

LETTER TO THE EDITOR

Effect of chemical-potential fluctuations on short-range order in disordered alloys

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Received 12 December 2001

Published 15 February 2002

Online at stacks.iop.org/JPhysCM/14/L193

Abstract

By taking into account the chemical-potential fluctuations, we propose a generalization of the formalism elaborated by R V Chepulskii and V N Bugaev (1998 *J. Phys.: Condens. Matter* **10** 7309), which is based on the use of the thermodynamic fluctuation method in the first order of a modified thermodynamic perturbation theory under the choice of the inverse effective number of atoms interacting with one fixed atom as a small parameter of expansion. As a result, a new approximation for calculation of the short-range order parameters in the disordered (i.e. without the long-range order) state of alloys is obtained. Moreover, the rigorous equation for determination of the chemical potentials is derived to replace the heuristic one obtained earlier. Both analytical and numerical comparison of the results of old and new approximations is performed. By comparison with the results of the Monte Carlo simulation, the higher numerical accuracy of the new approximation is demonstrated. The importance of taking into account the chemical-potential fluctuations is shown at low temperatures.

In [1–3], by use of the thermodynamic fluctuation method [4], in the first order of a modified thermodynamic perturbation theory [5, 6] under the choice of the inverse effective number of atoms interacting with one fixed atom as a small parameter of expansion [7], the so-called ring approximation was elaborated for the calculation of the short-range order (SRO) in disordered (i.e. without the long-range order) alloys. However, the chemical-potential fluctuations corresponding to the fluctuations of the site concentrations of atoms were assumed to be small and were not taken into account in the developed formalism. Besides, the equation for determination of the chemical potentials was derived heuristically and (as shown below) is approximate. In this letter, the corresponding formalism is generalized by taking into account the chemical-potential fluctuations. As a result, the modified expression for the SRO parameters and the rigorous equation for the determination of the chemical potentials are derived.

In general, in the framework of the lattice gas model, the Hamiltonian H of a two-component A–B disordered alloy with a Bravais crystal lattice can be written in the following form [8]:

$$H = Nv_0 + \Phi \sum_{\mathbf{R}} C_{\mathbf{R}} + \frac{1}{2} \sum_{\mathbf{R}_1, \mathbf{R}_2} V_{\mathbf{R}_1 - \mathbf{R}_2} C_{\mathbf{R}_1} C_{\mathbf{R}_2}, \quad (1)$$

taking into account the atomic interactions of less than or equal to second order and of arbitrary radius of action (order of interactions means the number of interacting atoms). In (1) N is the number of sites of the crystal lattice, v_0 is the energy per site of the alloy in which all N sites are occupied by B-type atoms, Φ and $V_{\mathbf{R}_1 - \mathbf{R}_2}$ are the unary and pair mixing potentials, respectively,

$$C_{\mathbf{R}} = \begin{cases} 1, & \text{if the site } \mathbf{R} \text{ is occupied by an A-type atom} \\ 0, & \text{otherwise,} \end{cases} \quad (2)$$

and the summations on the radius-vectors \mathbf{R} , \mathbf{R}_1 and \mathbf{R}_2 are carried over all N sites of the crystal lattice.

Taking into account the chemical-potential fluctuations, the grand partition function Ξ of the alloy in question

$$\Xi = \sum_{\{C_{\mathbf{R}}\}} \exp[-(k_{\text{B}}T)^{-1}(H - \mu_{\text{A}}N_{\text{A}} - \mu_{\text{B}}N_{\text{B}})] \quad (3)$$

can be presented as follows:

$$\Xi = \sum_{\{C_{\mathbf{R}}\}} \exp \left\{ -(k_{\text{B}}T)^{-1} \left[H - \sum_{\mathbf{R}} \mu_{\mathbf{R}}^{\text{A}} C_{\mathbf{R}} - \sum_{\mathbf{R}} \mu_{\mathbf{R}}^{\text{B}} (1 - C_{\mathbf{R}}) \right] \right\}. \quad (4)$$

In equations (3) and (4) $\mu_{\mathbf{R}}^{\text{A}}$, N_{A} and $\mu_{\mathbf{R}}^{\text{B}}$, N_{B} are the chemical potentials and the total numbers of A- and B-type atoms, respectively, T is the absolute temperature, k_{B} is the Boltzmann constant and the summation on $\{C_{\mathbf{R}}\}$ is carried over all possible atomic configurations. In the determination of (4), the relationships $N_{\text{A}} + N_{\text{B}} = N$ and $N_{\text{A}} = \sum_{\mathbf{R}} C_{\mathbf{R}}$ were used. Substituting (1) into (4) and using the equality $[C_{\mathbf{R}}]^n = C_{\mathbf{R}}$ (n is a positive integer), one can write

$$\Xi = \Xi_0 \sum_{\{C_{\mathbf{R}}\}} \exp \left[-(2k_{\text{B}}T)^{-1} \sum_{\mathbf{R}_1, \mathbf{R}_2} (V_{\mathbf{R}_1 - \mathbf{R}_2} + \mu_{\mathbf{R}_1} \delta_{\mathbf{R}_1, \mathbf{R}_2}) C_{\mathbf{R}_1} C_{\mathbf{R}_2} \right], \quad (5)$$

where $\delta_{\mathbf{R}_1, \mathbf{R}_2}$ is the Kronecker delta,

$$\Xi_0 = \exp \left[-(k_{\text{B}}T)^{-1} \sum_{\mathbf{R}} (v_0 - \mu_{\mathbf{R}}^{\text{B}}) \right], \quad \mu_{\mathbf{R}} = 2(\Phi - \mu_{\mathbf{R}}^{\text{A}} + \mu_{\mathbf{R}}^{\text{B}}). \quad (6)$$

Going from the partition function Ξ in (5) to the grand thermodynamic potential $\Omega = -k_{\text{B}}T \ln \Xi$ in the same way as from the corresponding equations (2.4) to (5.2) in [2], and then to the free energy F

$$F = \Omega + \sum_{\mathbf{R}} [\mu_{\mathbf{R}}^{\text{A}} P_{\mathbf{R}} + \mu_{\mathbf{R}}^{\text{B}} (1 - P_{\mathbf{R}})], \quad (7)$$

we arrive at the following expression:

$$\begin{aligned} F = Nv_0 + \sum_{\mathbf{R}} \left[\Phi P_{\mathbf{R}} - \frac{\mu_{\mathbf{R}}}{2} P_{\mathbf{R}} (1 - P_{\mathbf{R}}) \right] + \frac{1}{2} \sum_{\mathbf{R}_1, \mathbf{R}_2} V_{\mathbf{R}_1 - \mathbf{R}_2} P_{\mathbf{R}_1} P_{\mathbf{R}_2} \\ + k_{\text{B}}T \sum_{\mathbf{R}} [P_{\mathbf{R}} \ln P_{\mathbf{R}} + (1 - P_{\mathbf{R}}) \ln(1 - P_{\mathbf{R}})] \\ - \frac{k_{\text{B}}T}{2} \sum_{n=1}^{\infty} \frac{1}{n} \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n} f_{\mathbf{R}_1 - \mathbf{R}_2} f_{\mathbf{R}_2 - \mathbf{R}_3} \dots f_{\mathbf{R}_n - \mathbf{R}_1}. \end{aligned} \quad (8)$$

Equation (8) was obtained within the ring approximation, i.e. taking into account the contributions from the terms corresponding to the first and second powers of Brout's parameter z^{-1} , where z is the effective number of atoms interacting with one fixed atom [7]. In equation (8)

$$P_R = \langle C_R \rangle \quad (9)$$

is the probability to find an A-type atom at the site \mathbf{R} , the sign $\langle \dots \rangle$ means the statistical average over all states with given values of the long-range order (LRO) parameters,

$$\frac{f_{R_l-R_m}}{\sqrt{P_{R_l}(1-P_{R_l})}\sqrt{P_{R_m}(1-P_{R_m})}} = \frac{(V_{R_l-R_m} + \mu_{R_l}\delta_{R_l,R_m})}{k_B T}. \quad (10)$$

The equations for determination of the chemical potentials are $\partial\Omega/\partial\mu_R^A = -P_R$ and $\partial\Omega/\partial\mu_R^B = -(1-P_R)$, which in terms of the free energy can be written as

$$\partial F/\partial\mu_R = 0. \quad (11)$$

The free energy functional derived above has the following form:

$$F = F[P_R, \mu_R(P_R)]. \quad (12)$$

Within the thermodynamic fluctuation method [4], the SRO is found through the calculation of the free energy variation of the second order with respect to the fluctuations δP_R . However, in [2], the dependence $\mu_R(P_R)$ was assumed to be small and was not taken into account in such calculation. From (12) it follows that the expression for the free energy variation δF up to second order with respect to the fluctuations δP_R should be

$$\begin{aligned} \delta F = \sum_R \left[\frac{\partial F}{\partial P_R} \delta P_R + \frac{\partial F}{\partial \mu_R} \delta \mu_R \right] + \frac{1}{2} \sum_{R_1, R_2} \left[\frac{\partial^2 F}{\partial P_{R_1} \partial P_{R_2}} \delta P_{R_1} \delta P_{R_2} \right. \\ \left. + \frac{2\partial^2 F}{\partial P_{R_1} \partial \mu_{R_2}} \delta P_{R_1} \delta \mu_{R_2} + \frac{\partial^2 F}{\partial \mu_{R_1} \partial \mu_{R_2}} \delta \mu_{R_1} \delta \mu_{R_2} \right]. \quad (13) \end{aligned}$$

From (11), by taking the first derivative with respect to P_R , one can write that

$$\frac{d}{dP_{R_1}} \frac{\partial F}{\partial \mu_{R_2}} = \frac{\partial^2 F}{\partial P_{R_1} \partial \mu_{R_2}} + \sum_{R'} \frac{\partial^2 F}{\partial \mu_{R'} \partial \mu_{R_2}} \frac{d\mu_{R'}}{dP_{R_1}} = 0. \quad (14)$$

Besides, for the variation $\delta \mu_R$, we generally have up to second order with respect to the fluctuations δP_R

$$\delta \mu_R = \sum_{R_1} \frac{\partial \mu_R}{\partial P_{R_1}} \delta P_{R_1} + \frac{1}{2} \sum_{R_1, R_2} \frac{\partial^2 \mu_R}{\partial P_{R_1} \partial P_{R_2}} \delta P_{R_1} \delta P_{R_2}. \quad (15)$$

Thus, from (13), taking into account (11), (14) and (15), we obtain up to second order with respect to the fluctuations δP_R

$$\delta F = \frac{1}{2} \sum_{R_1, R_2} \left[\frac{\partial^2 F}{\partial P_{R_1} \partial P_{R_2}} + \sum_{R'} \frac{\partial^2 F}{\partial P_{R_1} \partial \mu_{R'}} \frac{d\mu_{R'}}{dP_{R_2}} \right] \delta P_{R_1} \delta P_{R_2}. \quad (16)$$

Note that the term in δF which is linear with respect to δP_R is equal to zero, because the fluctuations are considered in the disordered state, which is supposed to be thermodynamically stable at the considered external conditions. In such a disordered state, which is investigated in this letter, we should also put

$$\mu_R^A \rightarrow \mu_A, \quad \mu_R^B \rightarrow \mu_B, \quad \mu_R \rightarrow \mu, \quad P_R \rightarrow c = N_A/N, \quad (17)$$

where c is the concentration of A-type atoms in the alloy. Below, the transformation (17) will be performed in all coefficients of series expansion in terms of the fluctuations and in all final expressions corresponding to the disordered state.

Let us define the Fourier transforms $\delta\mu_k$ and δP_k of the fluctuations $\delta\mu_R$ and δP_R , respectively, as

$$\delta\mu_R = \sum_k \delta\mu_k \exp(-i\mathbf{k}\mathbf{R}), \quad \delta P_R = \sum_k \delta P_k \exp(-i\mathbf{k}\mathbf{R}). \quad (18)$$

From (11) using (8), firstly, one can derive the following relationship:

$$\frac{c(1-c)}{k_B T} \delta\mu_k = \frac{1-2c}{c(1-c)} \left(1 - \frac{1}{I_k}\right) \delta P_k \quad (19)$$

where

$$I_k = N^{-1} \sum_q [A_{k-q} A_q]^{-1}, \quad A_k = 1 + \frac{c(1-c)}{k_B T} (\tilde{V}_k + \mu), \quad (20)$$

\tilde{V}_k is the Fourier transform of the pair mixing potential

$$\tilde{V}_k = \sum_R V_R \exp(-i\mathbf{k}\mathbf{R}). \quad (21)$$

Secondly, in the same way, one can also obtain the following equation for the determination μ :

$$N^{-1} \sum_k [A_k]^{-1} = 1. \quad (22)$$

From (16), using (8), (11), (19) and (22), we obtain

$$\delta F = \frac{N k_B T}{2} \sum_k \frac{|\delta P_k|^2}{c(1-c)} \beta_k^{-1}, \quad (23)$$

where

$$\beta_k^{-1} = A_k + \frac{(1-2c)^2}{2c(1-c)} \left(\frac{1}{I_k} - 1\right). \quad (24)$$

Thus, from equation (23) it follows that, within the ring approximation, in the context of the thermodynamic fluctuation method, the Fourier transform α_k of the SRO parameters α_R

$$\alpha_{R_1-R_2} = (\langle C_{R_1} C_{R_2} \rangle)_{P_R=c} - c^2 [c(1-c)]^{-1}, \quad (25)$$

$$\alpha_k = \sum_R \alpha_R \exp(-i\mathbf{k}\mathbf{R}), \quad \alpha_R = N^{-1} \sum_k \alpha_k \exp(i\mathbf{k}\mathbf{R})$$

is determined (see e.g. equation (7.6) in [2]) as

$$\alpha_k = 1 - N^{-1} \sum_q \beta_q + \beta_k, \quad (26)$$

where β_k is defined in (24). Note that the term A_k in (24) corresponds to the spherical model (SM) approximation [7] and the other terms in (24) are just the corrections within the ring approximation.

Thus, within the considered ring approximation, taking into account the chemical-potential fluctuations, one can calculate the SRO Fourier transform α_k and then (by integration over the Brillouin zone—see equation (25)) the SRO parameters α_R . To do so, one has to use equation (26) with β_k from (24), where I_k and A_k are determined in (20). The quantity μ (see (20)) is determined from equation (22).

To compare the expression (26) with the corresponding expression for α_k derived in [2] (section 8), let us write the latter in such a form (see e.g. equation (1) in [10])

$$\alpha_k^{-1} = A_k + \frac{(1-2c)^2}{2c(1-c)} (1 - I_k) + \frac{1-3c(1-c)}{c(1-c)} \left(N^{-1} \sum_k [A_k]^{-1} - 1 \right), \quad (27)$$

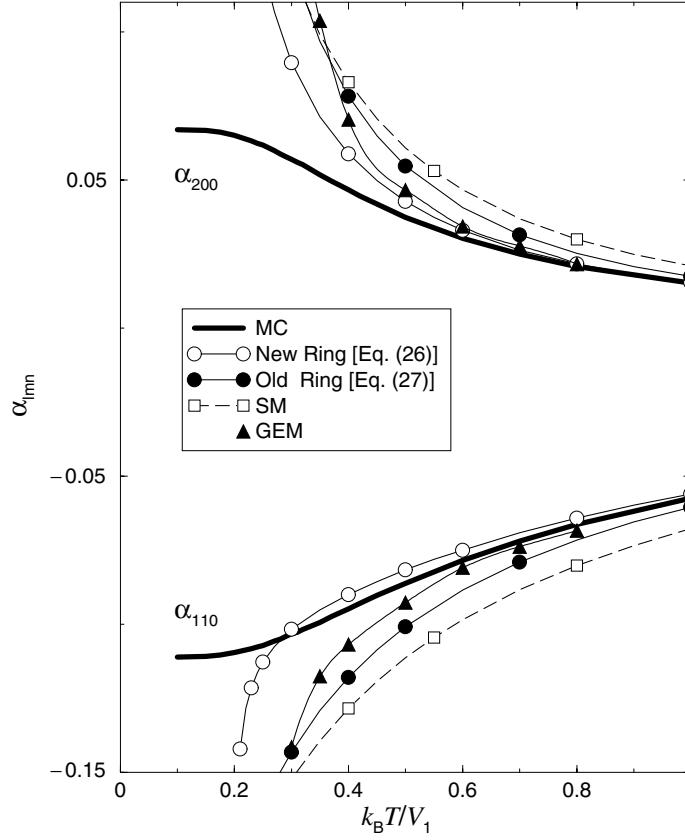


Figure 1. Evolution of the SRO parameters α_R for the first two coordination shells of the fcc crystal lattice on the reduced temperature obtained in the framework of both ‘new’ (26) and ‘old’ (27) ring approximations as well as calculated by Monte Carlo (MC) simulations [3], within the SM approximation [7] and by the γ -expansion method (GEM) [9] at $c = 0.10$, $V_1 > 0$, $V_s = 0$ ($s > 1$). l, m and n are the Cartesian coordinates of vector \mathbf{R} in $a/2$ units, where a is the fcc lattice parameter.

where the quantities I_k and A_k are the same as in (20) but μ is to be found from the equation

$$N^{-1} \sum_k \alpha_k = 1 \quad (28)$$

rather than from (22).

It should be emphasized that, in contrast to the heuristical derivation of (28) in [2], the new equation (22) for the determination μ was derived rigorously from the general grand canonical ensemble formalism. In fact, equation (28) was derived in [2] (see equation (8.3) there) in analogy with the SM approximation to satisfy the sum rule, which is equation (28) itself. However, one can see that equation (26) satisfies the sum rule (28) for any function β_k . Note also that (22) is much simpler than (28) because in (22) there is only one summation over the Brillouin zone. Besides, it was revealed that in the case of equation (22) there is no such problem as the choice of the ‘physically adequate solution’ for μ (see section 4 in [3]).

For the subsequent comparison of the two approximations, it is useful to present (24) in the following equivalent form:

$$\beta_k^{-1} = A_k + \frac{(1-2c)^2}{2c(1-c)} (1-I_k) \left(1 + \frac{1-I_k}{I_k} \right). \quad (29)$$

Using in equation (27) the rigorous equality (22) and then comparing (27) and (29), one can see that the difference between them lies in the term proportional to $(1 - I_k)^2$. Note that this term appears just due to taking account of the fluctuations of the chemical potential.

From (20), it follows that $I_k \rightarrow 1$ at $T \rightarrow \infty$. On the other hand, because the difference between the results of the 'old' ring (without the chemical-potential fluctuations) and SM approximations is proportional to $(1 - I_k)$ (see (27)) and can be large in the vicinity of the order–disorder phase transformation (see figures 4–11 in [3]), one can expect that the quantity $(1 - I_k)^2$ and thus the contribution from the chemical-potential fluctuations can be considerable when the alloy temperature approaches the critical temperature of the order–disorder phase transformation.

To test the validity of the last statement, let us calculate the SRO parameters for the first two coordination shells of face-centred cubic (fcc) crystal lattice in the case of $c = 0.10$, $V_1 > 0$, $V_s = 0$ ($s > 1$) (V_s is the pair mixing potential for the s th coordination shell) within both the 'new' (26) and the 'old' (27) ring approximations. We chose such a case because here the difference between the 'old' ring and SM approximations is comparatively large (see figure 6 in [3]). The results are presented in figure 1. In this figure, we have also included the corresponding results obtained from MC simulations [3] as well as calculated within the SM approximation [7] and by the γ -expansion method [9].

From figure 1, one can see that indeed the difference between the 'old' and 'new' ring approximations (i.e. with and without taking into account the chemical-potential fluctuations) is considerable at low temperatures and so is the contribution from the chemical-potential fluctuations. Accepting the MC simulation results as a standard, we find also that the numerical accuracy of the approximation (26) derived in this letter is highest among all the approximations considered.

In conclusion, it should be noted that the zero value of the function β_k^{-1} determines the critical temperature of the instability of the disordered state (see equation (23)). Elsewhere, in a paper devoted to phase diagrams calculation within the ring approximation [11], it is shown that the neglect of the chemical-potential fluctuations can erroneously make the value of such a critical temperature be even more than the temperature of the order–disorder phase transformation. Thus, taking into account the chemical-potential fluctuations is also important for a correct evaluation of the alloy phase diagram.

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