Pis'ma v ZhETF, vol. 76, iss. 2, pp. 105 – 109

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

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Submitted 27 May 2002
Resubmitted 10 June 2002

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 reveale 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 $L1_0$ and $L1_2$-type orderings.

PACS: 05.70.Fh, 61.50.Ks

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 asumptions 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 A_cB_{1-c} at $c \leq 1/2$. Various distributions of atoms over lattice sites i are described by the mean occupations $c_i = \langle n_i \rangle$ where n_i 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 [9]. The free energy $F\{c_i\}$ in the cluster description can be written as a series [13]:

$$F = \sum_i f^i = \sum_i \left(F_1^i + \sum_j F_2^{ij} + \cdots \sum_{j,\ldots k} F_m^{ij\ldots k} \right). \quad (1)$$

Here f^i is the free energy per site i; $F_1^i = T[c_i \ln c_i + (1-c_i)\ln(1-c_i)]$ is the mixing entropy contribution; $F_l^{i\ldots k} = F_l(c_i, \ldots, c_k)$ is the contribution of interactions within l-site cluster of sites $i, \ldots, k$; 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 $L1_2$ and $L1_0$-type orderings [9]) Eq. (1) includes also 4-site terms F_4^{ijkl} [13].

For the homogeneous ordered structure, the mean occupation $c_j = c(\mathbf{r}_j)$ at site j with the lattice vector $\mathbf{r}_j$ can be written as a superposition of concentration waves with some superstructure vectors $\mathbf{k}_s$ [8 – 12]:

$$c_j = c + \sum_s \eta_s \exp(i\mathbf{k}_s\mathbf{r}_j) \equiv \sum_p \eta_p \exp(i\mathbf{k}_p\mathbf{r}_j). \quad (2)$$

Here amplitudes η_s can be considered as order parameters; the last expression includes also term with $\eta_p = c$ and $\mathbf{k}_p = 0$; and for simplicity both parameters η_s and factors $\exp(i\mathbf{k}_s\mathbf{r}_i)$ are supposed to be real which is the case, in particular, for the B2, $L1_0$ and $L1_2$-type order.

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For weakly inhomogeneous states, amplitudes η_p in (2) are not constants but smooth functions of coordinates $\mathbf{r}_i$. Thus functions $f^i\{c_j\}$ in (1) can be expanded in powers of differences $\delta c_j = \sum_p \delta\eta_p^j \exp(i\mathbf{k}_p\mathbf{r}_j)$ where

$$\delta\eta_p^j = \eta_p^j - \eta_p^i = \mathbf{r}_{ji}\nabla\eta_p + \frac{1}{2}r_{ji}^\alpha r_{ji}^\beta \nabla_{\alpha\beta}\eta_p. \qquad (3)$$

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

$$F = \frac{1}{v_a}\int d^3r\Big[\sum_{p,q} g_{pq}^{\alpha\beta}\nabla_\alpha\eta_p\nabla_\beta\eta_q + f\{\eta_p\}\Big]. \qquad (4)$$

Here v_a is volume per atom; $f\{\eta_p\}$ is function $f^i\{c_j\}$ in (1) averaged over all sublattices with c_j given by Eq. (2); and $g_{pq}^{\alpha\beta}$ is given by the expression:

$$g_{pq}^{\alpha\beta} = -\frac{1}{2}\sum_j r_{ij}^\alpha r_{ij}^\beta S_{ij}^i \exp[i(\mathbf{k}_p\mathbf{r}_j - \mathbf{k}_q\mathbf{r}_i)] +$$
$$+\frac{1}{2}\sum_{k,j;\, j\neq i} r_{ki}^\alpha (r_{ji}^\beta - r_{ki}^\beta) S_{kj}^i \exp[i(\mathbf{k}_p\mathbf{r}_j - \mathbf{k}_q\mathbf{r}_i)] \qquad (5)$$

where $S_{kj}^i = \partial^2 f^i/\partial c_k \partial c_j$. Note that the last term of (5) is nonzero only when all three sites i, j and k are different, and so it is present only when the non-pairwise contributions $F_{m>2}^{ij\ldots k}$ in (1) are taken into account, such as the TCA terms F_4^{ijkl} [13].

For the $L1_2$ and $L1_0$ phases in face-centred-cubic (FCC) alloys, Eq. (2) includes waves with three vectors $\mathbf{k}_s$: $\mathbf{k}_1 = (100)2\pi/a$, $\mathbf{k}_2 = (010)2\pi/a$, and $\mathbf{k}_3 = (001)2\pi/a$ 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 (η_1, η_2, η_3) of the type (ζ, η, η) and corresponds to the tetragonal symmetry [6, 9, 11]. 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, $g_{pq}^\perp = g_{pq}^{22} = g_{pq}^{33}$ and $g_{pq}^a = (g_{pq}^{11} - g_{pq}^{22})$. Using for simplicity the 2-neighbor-interaction model: $v_{n>2} = 0$, one obtains in the MFA:

$$g_{\zeta\zeta}^\perp = -\frac{1}{2}a^2 v_2;\; g_{\zeta\zeta,\eta\eta}^a = \pm\frac{1}{2}a^2 v_1;\; g_{\eta\eta}^\perp = \frac{1}{2}a^2(v_1 - 2v_2);$$
$$g_{cc}^\perp = -\frac{1}{2}a^2(v_1 + v_2); \qquad g_{cc}^a = g_{\eta c,\zeta c,\eta\zeta}^{\perp,a} = 0, \qquad (6)$$

while the PCA expressions for $g_{pq}^\perp$ and g_{pq}^a are:

$$g_{\zeta\zeta,cc}^\perp = \frac{1}{4}a^2(-\varphi_1^+ \pm \psi_1^+ - \chi_2^+ - \varphi_2^{dd});\;\; g_{\zeta c}^a = \frac{1}{4}a^2\varphi_1^-;$$
$$g_{\zeta\zeta,cc}^a = \frac{1}{4}a^2(\varphi_1^+ \pm \psi_1^+);\; g_{\zeta c}^\perp = \frac{1}{4}a^2(-\varphi_1^- - \chi_2^+ + \varphi_2^{dd});$$
$$g_{\eta\eta}^\perp = \frac{1}{2}a^2(\varphi_1^{ab} - 2\,\chi_2^+); \quad g_{\eta\eta}^a = -\frac{1}{2}a^2\varphi_1^{ab};$$
$$g_{\eta\zeta,\eta c}^\perp = \frac{1}{4}a^2(\pm\psi_1^- - 2\varphi_2^-); \quad g_{\eta\zeta,\eta c}^a = \pm\frac{1}{4}a^2\psi_1^-. \qquad (7)$$

Here plus or minus in $(\pm)$ corresponds to the first or the second pair of lower indices in the left-hand-side of Eqs. (6), (7);

$$\varphi_n^{ij} = -Tf_n/R_n^{ij}; \qquad \varphi_n^\pm = \frac{1}{2}(\varphi_n^{ab} \pm \varphi_n^{dd});$$
$$\psi_n^\pm = \frac{1}{2}(\varphi_n^{ad} \pm \varphi_n^{bd}); \qquad \chi_n^\pm = \frac{1}{2}(\varphi_n^{aa} \pm \varphi_n^{bb});$$
$$R_n^{ij} = [1 + 2f_n(c_i + c_j - 2c_ic_j) + f_n^2(c_i - c_j)^2]^{1/2}; \quad (8)$$

$f_n = \exp(-v_n/T) - 1$ is the Mayer function; and index i or j equal to a, b or d corresponds to the mean occupation c_i or c_j of one of three different sublattices:

$$c_a = c + \zeta + 2\eta; \quad c_b = c + \zeta - 2\eta; \quad c_d = c - \zeta. \quad (9)$$

If the TCA is used, the nearest-neighbor contributions φ_1^{ij} in Eqs. (7) are replaced by the relevant tetrahedron contributions S_{ij}^i presented in Ref. [14]. For the B2 order, there is only one order parameter $\eta_s = \eta$ [9]; 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} are similar to those for $g_{pq}^\perp$ in Eqs. (6) and (7).

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

Let us now consider the case of a plane APB (or IPB) when parameters η_p in (2) depend only on the distance $\xi = \mathbf{r}\mathbf{n}_0$ where $\mathbf{n}_0 = (\cos\alpha, \sin\alpha\cos\varphi, \sin\alpha\sin\varphi)$ is normal to the APB plane. To find the equilibrium structure, one should minimize the functional (4) over functions $\eta_p(\xi)$ at the fixed total number of atoms [2]. 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:

$$g_{\eta\eta}\eta'' + g_{\eta c}c'' + \frac{1}{2}g_\eta^{\eta\eta}(\eta')^2 + g_c^{\eta\eta}\eta'c' +$$
$$+ (g_c^{\eta c} - \frac{1}{2}g_\eta^{cc})(c')^2 = \frac{1}{2}f_\eta;$$
$$g_{\eta c}\eta'' + g_{cc}c'' + (g_\eta^{\eta c} - \frac{1}{2}g_c^{\eta\eta})(\eta')^2 + g_\eta^{cc}\eta'c' +$$
$$+ \frac{1}{2}g_c^{cc} = \frac{1}{2}(f_c - \mu). \qquad (10)$$

Here prime means taking derivative over ξ; the lower index η or c means taking derivative over η or c; and μ is the chemical potential. At $\xi \to \infty$ functions c and η tend to their equilibrium values, c_0 and $\eta_0(c_0)$.

Multiplying first and second Eq. (10) by η' and c', respectively, summing them, and integrating the result, one obtains the first integral of this system of equations:

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

where Ω is the non-gradien part of the local excess grand canonical potential per atom:

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

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 η as an independent variable, while c and Ω, as its functions determined by Eqs. (10)–(12). Then the dependence $\eta'(\eta)$ is determined by Eq. (11):

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

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

$$\begin{aligned}&[\ddot{c}\,(g_{\eta c}^2 - g_{cc}g_{\eta\eta}) + \Phi]\,2\,\Omega\,/G = \\ &= (\mu - f_c)(g_{\eta\eta} + g_{\eta c}\dot{c}) + f_\eta(g_{\eta c} + g_{cc}\dot{c})\end{aligned} \tag{14}$$

where Φ is a linear function of derivatives g_r^{pq}:

$$\begin{aligned}\Phi = (g_{\eta c} + g_{cc}\dot{c})\Big[\frac{1}{2}g_\eta^{\eta\eta} + g_c^{\eta\eta}\dot{c} + \Big(g_c^{\eta c} - \frac{1}{2}g_\eta^{cc}\Big)\dot{c}^2\Big] - \\ -(g_{\eta\eta} + g_{\eta c}\dot{c})\Big(g_\eta^{\eta c} - \frac{1}{2}g_c^{\eta\eta} + g_\eta^{cc}\dot{c} + \frac{1}{2}g_c^{cc}\dot{c}^2\Big).\end{aligned} \tag{15}$$

Because of the equilibrium conditions: $f_\eta^0 = 0$, $f_c^0 = \mu$, 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):

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

where the reference point ξ_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, Ω and G are even in η, 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 ξ_1 should be chosen at some intermediate value η_1.

The surface energy σ and the surface segregation Γ 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:

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

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

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

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

Relations similar to (11)–(18) can also be derived for phases with several order parameters, such as the $L1_2$ or $L1_0$ phase. In particular, for an APB separating two $L1_2$-ordered domains, the order parameters (η_1, η_2, η_3) have the form (ζ, η, η) mentioned above with the limiting values (η_0, η_0, η_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. (10) and (11) but include three functions, $c(\xi)$, $\zeta(\xi)$ and $\eta(\xi)$. It is again convenient to consider c and ζ as functions of η (while for APBs in the $L1_0$ phase, c and η as functions of ζ) and obtain a system of equations for $c(\eta)$ and $\zeta(\eta)$ analogous to COE (14). Equations for $\xi(\eta)$, σ and Γ preserve their form (16)–(18) but $G(\eta)$ now includes the derivative $\dot{\zeta} = d\zeta/d\eta$ and six functions g_{pq} which are related to $g_{pq}^{\perp,a}$ in Eqs. (6), (7) as follows:

$$g_{pq}(\alpha) = g_{pq}^{\perp} + g_{pq}^{a}\cos^2\alpha, \tag{19}$$

where α 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. (6): $g_{\eta\eta} \sim \sim \sin^2\alpha$; $g_{\zeta\zeta} \sim \cos^2\alpha$. It results in a notable anisotropy of distributions of APBs, including the presence of many low-energy "conservative" APBs with $\alpha \simeq 0$ in the $L1_2$ phase and $\alpha \simeq \pi/2$ in the $L1_0$ phase, as well as a peculiar alignment of APBs in "twinned" $L1_0$ structures [9 – 11]. In more detail, COE and Eqs. (16)–(19) for the $L1_2$ and $L1_0$ phases will be discussed elsewhere.

Let us now discuss some applications of Eqs. (14)–(19). First I consider the case when the equilibrium order parameter η_0 is small. Then the function f in (4) can be written as the Landau expansion:

$$f(\eta, c) = \varphi + a\eta^2 + b\eta^4 + d\eta^6 \tag{20}$$

where φ, a, b and d are some functions of concentration c and temperature T. The equilibrium value η_0 is determined by the equation $f_\eta^0 = 0$, while the ordering spinodal $T = T_s(c)$ (the disordered phase stability limit) is determined by the equation: $a(c,T) = 0$. Small values η_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 η_0 is small, too. Therefore, functions $(f_c - \mu)$ and f_η in Eq. (14) can be expanded in powers of $(c - c_0)$, η and η_0:

$$f_c - \mu = a_c^0\,(\eta^2 - \eta_0^2) + \varphi_{cc}^0\,(c - c_0) + \ldots\,, \tag{21}$$

$$f_\eta = 4\eta\, b_0\,(\eta^2 - \eta_0^2) + 2\eta\, a_c^0\,(c - c_0) + \ldots \tag{22}$$

Here φ_{cc}^0 is $(\partial^2\varphi/\partial c^2)_0$, and dots mean terms of higher orders in η_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 $g_{\eta c}$ and $\dot{c}$ the expansions start with terms linear in η. Thus terms with Ω and f_η in (14) are proportional to η_0^4 being small compared to $(f_c - \mu) \sim \eta_0^2$, and COE is reduced to the equation $f_c = \mu$, which yields:

$$c_0 - c(\eta) = (\eta_0^2 - \eta^2)(-a_c^0)/\varphi_{cc}^0. \tag{23}$$

Taking derivative of equation $a(c,T) = 0$ one obtains: $(-a_c^0) = T_s'\alpha$ where α is $(\partial a/\partial T)_0$ and $T_s' = dT_s/dc$. Thus the surface segregation at APB is proportional to the ordering spinodal slope $T_s'(c_0)$, and so it decreases with approaching the critical point where $T_s' = 0$.

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:

$$\Omega(\eta) = \tilde{b}\,(\eta_0^2 - \eta^2)^2; \qquad \tilde{b} = b_0 - (\alpha\, T_s')^2/2\varphi_{cc}^0. \tag{24}$$

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

$$\eta(\xi) = \eta_0\tanh(\xi/\delta); \quad c_0 - c(\xi) = \eta_0^2\,\lambda\cosh^{-2}(\xi/\delta);$$
$$\sigma = \frac{8}{3v_a}\,\eta_0^3\left(g\,\tilde{b}\right)^{1/2}; \; \Gamma = \frac{2}{v_a}\,\eta_0\,\lambda(g/\tilde{b})^{1/2} \tag{25}$$

where λ is $\alpha\, T_s'/\varphi_{cc}^0$; g is $g_{\eta\eta}^0$; and $\delta = (g/\eta_0^2\tilde{b})^{1/2}$ is the APB width. These expressions generalize the earlier MFA results [12] to the case of any GL functional. The dependences $\eta(\xi)$ and $c(\xi)$ in Eqs. (25) are similar to those observed in the Monte-Carlo study of segregation at APBs [5]. The temperature dependence of this segregation at small η_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 σ and an increase of its width δ and segregation Γ under decreasing temperature T along the ordering spinodal $T = T_s(c)$.

The point c_0, T at which both $a(c_0,T)$ in (20) and $\tilde{b}$ 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 Ω (12) at small $x = (c_0 - c_t)$ and $t = (T - T_t)$ takes the form:

$$\Omega(\eta) = A\,(\eta_0^2 - \eta^2)^2(\eta^2 + h). \tag{26}$$

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 ν are some positive constants. Using Eqs. (16)–(18) and (26) one obtains for the characteristics of APB near T_t:

$$\eta(\xi) = \frac{\eta_0\,\sinh y}{(\cosh^2 y + \alpha)^{1/2}}; \quad c_0 - c(\xi) = \frac{\lambda\,\eta_0^2(1+\alpha)}{(\cosh^2 y + \alpha)};$$
$$\sigma = \frac{J(\alpha)}{v_a}(gA\eta_0^4)^{1/2}; \quad \Gamma = \frac{2\lambda L(\alpha)}{v_a}\,(g/A)^{1/2}. \tag{27}$$

Here y is $\xi/\tilde{\delta}$; α is η_0^2/h; while $\tilde{\delta}$, $L(\alpha)$ and $J(\alpha)$ are:

$$\tilde{\delta} = [g/A\eta_0^2(h + \eta_0^2)]^{1/2}; L(\alpha) = \ln\left[(1+\alpha)^{1/2} + \alpha^{1/2}\right];$$
$$J(\alpha) = \frac{1}{2\alpha^2}[(1 + 4\alpha)L(\alpha) + (2\alpha - 1)(\alpha + \alpha^2)^{1/2}]. \tag{28}$$

Function $h(x,t)$ in (26)-(28) is proportional to the distance in the c,T plane from point c_0, T to the binodal $c_{bo}(T)$, while η_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 $\tilde{b} = Ah$ 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 [3, 6, 15]. Value $h = 0$ corresponds to the ordered state with $c_0 = c_{bo}(T)$, and then COE (14) describes an IPB betwen this state and the disordered state with $\eta_d = 0$ and $c_d = c_{bd}(T)$. Substituting Eq. (26) with $h = 0$ into Eqs. (16) and (17) one obtains for this IPB:

$$\eta(\xi) = \frac{\eta_0}{(1 + e^{-z})^{1/2}}; \quad c(\xi) - c_d = \frac{\lambda\,\eta_0^2}{(1 + e^{-z})}; \tag{29}$$

$$\sigma_{\mathrm{APB}} = 2\sigma_{\mathrm{IPB}}. \tag{30}$$

Here z is ξ/δ_1; $\delta_1 = (g/A)^{1/2}/2\eta_0^2$ is the IPB width; $\sigma_{\mathrm{IPB}} = (gA\eta_0^4)^{1/2}/2v_a$ is the IPB energy; c_d is $c_0 - \lambda\eta_0^2$;

and the coordinate $\xi_1 = 0$ in (16) 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 η 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 α, 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 Γ for such APB are proportional to $\ln(1/h)$ while the energy difference $(\sigma_{\rm APB} - 2\sigma_{\rm IPB})$ is proportional to $h\ln(1/h)$, 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 (30) for the phases with several order parameters, in particular, for the $\rm L1_2$ phase in equilibrium with the $\rm L1_0$ or the disordered FCC (A1) phase. This problem was discussed by a number of authors [3, 6, 15] 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,η) values equal to either (c_0,η_0) or $(c_d,0)$, while the solution $c_{\rm IPB}(\eta)$ at either choice is the same and unique. Therefore, in consideration of APB with the same initial values c_0,η_0, the solution $c_{\rm APB}(\eta)$ coincides with $c_{\rm IPB}(\eta)$ at $\eta>0$, it is $c_{\rm APB}(-\eta)$ at $\eta<0$, and so Eq. (30) follows from Eq. (17). For the APB or IPB in the $\rm L1_2$ phase, the local order can be described by the parameters (c,ζ,η) mentioned above, and their initial values in COE are (c_0,η_0,η_0), while the final ones are $(c_0,\eta_0,-\eta_0)$, $(c_d,0,0)$, and $(c_l,\eta_l,0)$ for the case of an APB, $\rm IPB(L1_2-A1)$, and $\rm IPB(L1_2-L1_0)$, respectively, where c_l and η_l correspond to the second binodal $\rm L1_2 - L1_0$. Therefore, the wetting relation (30) for the $\rm L1_2 - A1$ or $\rm L1_2 - L1_0$ phase equilibrium follows from COE and Eq. (17), just as for the single-order-parameter case. Note, however, that at the given orientation $\mathbf{n}_0$ there are three types of an APB in the $\rm L1_2$ phase with the local order (η_1,η_2,η_3) of the form (ζ,η,η), (η,ζ,η) or (η,η,ζ), and the structure and energy for each type is, generally, different. Therefore, there are at least three types of an $\rm IPB(L1_2-A1)$ corresponding to "a half" of the relevant APB in the wetting limit. In the course of the kinetical wetting (for example, under $\rm A1 \to A1 + L1_2$ transformations studied in [7, 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. (16)–(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 σ and Γ under wetting $\rm L1_2$-APB by the A1 or $\rm L1_0$ phase correspond to the region of small η where Ω has the same form as in Eq. (26), while $G(\eta)$ is reduced to its first term $g_{\eta\eta}$ as functions $g_{\eta\zeta}$, $g_{\eta c}$, $\dot\zeta$ and $\dot c$, being odd in η, vanish at small η. Thus the main contributions to the APB width and energy take the form:

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

where the angular dependence $g_{\eta\eta}$ is given by (19). Therefore, the wetting effects can reveale a significant anisotropy, particularly in the short-range interaction systems. It agrees with some previous results [3, 6, 15].

The author is much indebted to I.R. Pankratov for the help in this work. The work was supported by the Russian Fund of Basic Research under Grants # 00-02-17692 and # 00-15-96709.

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