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Analytical method for the calculation of the phase diagram of a two-component lattice gas

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Abstract

We propose a new analytical method for calculating the phase diagram of a two-component lattice gas with arbitrary complex crystal lattice and any long-range order in atomic distribution. The method is elaborated in the context of a modified thermodynamic perturbation theory with the use of the inverse effective number of atoms interacting with one fixed atom as a small parameter of expansion. By a comparison with the results of the Monte Carlo simulation, the high numerical accuracy of the method is demonstrated in a wide concentration interval. The effective radius of atomic interactions is not limited within the method and the numerical accuracy of the method becomes higher with increasing radius. The developed approach may also be followed in studies of magnetics within the Ising model, of alloys, fluids and amorphous materials within the lattice gas model as well as in investigations of the low-dimension lattice systems. © 2000 Published by Elsevier Science Ltd.

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1. Introduction

The statistical-thermodynamic investigation of the lattice gas model [1] is of interest for studies of not only solid compounds, but also magnetics, fluids and amorphous materials as well as for the general theory of phase transitions. At present, the Monte Carlo [2] and cluster-variation methods [3] are most widely used for such an investigation. However, within both methods, the calculations have a strong tendency to become more complicated with an increase of the effective radius of atomic interactions, which is the grave practical disadvantage in the case, for example, of actual alloys [4]. Moreover, these methods have a principal disadvantage because they approximate the interatomic potential by its values for a finite number of co-ordination shells, whereas such a specific feature of the potential of actual alloys as the non-analyticity of its Fourier-transform (see Ref. [3]) cannot be described in terms of the values of the potential for any great but finite number of co-ordination shells.

To overcome the denoted drawbacks, there have been advanced a number of analytical approximations [4–21]. The consideration of the lattice gas with arbitrarily long-range atomic interactions is possible within all these approximations, because the interaction's parameters appear in the corresponding expressions only through the Fourier transform of the interatomic potential.

One of such approximations (the so-called ring one) was elaborated in the context of a modified thermodynamic perturbation theory with the use of the inverse effective number of atoms interacting with one fixed atom as a small parameter of expansion [4,18–20,22,23]. These approximations have demonstrated a high numerical accuracy of results in a wide temperature–concentration interval and the numerical accuracy turns higher with the increase of the effective radius of atomic interactions. The ring approximation also permits us to take into account the many-body atomic interactions of arbitrary order and effective radius of action. However, these approximations have been developed only in case of the disordered lattice gas with a Bravais crystal lattice.

The aim of the present article is to generalize the ring approximation to the case of a two-component lattice gas with arbitrary complex crystal lattice and any long-range order (LRO) in atomic distribution. Such generalization

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allows the development of the new analytical method for calculation of the phase diagram of the lattice gas model.

2. Free energy within the ring approximation

Let us consider a two-component A–B lattice gas whose primitive unit cell consists of ν crystal lattice sites. In general, the Hamiltonian H of it can be written in the following form [24]:

$$H = N\nu v_0 + \sum_i \Phi_i \sum_{\mathbf{R}} C_{\mathbf{R}}^{(i)} + \frac{1}{2}\sum_{i_1,i_2}\sum_{\mathbf{R}_1,\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2}^{i_1,i_2} C_{\mathbf{R}_1}^{(i_1)} C_{\mathbf{R}_2}^{(i_2)}, \tag{1}$$

taking into account the atomic interactions of less than or equal to the second order and of arbitrary radius of action. In Eq. (1), N is the number of primitive unit cells of the crystal lattice, v_0 the energy per site of the lattice gas in which all $N\nu$ sites are occupied by B-type atoms, Φ_i and $V_{\mathbf{R}_1-\mathbf{R}_2}^{i_1,i_2}$ are the unary and pair mixing potentials, respectively,

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

the summations on the indices i,i_1,i_2 and on the radius-vectors $\mathbf{R}$, $\mathbf{R}_1$, $\mathbf{R}_2$ are carried over all ν sublattices and N primitive unit cells of the crystal lattice, respectively.

Following the procedure described in Refs. [4,18–20], the expression for the free energy f per one primitive unit cell of the system in question may be presented in such a form [25]:

$$f = \nu v_0 + \sum_i \left\{ P_i\left(\Phi_i - \frac{\mu_i}{2}\right) + \mathrm{k_B}T\,[P_i \ln P_i + (1-P_i)\ln(1-P_i)] \right\} + \Delta f, \tag{3}$$

where

$$\Delta f = -\mathrm{k_B}TN^{-1}\ln\left\langle \exp\left[-(2\mathrm{k_B}T)^{-1}\sum_{i_1,i_2}\sum_{\mathbf{R}_1,\mathbf{R}_2} W_{\mathbf{R}_1-\mathbf{R}_2}^{i_1,i_2} C_{\mathbf{R}_1}^{(i_1)} C_{\mathbf{R}_2}^{(i_2)}\right]\right\rangle, \tag{4}$$

$$W_{\mathbf{R}_1-\mathbf{R}_2}^{i_1,i_2} = V_{\mathbf{R}_1-\mathbf{R}_2}^{i_1,i_2} + \mu_{i_1}\delta_{i_1,i_2}\delta_{\mathbf{R}_1,\mathbf{R}_2}, \tag{5}$$

$$\mu_i = 2(\Phi_i - \mu_i^{\mathrm{A}} + \mu_i^{\mathrm{B}}), \tag{6}$$

μ_i^{A} and μ_i^{B} are the chemical potentials of A- and B-type atoms situated at the ith sublattice, respectively, T is the absolute temperature, $\mathrm{k_B}$ is the Boltzmann constant, the sign $\langle\ldots\rangle$ means the statistical average over all states with given values of the LRO parameters, δ_{i_1,i_2} and $\delta_{\mathbf{R}_1,\mathbf{R}_2}$ are the Kronecker's deltas,

$$P_i = \langle C_{\mathbf{R}}^{(i)} \rangle \tag{7}$$

and is equal to the probability of finding an A-type atom at the site belonging to the ith sublattice. Note that the quantities P_i are independent from the radius-vector $\mathbf{R}$ of primitive unit cells due to the translational invariance of these cells. The values of the chemical potentials $\mu_{\mathrm{A}}^i, \mu_{\mathrm{B}}^i$ and, therefore (see Eq. (6)), the values of μ_i $(i = 1,2,\ldots,\nu)$ must satisfy the following relationships:

$$\partial f/\partial \mu_i = 0, \tag{8}$$

which follow from the general thermodynamic ones.

According to the general approach of the thermodynamic perturbation theory [4,5,10,18–20,26,27], the expression (4) for Δf can be expanded in a cumulant series in powers of the inverse temperature. Following Brout's approach [4,5,18–20], let us select the contributions to the cumulant expansion from the summands proportional, respectively, to zeroth and first powers of the quantity z^{-1} with z being equal to the effective number of atoms interacting with one fixed atom:

$$\Delta f = \frac{1}{2N}\sum_{i_1,i_2}\sum_{\mathbf{R}_1,\mathbf{R}_2} W_{\mathbf{R}_1-\mathbf{R}_2}^{i_1,i_2} P_{i_2} P_{i_2} - \frac{\mathrm{k_B}T}{2N}\sum_{n=1}^{\infty}\frac{1}{n(-\mathrm{k_B}T)^n}\sum_{i_1,i_2,\ldots,i_n}\sum_{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_n} f_{\mathbf{R}_1-\mathbf{R}_2}^{i_1,i_2} f_{\mathbf{R}_2-\mathbf{R}_3}^{i_2,i_3},\ldots,f_{\mathbf{R}_n-\mathbf{R}_1}^{i_n,i_1}, \tag{9}$$

where

$$f_{\mathbf{R}_l-\mathbf{R}_m}^{i_l,i_m} = \sqrt{P_{i_l}(1-P_{i_l})}\,W_{\mathbf{R}_l-\mathbf{R}_m}^{i_l,i_m}\sqrt{P_{i_m}(1-P_{i_m})}. \tag{10}$$

Introducing the Fourier transform $\tilde{V}_{\mathbf{k}}^{i_1,i_2}$ of the pair mixing potential

$$\tilde{V}_{\mathbf{k}}^{i_1,i_2} = \sum_{\mathbf{R}} V_{\mathbf{R}}^{i_1,i_2}\exp(-\mathrm{i}\mathbf{kR}) \tag{11}$$

and performing a number of matrix transformations, one can obtain [25]

$$\Delta f = \tfrac{1}{2}\sum_{i_1,i_2}\tilde{W}_{\mathbf{k}=0}^{i_1,i_2} P_{i_1} P_{i_2} + \frac{\mathrm{k_B}T}{2N}\sum_{\mathbf{k}}\ln\det \mathbf{A_k}, \tag{12}$$

where

$$\tilde{W}_{\mathbf{k}}^{i_1,i_2} = \tilde{V}_{\mathbf{k}}^{i_1,i_2} + \mu_{i_1}\delta_{i_1,i_2}, \tag{13}$$

the summation on $\mathbf{k}$ is carried over all the points specified by the cyclic boundary conditions in a corresponding first Brillouin zone and the designation $\det \mathbf{A_k}$ means the determinant of the matrix $\mathbf{A_k}$ with the following elements:

$$A_{\mathbf{k}}^{i_1,i_2} = \delta_{i_1,i_2} + \frac{\sqrt{P_{i_1}(1-P_{i_1})}\,\tilde{W}_{\mathbf{k}}^{i_1,i_2}\sqrt{P_{i_2}(1-P_{i_2})}}{\mathrm{k_B}T}. \tag{14}$$

Using Eq. (8), we obtain the following equations for determination of the quantities μ_i $(i = 1,2,\ldots,\nu)$

$$N^{-1}\sum_{\mathbf{k}}[\mathbf{A_k}]_{ii}^{-1} = 1, \tag{15}$$

where the designation $[\mathbf{A_k}]_{ii}^{-1}$ means the ith diagonal element of the matrix inverse to $\mathbf{A_k}$.

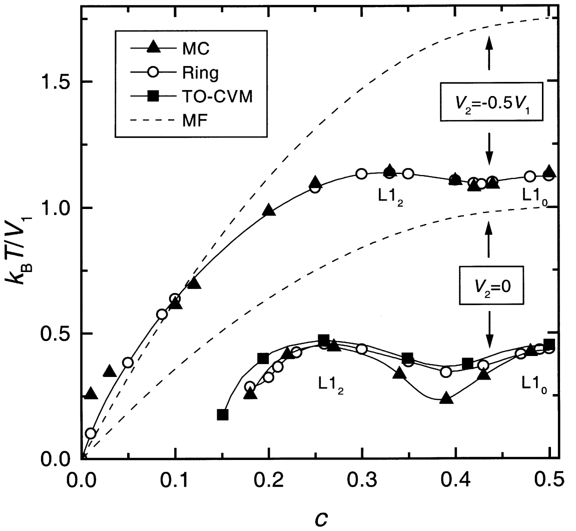

Fig. 1. The values of the order–disorder phase transformation temperatures calculated within the ring approximation (3), (12)–(15) (Ring) as well as by the Monte Carlo simulation (MC) and by the cluster variation method in tetrahedron–octahedron approximation [29] (TO-CVM) in case of the f.c.c. crystal lattice with $\Phi_i = 0$ and two model types of the pair mixing potential: (a) $V_1 > 0$, $V_s = 0$ $(s > 1)$; and (b) $V_1 > 0$, $V_2 = -0.5V_1$, $V_s = 0$ $(s > 2)$ (V_s is the value of the pair mixing potential for the sth co-ordination shell). The MC data were obtained in accordance with the procedure described in Ref. [4]. The designation MF is appropriate to the critical temperature of the order–disorder phase transformation calculated within the mean-field approximation. For the superstructures designations see e.g. in Ref. [29].

Note that in a particular case of the disordered lattice gas with a Bravais crystal lattice, when $P_i = c = N_A/(\nu N)$ for any $i = 1, 2, \ldots, \nu$ (c is the concentration of the A-type atoms, N_A is the total number of these atoms in the considered system), the obtained expressions (3), (12)–(14) for the free energy correspond to those for the grand thermodynamic potential derived within the ring approximation in Ref. [4]. We shall also call the approximation obtained above the ring one, because it is the same approximation as in Ref. [4], but applied in the case of a more complex system. Note that the name of the approximation is in accordance with the topology of the diagrams being taken into account within the ring approximation in the context of the corresponding diagram technique.

3. Calculation of the phase diagrams

Using the expressions obtained above, one can calculate the free energy of any two-component lattice gas. To achieve this aim in case of presence of a LRO in the atomic distribution, the minimization of the free energy with respect to the corresponding LRO parameters have to be performed. Such minimization can be made either by a direct numerical minimization of the free energy functional (as it was done in the present paper—see below) or by the usual solving of the corresponding "equations of equilibria" derived by putting the first derivatives to zero [25]. The energy parameters (v_0, Φ_i, $V^{i_1,i_2}_{\mathbf{R}_1-\mathbf{R}_2}$) should be calculated independently, for example, by ab initio methods or through the experimental data on diffuse scattering intensity (see for e.g. Refs. [18–20,28] and references therein) in case of alloy study. By a comparison of the free energies of all structures supposed to be competitive at the considered external conditions as well as the free energies of their mixtures, one can calculate the complete phase diagram of the system in question.

As an example and with the aim to study the numerical accuracy of the ring approximation, we considered two model cases. Both cases are appropriate to the face-centered cubic (f.c.c.) crystal lattice with $\Phi_i = 0$ and two following model types of the pair mixing potential: (a) $V_1 > 0$, $V_s = 0$ $(s > 1)$; and (b) $V_1 > 0$, $V_2 = -0.5V_1$, $V_s = 0$ $(s > 2)$ (V_s is the value of the pair mixing potential for the sth co-ordination shell of the f.c.c. crystal lattice). In Fig. 1, we present the values of the order–disorder phase transformation temperatures calculated within the ring approximation from the condition of the equality of the free energies of the disordered and corresponding ordered states. In Fig. 1, we do not include the two-phase regions. This will be done elsewhere [25]. The corresponding results obtained by the Monte Carlo simulation and by the cluster variation method in tetrahedron–octahedron approximation are also presented in Fig. 1. Note that the consideration of the concentrations greater than the equiatomic one is not required due to the symmetry of the phase diagram with respect to equiatomic concentration in case of lattice gas with concentration-independent atomic interactions of less than or equal to the second order [18].

4. Conclusions

Accepting the results of the Monte Carlo simulation as a standard, on the basis of the data presented in Fig. 1, one may conclude the following. In both considered cases, the ring approximation yields the adequate results at the entire concentration interval. The data of this approximation differ noticeably from those of the Monte Carlo simulation only in the vicinity of the triple point (near $c = 0.40$) in the case of $V_2 = 0$. However, the problem of adequate description of this vicinity is well known and is attributed to the "frustration" character of the corresponding model case due to the highly degenerate ground states [29]. One encounters this problem within both the Monte Carlo [30] and cluster variation [29,31] methods. Taking into account the next neighbor interactions allows us to resolve the problem (see Fig. 1). Note that the numerical accuracy of the ring approximation occurs higher than that of the cluster variation method in the widely used tetrahedron–octahedron approximation.

It should be emphasized that both considered cases corresponding to atomic interactions for only nearest and next nearest neighbors are obviously most unfavorable for a high numerical accuracy of the ring approximation in which the inverse effective number of atoms interacting with one fixed atom is chosen as a small parameter in the corresponding perturbation theory. Besides, the consideration of the f.c.c. crystal lattice (in contrast to the b.c.c. one) is also most unfavorable for such self-consistent-field type theories as the mean-field and ring approximations (see the MF curves in Fig. 1 and Ref. [3]). Surprisingly, even in these unfavorable cases the ring approximation demonstrates its adequacy. The high numerical accuracy of this approximation even in the cases of the short-range atomic interactions as well as the essential increase of the accuracy, when the atomic interactions for the second co-ordination shell are taken into account, clearly demonstrates the quick convergence of the cumulant expansion under such a choice of a small parameter as in the ring approximation.

The comparative generality and analytical simplicity of the ring approximation should be noted. The corresponding expressions (3), (12)–(14) for the free energy do not change their form at an increase of the effective radius of atomic interactions and are valid in case of any structure. The number n of the "variational" parameters of the free energy is equal to the sum of the number $n(\eta)$ of the LRO parameters and the number $n(\mu_i)$ of different quantities μ_i. The last, in its turn, is equal to the number of symmetry unequivalent sublattices in a structure, and therefore [10] we have:

$$n = n(\eta) + n(\mu_i) = 2n(\eta) + 1. \tag{16}$$

Such a number of the "variational" parameters is considerably less than that within the cluster variation method [3]. For example, in the above considered case of the f.c.c. crystal lattice with only nearest neighbors interactions, within the ring approximation we have 1, 3 and 3 "variational" parameters in the disordered state, $L1_0$ and $L1_2$ structures, respectively, in comparison with 10, 27 and 22 ones [31] within the cluster variation method in tetrahedron–octahedron approximation. It is important that, within the ring approximation, these numbers are determined only by the type of the structure and are independent from the value of the effective radius of atomic interactions in contrast to the cluster variation method. The considerably fewer number of the "variational" parameters obviously results in much less time of the corresponding computer calculations. Of course, this time within the ring approximation is much less in comparison with that of the Monte Carlo simulation due to the analytical nature of the ring approximation. Note that, within this approximation, the difference of the space symmetries of the interatomic potentials in different structures [24] is also taken into account.

The approach advanced in the present work may be extended [25] to the cases of a multicomponent lattice gas and/or of a lattice gas with non-pair atomic interactions (which are important for investigation of actual alloys [18–20]) as well as to the case of the Ising model. The absence of a priori assumptions about the space dimensionality of a crystal lattice in the developed formalism permits readily to apply it in investigations of low-dimension lattice systems. The approximation elaborated in the present work may also be useful in the investigations of fluids and amorphous materials within the framework of the lattice gas model [5].

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