g_{pq}^n + g_{pq}^\alpha c}{g_{pq}^n} + \left(\frac{g_{pq} - \frac{1}{2}g_{pq}^n c^2}{g_{pq}}\right)^2\right] - g_{\eta\eta}g_{cc}$

$$-\left[g_{\eta\eta}g_{\eta c} + g_{cc}\dot{c}\left(g_{pq}^n - \frac{1}{2}g_{pq}^n g_{\eta c} + g_{cc}c + \frac{1}{2}g_{cc}c^2\right)\right].$$  (15)

Because of the equilibrium conditions: $f_\eta = 0$, $f_{cc} = \mu$, function $\Omega(\eta)$ (12) at $\eta \to \eta_0$ is proportional to $(\eta - \eta_0)^2$. Therefore, the initial value $\dot{c}(\eta_0)$ can be found by taking the $\eta \to \eta_0$ limit of Eq. (14).

For the given solution $c(\eta)$ of COE, the coordinate dependence $\eta(\xi)$ is determined by integrating Eq. (13):

$$\xi = \xi_1 + \int_{\eta_1}^{\eta} d\eta (G/\Omega)^{1/2}$$  (16)

where the reference point $\xi_1$ is determined by the choice of value $\eta_1 = \eta(\xi_1)$. For the symmetrical APB for which $\eta \to \pm \eta_0$ at $\xi \to \pm \infty$, functions $c$, $\Omega$ and $G$ are even in $\eta$, and it is natural to put $\xi_1 = 0$ at $\eta_1 = 0$. But for an IPB separating the ordered and the disordered phase, values $\eta_1 \to 0$ correspond to $\xi \to (-\infty)$, and so $\xi_1$ should be chosen at some intermediate value $\eta_1$.

The surface energy $\sigma$ and the surface segregation $\Gamma$ is the excess of the grand canonical potential and of B atoms, respectively, per unit area $[2]$. Taking into account Eqs. (11)–(13) one obtains for the surface energy:

$$\sigma = \frac{2}{v_a} \int_{\eta_{min}}^{\eta_0} d\eta (G/\Omega)^{1/2}$$  (17)

where $\eta_{min}$ is $(-\eta_0)$ for an APB and zero for an IPB, while the surface segregation is given by the expression:

$$\Gamma = \frac{1}{v_a} \int_{-\eta_0}^{\eta_0} d\eta (c_0 - c) (G/\Omega)^{1/2}.$$  (18)

For a symmetrical APB, the integral in (17) or (18) can be written as twice of the integral over positive $\eta$.

Relations similar to (11)–(13) can also be derived for phases with several order parameters, such as the L12 or L10 phase. In particular, for an APB separating two L12-ordered domains, the order parameters $(\eta_1, \eta_2, \eta_3)$ have the form $(\zeta, \eta, \eta)$ mentioned above with the limiting values $(\eta_0, \eta_0, \eta_0)$ and $(\eta_0, -\eta_0, -\eta_0)$ at $\xi \to \pm \infty$. The variational equations and their first integral have the form analogous to Eqs. (11) and (13) but include three functions, $c(\xi)$, $\zeta(\xi)$ and $\eta(\xi)$. It is again convenient to consider $c$ and $\xi$ as functions of $\eta$ (while for APBs in the L10 phase, $c$ and $\eta$ as functions of $\zeta$) and obtain a system of equations for $c(\eta)$ and $\zeta(\eta)$ analogous to COE (14). Equations for $\xi(\eta)$, $\sigma$ and $\Gamma$ preserve their form (14)–(16) but $G(\eta)$ now includes the derivative $\dot{\xi} = d\xi/d\eta$ and six functions $g_{pq}$ which are related to $g_{pq}$ in Eqs. (14), (15) as follows:

$$g_{pq}(\alpha) = g_{pq}^1 + g_{pq}^b \cos^2 \alpha,$$  (19)

where $\alpha$ is the angle between the APB orientation and the local tetragonality axis. When the nearest-neighbor interaction $v_1$ much exceeds the rest ones (as in CuAu-based alloys [9–11]), the functions $g_{pq}(\alpha)$ are highly anisotropic which is illustrated by Eqs. (14): $g_{pq}^n \sim \sin^2 \alpha$; $g_{pq}^\alpha \sim \cos^2 \alpha$. It results in a notable anisotropy of distributions of APBs, including the presence of many low-energy “conservative” APBs with $\alpha \approx 0$ in the L12 phase and $\alpha \approx \pi/2$ in the L10 phase, as well as a peculiar alignment of APBs in “twinned” L10 structures [9–11]. In more detail, COE and Eqs. (14)–(16) for the L12 and L10 phases will be discussed elsewhere.

Let us now discuss some applications of Eqs. (14)–(16). First I consider the case when the equilibrium order parameter $\eta_0$ is small. Then the function $f$ in (14) can be written as the Landau expansion:

$$f(\eta, c) = \varphi + a\eta^2 + b\eta^4 + d\eta^6$$  (20)
where $\varphi$, $a$, $b$ and $d$ are some functions of concentration $c$ and temperature $T$. The equilibrium value $\eta_0$ is determined by the equation $f^0_a = 0$, while the ordering spinodal $T_s(c)$ (the disordered phase stability limit) is determined by the equation: $a(c, T) = 0$. Small values $\eta_0$ under consideration correspond to $c_0$, $T$ points near the ordering spinodal where $a(c_0, T)$ is small.

It is clear from both physical considerations and the results below that the difference $(c - c_0)$ at small $\eta_0$ is small, too. Therefore, functions $(f_c - \mu)$ and $f_\eta$ in Eq. (14) can be expanded in powers of $(c - c_0)$, $\eta$ and $\eta_0$:

$$f_c - \mu = a^0_c (\eta^2 - \eta_0^2) + \varphi^0_c (c - c_0) + \ldots$$

$$f_\eta = 4 \eta b_0 (\eta^2 - \eta_0^2) + 2 \eta a^0_c (c - c_0) + \ldots$$

Here $\varphi^0_c$ is $(\partial^2 \varphi/\partial c^2)_0$, and dots mean terms of higher orders in $\eta_0^2$. The analogous expansion of $\Omega(c, \eta)$ starts with terms bilinear in $(c - c_0)$ and $(\eta^2 - \eta_0^2)$, while for functions $g_{\varphi c}$ and $\tilde{c}$ the expansions start with terms linear in $\eta$. Thus terms with $\Omega$ and $f_\eta$ in (14) are proportional to $\eta_0^2$ being small compared to $(f_c - \mu) \sim \eta_0^2$, and COE is reduced to the equation $f_c = \mu$, which yields:

$$c_0 - c(\eta) = (\eta_0^2 - \eta^2)(-a^0_c)/\varphi^0_c.$$  

(23)

Taking derivative of equation $a(c, T) = 0$ one obtains:

$$-a^0_c = T_s^o \alpha$$

where $\alpha$ is $(\partial a/\partial T)_0$ and $T_s^o = d T_s^o/dc$. Thus the surface segregation at ABP is proportional to the ordering spinodal slope $T_s^o(c_0)$, and so it decreases with approaching the critical point where $T = 0$.

Let us now suppose the alloy state $c_0, T$ in the $c, T$ plane to be close to the second-order transition line $T_s(c)$ far from possible tricritical points. Then the higher-order terms in expansions (20)-(22) can be neglected, and for the function $\Omega(\eta)$ (12) such expansion yields:

$$\Omega(\eta) = \tilde{\eta}(\eta_0^2 - \eta^2)^2; \quad \tilde{\eta} = b_0 - (\alpha T_s^o)^2/2\varphi^0_c.$$  

(24)

Using Eqs. (16)-(18) and (24) one obtains in this case for $\eta(\xi), c(\xi)$, the APB energy $\sigma$ and the segregation $\Gamma$:

$$\eta(\xi) = \eta_0 \tanh(\xi/\delta); \quad c_0 - c(\xi) = \eta_0^2 \lambda \cosh^{-2}(\xi/\delta);$$

$$\sigma = \frac{8}{3 v_a} \eta_0^3 \left(\frac{g \tilde{b}}{v_a}\right)^{1/2}; \quad \Gamma = \frac{2}{v_a} \eta_0 \lambda (g \tilde{b})^{1/2}$$

(25)

where $\lambda = \alpha T_s^o/\varphi^0_c$; $g$ is $\eta_0^2 \eta_0$; and $\delta = (g/\eta_0^2 \tilde{b})^{1/2}$ is the APB width. These expressions generalize the earlier MFA results (2) to the case of any GL functional. The dependencies $\eta(\xi)$ and $c(\xi)$ in Eqs. (25) are similar to those observed in the Monte Carlo study of segregation at APBs (3). The temperature dependence of this segregation at small $\eta_0$ is more sharp than that of the APB energy: $\Gamma \propto \eta_0 \sim (T_s - T)^{1/2}$ while $\sigma \propto \eta_0^3 \sim (T_s - T)^{3/2}$. Eqs. (24)-(25) also show that the presence of segregation results in a renormalization of the Landau parameter $b_0$ entering characteristics of APB to the lesser value $\tilde{b}$ given by Eq. (24). It results in a decrease of the APB energy $\sigma$ and an increase of its width $\delta$ and segregation $\Gamma$ under decreasing temperature $T$ along the ordering spinodal $T_s(c)$.

The point $c_0, T$ at which both $a(c_0, T)$ in (24) and $b$ in (24) vanish corresponds to the tricritical point $c_t, T_t$. At $T < T_t$ the second-order transition line $T_s(c)$ in the $c, T$ plane splits into two binodals, $c_{bo}(T)$ and $c_{bd}(T)$, delimiting the single-phase ordered and disordered field, respectively. Such tricritical point is observed, for example, in alloys Fe–Al (4). At this point the lowest order terms in Eqs. (22) and (24) vanish, one should consider the next-order terms, and function $\Omega(\eta)$ (12) at small $x = (c_0 - c_t)$ and $t = (T_c - T_t)$ takes the form:

$$\Omega(\eta) = A (\eta_0^2 - \eta^2)^2 (\eta^2 + h).$$

(26)

Here $h = h(x, t)$ is a linear function of $x$ and $t$ which can be written in terms of the binodal temperature derivative $c_{bo} = dc_{bo}/dT$ as: $h = \nu (x - t c_{bo})$, while $A$ and $\nu$ are some positive constants. Using Eqs. (14)-(18) and (24) one obtains for the characteristics of APB near $T_t$:

$$\eta(\xi) = \frac{\eta_0 \sinh y}{(\cosh^2 y + \alpha)^{1/2}}; \quad c_0 - c(\xi) = \frac{\lambda \eta_0^2 (1 + \alpha)}{(\cosh^2 y + \alpha)^{1/2}}; \quad \sigma = \frac{J(\alpha)}{v_a} (g A \eta_0)^{1/2}; \quad \Gamma = \frac{2 \lambda L(\alpha)}{v_a} (g A)^{1/2}.$$  

(27)

Here $y = \xi/\tilde{\delta}$; $\alpha$ is $\eta_0^2 / h$; while $\tilde{\delta}, L(\alpha)$ and $J(\alpha)$ are:

$$\tilde{\delta} = [g A \eta_0^2 (h + \eta_0^2)]^{1/2}; \quad L(\alpha) = \ln [(1 + \alpha)^{1/2} + \alpha^{1/2}]; \quad J(\alpha) = \frac{1}{\alpha^2} [(1 + 4 \alpha) L(\alpha) + (2 \alpha - 1)(\alpha + \alpha^2)^{1/2}].$$

(28)

Function $h(x, t)$ in (24)-(28) is proportional to the distance in the $c, T$ plane from point $c_0, T$ to the binodal $c_{bo}(T)$, while $\eta_0^2$ is proportional to the distance to the ordering spinodal $T_s(c)$. Thus at small $\alpha \ll 1$, Eqs. (26)-(28) turn into (24)-(25) with $\tilde{b} = Ab$ and describe the critical behaviour of APB near $T_s(c)$ discussed above. The opposite case, $\alpha \gg 1$, corresponds to the region of “wetting” APBs which received recently much attention (4-6). Value $h = 0$ corresponds to the ordered state with $c_0 = c_{bo}(T)$, and then COE (14) describes an IPB between this state and the disordered state with $\eta_0 = 0$ and $c_d = c_{bd}(T)$. Substituting Eq. (24) with $h = 0$ into Eqs. (16) and (17) one obtains for this IPB:

$$\eta(\xi) = \frac{\eta_0}{(1 + e^{-\xi})^{1/2}}; \quad c(\xi) - c_d = \frac{\lambda \eta_0^2}{(1 + e^{-\xi})^{1/2}}; \quad \sigma_{APB} = 2 \sigma_{IPB}.$$  

(29)
Here $z$ is $\xi/\delta_1$; $\delta_1 = (g/A)^{1/2}/2z^2$ is the IPB width; $\sigma_{\text{IPB}} = (gA\kappa_0)^{1/2}/2c_0$ is the IPB energy; $c_d$ is $c_0 - \lambda n_0^2$; and the coordinate $\xi_1 = 0$ in (14) is chosen at $\eta_1 = \eta_0/\sqrt{2}$ where $c(\eta_1)$ is $(c_0 + c_d)/2$. Eqs. (29) show that the order parameter $\eta$ in the disordered phase decreases with moving from IPB much more slowly than the concentration deviation: $\eta \sim (c - c_d)^{1/2}$. Eqs. (27)-(30) also show that in the “wetting” regime of large $\alpha$, the profiles $\eta(\xi)$ and $c(\xi)$ in Eq. (27) correspond to the presence at $\xi_\pm = \pm \delta_1 \ln \alpha$ of two almost independent IPBs described by Eqs. (29). The total width $l \simeq (\xi_+ - \xi_-)$ and the segregation $\Gamma$ for such APB are proportional to $\ln(1/\alpha)$ while the energy difference $(\sigma_{\text{APB}} - 2\sigma_{\text{IPB}})$ is proportional to $h \ln(1/\alpha)$, which are usual dependences for the wetting regime (16). Eqs. (27)-(30) specify these relations for the vicinity of tricritical points and enable one to follow the transition from wetting to the critical behaviour of APBs under variation of $T$ or $c_0$.

Let us now apply Eqs. (14)-(17) to derive the wetting relation (18) for the phases with several order parameters, in particular, for the $L_12$ phase in equilibrium with the $L1_0$ or the disordered FCC (A1) phase. This problem was discussed by a number of authors (1, 3, 5, 7) but the general proof seems to be absent yet. Let us first note that in consideration of IPB, the initial condition to COE (14) can be put in either the ordered or the disordered phase, i.e. at $(c, \eta)$ values equal to either $(c_0, \eta_0)$ or $(c_d, 0)$, while the solution $c_{\text{IPB}}(\eta)$ at either choice is the same and unique. Therefore, in consideration of APB with the same initial values $c_0, \eta_0$, the solution $c_{\text{APB}}(\eta)$ coincides with $c_{\text{IPB}}(\eta)$ at $\eta > 0$, it is $c_{\text{IPB}}(-\eta)$ at $\eta < 0$, and so Eq. (19) follows from Eq. (17). For the APB or IPB in the $L1_2$ phase, the local order can be described by the parameters $(c, \zeta, \eta)$ mentioned above, and their initial values in COE are $(c_0, \eta_0, \eta_0)$, while the final ones are $(c_0, \eta_0, -\eta_0)$, $(c_d, 0, 0)$, and $(c_d, \eta_0, 0)$ for the case of an APB, IPB($L1_2-A1$), and IPB($L1_2-L1_0$), respectively, where $c_d$ and $\eta_0$ correspond to the second binodal $L1_2-L1_0$. Therefore, the wetting relation (19) for the $L1_2-A1$ or $L1_2-L1_0$ phase equilibrium follows from COE and Eq. (17), just as for the single-order-parameter case. Note, however, that at the given orientation $\eta_0$ there are three types of an APB in the $L1_2$ phase with the local order $(\eta_1, \eta_2, \eta_3)$ of the form $(\zeta, \eta, \eta)$, $(\eta, \zeta, \eta)$ or $(\eta, \eta, \zeta)$, and the structure and energy for each type is, generally, different. Therefore, there are at least three types of an IPB($L1_2-A1$) corresponding to “a half” of the relevant APB in the wetting limit. In the course of the kinetical wetting (for example, under $A1 \to A1+L1_2$ transformations studied in (6, 9)) each APB first transforms into two “its own” IPBs, but later on these IPBs can evolve to other types.

The effects of anisotropy under wetting APBs in Eqs. (14)-(18) are described by a factor $G^{1/2}$, while the main contribution to $\Omega(\eta)$ here is determined by the thermodynamic relations. In particular, singular contributions to $\sigma$ and $\Gamma$ under wetting $L1_2$-APB by the $A1$ or $L1_0$ phase correspond to the region of small $\eta$ where $\Omega$ has the same form as in Eq. (27), while $G(\eta)$ is reduced to its first term $g_{\eta\eta}$ as functions $g_{\eta\kappa}$, $g_{\eta\zeta}$, $\hat{\zeta}$, and $\hat{\kappa}$, being odd in $\eta$, vanish at small $\eta$. Thus the main contributions to the APB width and energy take the form:

$$l \sim g_{\eta \eta}^{1/2} \ln (1/\alpha); \quad (\sigma_{\text{APB}} - 2\sigma_{\text{IPB}}) \sim g_{\eta \eta}^{1/2} h \ln (1/\alpha),$$

where the angular dependence $g_{\eta\eta}$ is given by (13).

Therefore, the wetting effects can reveal a significant anisotropy, particularly in the short-range interaction systems. It agrees with some previous results (3, 6, 7).

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1. J.W. Cahn and J.E. Hilliard, J. Chem. Phys. 28, 258 (1958).
2. R. Kikuchi and J.W. Cahn, J. Phys. Chem. Solids, 23, 38 (1962), and 27, 1305 (1966).
3. R. Kikuchi and J.W. Cahn, Acta Met. 27, 1337 (1979).
4. S.M. Allen and J.W. Cahn, Acta Met. 24, 425 (1976).
5. F. Schmid and K. Binder, Phys. Rev. B 46, 13553 (1992).
6. R.J. Braun, J.W. Cahn, G.B. McFadden and A.A. Wheeler, Phil. Trans. R. Soc. Lond. A 355, 1787 (1997).
7. Y. Wang, D. Banerjee, C.C. Su and A.G. Khachaturyan, Acta Mater. 46, 2983 (1998).
8. L. Proville and A. Finel, Phys. Rev. B 64, 054104 (2001).
9. K.D. Belashchenko, V.Yu. Dobretsov, I.R. Pankratov, G.D. Samolyuk and V.G. Vaks., J. Phys.: Condensed Matter 11,10593 and 10567 (1999).
10. K.D. Belashchenko, I.R. Pankratov, G.D. Samolyuk and V.G. Vaks, J. Phys.: Condensed Matter 14, 565 (2002).
11. V.G. Vaks, Pis. Zh. Eksp. Teor. Fiz. 73, 274 (2001) [JETP Lett. 73, 237 (2001)].
12. V.Yu. Dobretsov, G. Martin, F. Soisson and V.G. Vaks, Europhys. Lett. 31, 417 (1995).
13. V.G. Vaks and G.D. Samolyuk, Zh. Eksp. Teor. Fiz. 115, 158 (1999) [ Sov. Phys.–JETP 88, 89 (1999)]
14. V.G. Vaks, N.E. Zein and V.V. Kamysheenko, J. Phys. F: Metal Physics 18, 1641 (1988).
15. Y. Le Bouar, A. Loiseau, A. Finel and F. Ducastelle, Phys. Rev. B 61, 3317 (2000).
16. B. Widom, J. Chem. Phys. 68, 3878 (1978).