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Analytical methods for calculation of the short-range order in alloys: I. General theory

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Abstract. In the context of a modified thermodynamic perturbation theory within the grand canonical ensemble, by the use of the thermodynamic fluctuation method, a number of new analytical approximations for calculations of the grand thermodynamic potential as well as of the short-range order parameters and their Fourier transform in disordered binary alloys with a Bravais crystal lattice are elaborated. An alloy of an arbitrary composition is considered in the framework of the lattice gas model with pair atomic interactions of arbitrary effective radius of action. The inverse effective number of atoms interacting with one fixed atom and inverse temperature as well as the concentration of the impurity component are used as small parameters of expansion. The developed approach may be also followed in studies of magnetics within the framework of the Ising model, and of fluids and amorphous materials within the lattice gas model as well as in investigations of low-dimensional lattice systems.

1. Introduction

Currently, there exist a number of analytical approaches for calculation of the short-range order (SRO) parameters in disordered (i.e. without a long-range order) binary alloys (for an overview see [1–6]). One comparatively simple in a practical implementation but methodologically consistent approach is based on the joint application of the thermodynamic perturbation theory and the fluctuation method [1–5, 7–10]. The important advantage of such an approach is the potential of taking into account the long-range contributions to atomic interactions without the complication of a consideration. Such potential is topical for a statistical–thermodynamic description of actual alloys, because the long-range character of atomic interactions in alloys was clearly demonstrated through the direct calculations of the distance dependencies of the energies of these interactions on the basis of the experimental data on diffuse scattering intensity [11–17]. In the framework of the electronic theory, the microscopic nature and the universal character of the long-range interatomic forces were revealed [18–23]. Besides, it was shown (see e.g. [2–5]) that the indirect elastic (strain-induced) interactions of the impurity atoms (caused by the relaxation of the elastic distortion fields induced by such atoms) also have long-range character.

To date, the essential disadvantage of the joint application of the thermodynamic perturbation theory and the fluctuation method in alloy studies lies in taking account of only the *finite* (as a rule small) number of terms in a perturbation series under the choice of the inverse temperature as a small parameter of expansion, whereas the convergence of this

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series is relatively weak. At the same time, considerable progress in the development of the thermodynamic perturbation theory within the Ising model was achieved in the works of Brout [24–27], where the possibility of analytical summation of the infinite number of terms that mainly contribute to the corresponding series was demonstrated in the realistic case of long-range atomic interactions. In this case, the inverse effective number of atoms interacting with one fixed atom was chosen as a small parameter of expansion. However, such an approach has not found the deserved applications in alloy studies, and no more than two corresponding works [28, 29] are familiar to us.

Besides, thus far, the thermodynamic perturbation theory was applied in alloy studies within the framework of the canonical ensemble only. At the same time, it is known [21, 30] that, within the approximate methods (unlike the rigorous ones), the step from the canonical ensemble to the grand canonical one may ensure the considerable rise of the numerical accuracy of calculations of thermodynamic characteristics. Moreover, as a result of such a step, one may expect the rise of the accuracy of the thermodynamic fluctuation method itself, because, within the grand canonical ensemble, the fluctuations of the occupation probabilities for the different sites of an alloy crystal lattice are not constrained by the requirement of the constancy of the total number of alloy atoms and, hence, these fluctuations are absolutely independent of one another. Thus, within the grand canonical ensemble, the necessary condition of the usability of the thermodynamic fluctuation method [31] is satisfied in contrast to the case of the canonical ensemble, when the above-mentioned requirement takes place.

The aim of the present study is to work out new analytical methods of calculation of the SRO parameters in disordered binary alloys with a Bravais crystal lattice by means of the joint application of the thermodynamic fluctuation method and perturbation theory within the grand canonical ensemble, adopting the inverse effective number of atoms interacting with one fixed atom and the inverse temperature as well as the concentration of the impurity atoms as small parameters of expansion.

In section 2, the expressions for the grand partition function and for the grand thermodynamic potential of an alloy are obtained within the framework of the lattice gas model.

In section 3 and the appendix, the traditional cumulant expansion in the thermodynamic perturbation theory is generalized to the case of the grand canonical ensemble and the corresponding diagram technique is developed.

In sections 4 and 5, the expressions for the grand thermodynamic potential within two approximations corresponding to taking account of the terms in the cumulant expansion that are proportional to the zeroth and first powers of the inverse effective number of atoms interacting with one fixed atom are obtained. In sections 6, 7 and 8, within such approximations both the method of differentiation with respect to the potential and the thermodynamic fluctuation method are used to obtain expressions for the SRO parameters. The comparative qualitative analysis of the accuracy of these two methods is performed.

In section 9, the expressions for the grand thermodynamic potential and for the SRO parameters are obtained within three high-temperature approximations corresponding to taking account of the terms in the cumulant expansion that are proportional to the zeroth, first and second powers of the inverse temperature.

In section 10, the expressions for the grand thermodynamic potential and for the SRO parameters are obtained within the approximation that corresponds to taking account of all chain-type diagrams (both reducible and irreducible) whose contribution in the cumulant expansion is proportional to the zeroth power of the inverse effective number of atoms interacting with one fixed atom.

In section 11, the expressions for the grand thermodynamic potential and for the SRO parameters are obtained within the low-concentration approximation.

In section 12, the conclusions and perspectives are presented.

2. Grand thermodynamic potential

In the general case, within the framework of the lattice gas model, the Hamiltonian H of a two-component A–B alloy with a Bravais crystal lattice and with atomic interactions of less than or equal to second order and arbitrary radius of action can be written in the following form [32, 33]

$$H = N\nu_0 + \Phi \sum_{\mathbf{R}} C_{\mathbf{R}} + 1/2 \sum_{\mathbf{R}_1, \mathbf{R}_2} V_{\mathbf{R}_1 - \mathbf{R}_2} C_{\mathbf{R}_1} C_{\mathbf{R}_2} \quad (2.1)$$

where ν_0 is the energy per site of an ‘alloy’ in which all N sites are occupied by B-type atoms, Φ is the potential of the injection of an A-type atom in a crystal lattice site, $V_{\mathbf{R}_1 - \mathbf{R}_2}$ is the (pair) mixing potential,

$$C_{\mathbf{R}} = \begin{cases} 1 & \text{if the site } \mathbf{R} \text{ is occupied by an A-type atom} \\ 0 & \text{otherwise} \end{cases} \quad (2.2)$$

and the summations on the vectors \mathbf{R} , \mathbf{R}_1 and \mathbf{R}_2 are carried out over all N crystal lattice sites. It should be emphasized that the expression (2.1) is valid only under the assumption that all crystal lattice sites are symmetry equivalent, because only in this case is the injection potential independent of \mathbf{R} and the mixing potential is a function of $\mathbf{R}_1 - \mathbf{R}_2$ [32, 33]. Such a situation takes place in the disordered state of an alloy, which is just under investigation in the present study.

The expression (2.1) can be presented as follows

$$H = N\nu_0 + 1/2 \sum_{\mathbf{R}_1, \mathbf{R}_2} (V_{\mathbf{R}_1 - \mathbf{R}_2} + 2\Phi\delta_{\mathbf{R}_1, \mathbf{R}_2}) C_{\mathbf{R}_1} C_{\mathbf{R}_2} \quad (2.3)$$

where $\delta_{\mathbf{R}_1, \mathbf{R}_2}$ is the Kronecker delta. Accordingly, the grand partition function Ξ of the system in question has the following form

$$\Xi = \Xi_0 \sum_{\{C_{\mathbf{R}}\}} \exp \left[-(2k_{\text{B}}T)^{-1} \sum_{\mathbf{R}_1, \mathbf{R}_2} W_{\mathbf{R}_1 - \mathbf{R}_2} C_{\mathbf{R}_1} C_{\mathbf{R}_2} \right] \quad (2.4)$$

where

$$\Xi_0 = \exp[-N(\nu_0 - \mu_{\text{B}})/(k_{\text{B}}T)] \quad (2.5)$$

$$W_{\mathbf{R}_1 - \mathbf{R}_2} = V_{\mathbf{R}_1 - \mathbf{R}_2} + \mu\delta_{\mathbf{R}_1, \mathbf{R}_2} \quad (2.6)$$

$$\mu = 2(\Phi - \mu_{\text{A}} + \mu_{\text{B}}) \quad (2.7)$$

μ_{A} and μ_{B} are the chemical potentials 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.

Note that the expression (2.4) for the grand partition function can be converted into the expression for the *canonical* partition function by setting $\mu = 0$ (under neglect of the configuration-independent multiplier). This allows us, if needs be, to make the step from the grand canonical ensemble to the canonical one in the expressions for the configurational statistical–thermodynamic characteristics of alloy by setting $\mu = 0$.

In the present section, we shall assume the presence of a long-range order (LRO) in the alloy with the purpose of further use of the thermodynamic fluctuation method, in which

the SRO is considered as fluctuations of the equilibrium LRO. In the following sections, after the application of the fluctuation method, the LRO parameters will be put equal to zero, according to the aim of the present paper to investigate just the disordered state of the alloy.

Thus, let us replace the summation on $\{C_R\}$ in the partition function (2.4) by the summation on $\{C_R\}_{\text{LRO}}$ over all states with some given values of the LRO parameters [1, 3, 4, 24–27, 34, 35]. The expression for the corresponding grand thermodynamic potential Ω can be presented as follows

$$\Omega = -k_B T \ln \Xi = \Omega_0 - k_B T \ln \Delta \Gamma + \Delta \Omega \quad (2.8)$$

where

$$\Omega_0 = -k_B T \ln \Xi_0 = N(\nu_0 - \mu_B) \quad (2.9)$$

$$\Delta \Omega = -k_B T \ln \left\langle \exp \left[-(2k_B T)^{-1} \sum_{R_1, R_2} W_{R_1-R_2} C_{R_1} C_{R_2} \right] \right\rangle \quad (2.10)$$

$$\Delta \Gamma = \sum_{\{C_R\}_{\text{LRO}}} 1. \quad (2.11)$$

$\Delta \Gamma$ is the number of configurations corresponding to a state with a given LRO, and (see e.g. [3, 4])

$$\ln \Delta \Gamma = - \sum_R [P_R \ln P_R + (1 - P_R) \ln(1 - P_R)] \quad (2.12)$$

where the value

$$P_R = \langle C_R \rangle \quad (2.13)$$

is equal to the probability of finding an A-type atom at the site R . In (2.10) and below, $\langle \dots \rangle$ means the statistical average over all states with given values of the LRO parameters:

$$\langle \dots \rangle = \Delta \Gamma^{-1} \sum_{\{C_R\}_{\text{LRO}}} \dots \quad (2.14)$$

Notice that the values of the chemical potentials μ_A and μ_B and, therefore (see (2.6), (2.7)), the value of μ must satisfy the general thermodynamic relationships [31]

$$\langle N_A \rangle = -(\partial \Omega / \partial \mu_A)_T \quad \langle N_B \rangle = -(\partial \Omega / \partial \mu_B)_T \quad (2.15)$$

where N_A and N_B are the numbers of atoms of types A and B, respectively.

3. Cumulant expansion

According to the general approach of the thermodynamic perturbation theory [3, 4, 24–27, 31, 34, 35], we expand the expression (2.10) in a cumulant series in powers of the inverse temperature

$$\Delta \Omega = -k_B T \ln \left\langle \exp \left(-\frac{X}{k_B T} \right) \right\rangle = -k_B T \sum_{n=1}^{\infty} \frac{1}{n!} \frac{M_n(X)}{(-k_B T)^n} \quad (3.1)$$

where

$$X = 1/2 \sum_{R_1, R_2} W_{R_1-R_2} C_{R_1} C_{R_2} \quad (3.2)$$

and $M_n(X)$ is the cumulant of the n th order determined as follows

$$M_n(X) = -n! \sum_{\substack{m_1, m_2, \dots, m_n=0 \\ \sum_{i=1}^n m_i = n}}^{\infty} \left(\sum_{i=1}^n m_i - 1 \right)! \prod_{j=1}^n \left[\frac{1}{m_j!} \left(-\frac{\langle X^j \rangle}{j!} \right)^{m_j} \right]. \quad (3.3)$$

In particular, from (3.3) one can obtain

$$\begin{aligned} M_1(X) &= \langle X \rangle \\ M_2(X) &= \langle X^2 \rangle - \langle X \rangle^2 \\ M_3(X) &= \langle X^3 \rangle - 3\langle X^2 \rangle \langle X \rangle + 2\langle X \rangle^3 \\ M_4(X) &= \langle X^4 \rangle - 4\langle X^3 \rangle \langle X \rangle - 3\langle X^2 \rangle^2 + 12\langle X^2 \rangle \langle X \rangle^2 - 6\langle X \rangle^4. \end{aligned} \quad (3.4)$$

In the work of Brout [24], it was shown that one can assign a linked irreducible diagram consisting of vertices linked by lines to each term that mainly contributes to the series (3.1). A linked diagram is defined as not consisting of several isolated parts, and an irreducible diagram as one that may not be transformed into an unlinked diagram by cutting at some vertex. To obtain the analytical expression corresponding to a given diagram, it is necessary [24–27, 36]:

- (1) to match up the multiplier $W_{\mathbf{R}_i - \mathbf{R}_j}$ to each line linking two arbitrary vertexes \mathbf{R}_i and \mathbf{R}_j ;
- (2) to match up the summation $\sum_{\mathbf{R}_i}$ and the multiplier

$$M_{l_i}^0(\mathbf{R}_i) = M_{l_i}(C_{\mathbf{R}_i}) \quad (3.5)$$

to each vertex \mathbf{R}_i with l_i lines entering it;

- (3) to multiply the expression obtained in the previous steps by a combinatorial factor K .

The expressions for the function $M_l^0(\mathbf{R})$ with different l can be easily obtained by the use of (3.5) and (3.3). Particularly, we have

$$\begin{aligned} M_1^0(\mathbf{R}) &= P_{\mathbf{R}} \\ M_2^0(\mathbf{R}) &= P_{\mathbf{R}}(1 - P_{\mathbf{R}}) \\ M_3^0(\mathbf{R}) &= P_{\mathbf{R}}(1 - P_{\mathbf{R}})(1 - 2P_{\mathbf{R}}) \\ M_4^0(\mathbf{R}) &= P_{\mathbf{R}}(1 - P_{\mathbf{R}})[1 - 6P_{\mathbf{R}}(1 - P_{\mathbf{R}})]. \end{aligned} \quad (3.6)$$

In the context of the above described traditional diagram technique we assumed the validity of the equality $W_{\mathbf{R}=\mathbf{0}} = 0$, whereas within the formalism of section 2 (see (2.6)), we have

$$W_{\mathbf{R}=\mathbf{0}} = \mu \quad (3.7)$$

where μ is not generally (see (2.7)) equal to zero. Thus, within the scope of the present study, one should take into account the diagrams in the cumulant expansion that have loops, i.e. the lines for which both the beginning and the end belong to the same vertex. For example, for the cumulant of the first order, we obtain

$$\begin{aligned} M_1(X) &= \langle X \rangle = 1/2 \sum_{\mathbf{R}_1, \mathbf{R}_2} W_{\mathbf{R}_1 - \mathbf{R}_2} \langle C_{\mathbf{R}_1} C_{\mathbf{R}_2} \rangle \\ &= 1/2 \left[\sum_{\mathbf{R}_1 \neq \mathbf{R}_2} W_{\mathbf{R}_1 - \mathbf{R}_2} \langle C_{\mathbf{R}_1} \rangle \langle C_{\mathbf{R}_2} \rangle + \sum_{\mathbf{R}} W_{\mathbf{R}=\mathbf{0}} \langle C_{\mathbf{R}}^2 \rangle \right] \end{aligned}$$

$$\begin{aligned}
&= 1/2 \left[\sum_{R_1, R_2} W_{R_1 - R_2} \langle C_{R_1} \rangle \langle C_{R_2} \rangle + \sum_R W_{R=0} (\langle C_R^2 \rangle - \langle C_R \rangle^2) \right] \\
&= 1/2 \left[\sum_{R_1, R_2} W_{R_1 - R_2} M_1^0(\mathbf{R}_1) M_1^0(\mathbf{R}_2) + \sum_R W_{R=0} M_2^0(\mathbf{R}) \right] \quad (3.8)
\end{aligned}$$

where the following relationship [27, 34, 37]

$$\langle C_{R_1} C_{R_2} \rangle = \langle C_{R_1} \rangle \langle C_{R_2} \rangle + O(1/N) \quad \mathbf{R}_1 \neq \mathbf{R}_2 \quad (3.9)$$

was used. By means of the diagram technique rules described above, the expression (3.8) may be written down in the following diagram form

$$M_1(X) = \bullet \text{---} \bullet + \textcirclearrowleft \bullet \quad (3.10)$$

It should be emphasized that, in the considered case, the diagram technique rules (1)–(3) still stand even for the diagram with a loop, because the correspondence between the multiplier $W_{R=0}$ and the loop obviously follows from rule (1).

In the appendix, it is shown that the above-mentioned rules of the diagram technique may be applied with no changes to any type of diagram containing loops, and the following general expression for the combinatorial factor K corresponding to such diagrams is derived:

$$K = S \left[(-k_B T)^{n-1} p! \prod_{i>j=1}^p (m_{ij}!) \prod_{i=1}^p (n_i! 2^{n_i}) \right]^{-1} \quad (3.11)$$

In (3.11): n and p are the total numbers of lines and vertices in a diagram, respectively; m_{ij} is the number of lines linking two different vertices i and j ; n_i is the number of loops corresponding to the vertex i ; S is the number of nonequivalent ways of distribution of p unequal fixed indices through the p vertices of the diagram:

$$S = p! / t \quad (3.12)$$

where t is the number of elements of the topological symmetry group of a diagram.

It should be emphasized that there exists a unique linked irreducible diagram with loops, namely



because any diagram (except this one) with a loop at some vertex may be transformed into an unlinked diagram by cutting just at this vertex. Thus, taking into account the linked irreducible diagrams only, in particular, we have

$$\begin{aligned}
-M_2(X)/(2k_B T) &= \textcirclearrowleft \bullet \\
M_3(X)/[6(k_B T)^2] &= \textcirclearrowleft \bullet \text{---} \bullet + \textcirclearrowleft \bullet \text{---} \bullet \\
-M_4(X)/[24(k_B T)^3] &= \textcirclearrowleft \bullet \text{---} \bullet \text{---} \bullet + \textcirclearrowleft \bullet \text{---} \bullet \text{---} \bullet + \textcirclearrowleft \bullet \text{---} \bullet \text{---} \bullet
\end{aligned} \quad (3.13)$$

4. Zero approximation

Brout [24–27] offered to choose the quantity z^{-1} as an expansion parameter in (3.1), where z is the number of sites within the imaginary shell whose radius is equal to the effective radius of atomic interactions. In the context of such an approach, the relative contribution

of a diagram with n lines and p vertices to the cumulant expansion (3.1) is determined by the value

$$Nz^{-(n+1-p)}.$$

Under such an estimation, the contribution of the unique linked irreducible diagram:



(for which $p = n + 1$) is proportional to the least, zeroth power of the quantity z^{-1} . Thus, just this diagram mainly contributes to the cumulant expansion (3.1) at $z \rightarrow \infty$ (i.e. at a sufficiently large value of the effective radius of atomic interactions). Let us call the approximation in which the contribution of this diagram alone is taken into account in (3.1) the zero approximation. Within such an approximation, the expression for the grand thermodynamic potential is the following

$$\Omega_{\text{zero}} = \Omega_0 + 1/2 \sum_{R_1, R_2} W_{R_1-R_2} P_{R_1} P_{R_2} - k_B T \ln \Delta \Gamma. \quad (4.1)$$

In the case of the disordered state of alloy, when for any R

$$P_R = c = \langle N_A \rangle / N \quad (4.2)$$

the expression (4.1) has the following form

$$\Omega_{\text{zero}}|_{P_R=c} = \Omega_0 + Nc^2 \tilde{W}_{k=0} / 2 + Nk_B T [c \ln c + (1 - c) \ln(1 - c)] \quad (4.3)$$

where

$$\tilde{W}_k = \tilde{V}_k + \mu \quad (4.4)$$

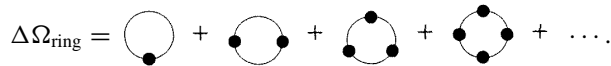
and \tilde{V}_k is the Fourier transform of the mixing potential V_R :

$$\tilde{V}_k = \sum_R V_R \exp(-ik \cdot R) \quad V_R = N^{-1} \sum_q \tilde{V}_q \exp(iq \cdot R). \quad (4.5)$$

In (4.5) and below, the summation on q is carried over all the points specified by the cyclic boundary conditions in a corresponding first Brillouin zone.

5. Ring approximation

According to Brout's classification, the contribution of the terms corresponding to linked irreducible diagrams of the ring type (for which $p = n$) is proportional to the first power of the quantity z^{-1} . Let us separate out the contribution $\Delta \Omega_{\text{ring}}$ corresponding to such diagrams in the expansion (3.1):



By the use of the diagram technique rules described in section 3, we obtain

$$\begin{aligned} \Delta \Omega_{\text{ring}} &= \frac{1}{2} \sum_{n=0}^{\infty} [(-k_B T)^n (n + 1)]^{-1} \sum_{R_1, R_2, \dots, R_{n+1}} W_{R_1-R_2} W_{R_2-R_3} \dots W_{R_{n+1}-R_1} \\ &\quad \times \prod_{i=1}^{n+1} P_{R_i} (1 - P_{R_i}). \end{aligned} \quad (5.1)$$

Note that the following expression [25, 26]

$$S_{\text{ring}} = \begin{cases} 1 & p = 1, 2 \\ (p - 1)! / 2 & p > 2 \end{cases}$$

for the quantity S (the knowledge of which is necessary for calculation of the combinatorial factor K (3.11)) was used in the derivation of (5.1).

Taking into account the contribution corresponding both to the diagram $\bullet\text{---}\bullet$ and to the ring-type diagrams in the cumulant expansion, we have the following form for the corresponding grand thermodynamic potential:

$$\Omega_{\text{ring}} = \Omega_{\text{zero}} + \Delta\Omega_{\text{ring}} \quad (5.2)$$

where Ω_{zero} and $\Delta\Omega_{\text{ring}}$ are determined by the expressions (4.1) and (5.1), respectively. We shall call this approximation ring one[†].

In the case of the disordered state of an alloy (see (4.2)), the expression (5.1) can be transformed as follows

$$\Delta\Omega_{\text{ring}}|_{P_R=c} = k_B T/2 \sum_k \ln[1 + \tilde{W}_k c(1-c)/(k_B T)]. \quad (5.3)$$

The expression analogous to (5.3) was first obtained by Brout [25–27] (see also [29, 39–43]).

6. Method of differentiation with respect to potential

There exist a number of methods for calculation of the Warren–Cowley short-range order parameters α_R [44, 45]

$$\alpha_{R_1-R_2} = ((C_{R_1} C_{R_2})|_{P_R=c} - c^2)[c(1-c)]^{-1}. \quad (6.1)$$

The basic method used in the present study (see the next section) is the thermodynamic fluctuation method. However, for the derivation of an equation in the quantity μ (required for the calculation of α_R within the grand canonical ensemble), it is helpful first to apply the other generally accepted method—the method of differentiation with respect to potential. Within this method (see e.g. [1]), differentiating the general expression for the grand thermodynamic potential (see (2.4) and (2.8)) with respect to $W_{R_1-R_2}$, we obtain

$$\alpha_{R_1-R_2} = \begin{cases} (2\partial\Omega/\partial W_{R_1-R_2}|_{P_R=c} - c^2)[c(1-c)]^{-1} & R_1 \neq R_2 \\ 1 & R_1 = R_2. \end{cases} \quad (6.2)$$

Within the zero approximation, substituting (4.3) into (6.2), we get

$$\alpha_R = 0 \text{ at } R \neq 0. \quad (6.3)$$

Thus, within the zero approximation, the method of differentiation with respect to potential yields the absence of the interatomic correlations for all coordination shells (except the ‘zeroth’ one corresponding to $R_1 = R_2$).

Within the ring approximation, substituting (5.2) into (6.2), we obtain

$$\alpha_k = 1 - N^{-1} \sum_q [1 + \tilde{W}_q c(1-c)/(k_B T)]^{-1} + [1 + \tilde{W}_k c(1-c)/(k_B T)]^{-1} \quad (6.4)$$

where α_k is the Fourier transform of the SRO parameters α_R

$$\alpha_k = \sum_R \alpha_R \exp(-ik \cdot R) \quad \alpha_R = N^{-1} \sum_q \alpha_q \exp(iq \cdot R). \quad (6.5)$$

The quantity μ must satisfy the relationships (2.15). Thus, substituting the expression (5.2) into (2.15), we obtain the following equation for calculation of μ

$$N^{-1} \sum_q [1 + \tilde{W}_q c(1-c)/(k_B T)]^{-1} = 1. \quad (6.6)$$

[†] Notice that within the framework of just the same approximation, the statistical–thermodynamic derivation of the Debye theory for a system of electrically charged particles was performed [30, 38].

By the use of (6.6), the expression (6.4) becomes

$$\alpha_k = [1 + \tilde{W}_k c(1 - c)/(k_B T)]^{-1}. \quad (6.7)$$

Thus, in the case of the disordered state of the alloy, within the ring approximation, the method of differentiation with respect to potential leads to the well known expression obtained within the spherical model [25–27, 42, 43, 46–51]. It should be emphasized that the equation (6.6) for calculation of μ was obtained here from the general thermodynamic relationships (2.15) rather than from the requirement $\alpha_{R=0} = 1$ (as in [27]), which is satisfied for an *arbitrary* value of μ (see (6.4)) within our consideration.

7. Thermodynamic fluctuation method within the zero-approximation

In the context of the thermodynamic fluctuation method [1–5, 31], let us expand the function $\delta P_R = P_R - c$ in the Fourier series

$$\delta P_R = \sum_q \delta P_q \exp(-iq \cdot R) \quad (7.1)$$

and choose δP_q corresponding to different q as independent fluctuations. Within the zero approximation, substituting $P_R = c + \delta P_R$ into (4.1), introducing the Fourier transforms and expanding the obtained expression in the series in powers of δP_q , we obtain the following fluctuational change of the grand thermodynamic potential

$$\delta \Omega_{\text{zero}} = N k_B T \sum_q [2c(1 - c)\beta_{\text{zero}}(q)]^{-1} |\delta P_q|^2 \quad (7.2)$$

where all the terms that are proportional to the powers of δP_q greater than the second power are neglected and

$$\beta_{\text{zero}}(\mathbf{k}) = [1 + \tilde{W}_k c(1 - c)/(k_B T)]^{-1}. \quad (7.3)$$

Taking into account that, in the context of the *grand* canonical ensemble, the fluctuations δP_q corresponding to different q are absolutely independent of one another (see section 1), following the general formalism of the thermodynamic fluctuation method, we have:

$$\langle \delta P_{k_1} \delta P_{k_2}^* \rangle_{\text{fluct}} = N^{-1} c(1 - c) \delta_{k_1, k_2} \beta_{\text{zero}}(\mathbf{k}_1) \quad (7.4)$$

where δ_{k_1, k_2} is the Kronecker delta and $\langle \dots \rangle_{\text{fluct}}$ means the statistical average over the Gaussian distribution of the probabilities of fluctuations [31]. In the case of the disordered state of alloy, we have

$$\alpha_{R_1 - R_2} = [c(1 - c)]^{-1} (\langle P_{R_1} P_{R_2} \rangle_{\text{fluct}} - c^2) = [c(1 - c)]^{-1} \langle \delta P_{R_1} \delta P_{R_2} \rangle_{\text{fluct}} \quad R_1 \neq R_2 \quad (7.5)$$

taking into account that $\langle \delta P_R^2 \rangle_{\text{fluct}}$ determines the square dispersion of the fluctuating quantity P_R rather than the correlation function at $R = 0$.

Using (7.1)–(7.5), we obtain

$$\alpha_k = 1 - N^{-1} \sum_q \beta_{\text{zero}}(q) + \beta_{\text{zero}}(\mathbf{k}). \quad (7.6)$$

Taking into account (7.3), it becomes obvious that the expression (7.6) is identical to (6.4). Thus, the application of the thermodynamic fluctuation method to Ω_{zero} gives just the same result as the application of the method of differentiation with respect to potential to Ω_{ring} . Nevertheless, although at the derivation of the expression (7.6), the fluctuation method was applied to Ω_{zero} , one should substitute Ω_{ring} rather than Ω_{zero} into (2.15) to obtain the correct equation (6.6), which determines the value of μ corresponding to (7.6), whereas the

substitution of Ω_{zero} into (2.15) leads to the incorrect equation $c(1 - c) = 0$. Note that, in terms of the function $\beta_{\text{zero}}(\mathbf{k})$, the equation (6.6) has the following form

$$N^{-1} \sum_{\mathbf{k}} \beta_{\text{zero}}(\mathbf{k}) = 1. \quad (7.7)$$

Substituting (7.7) into (7.6), we obtain

$$\alpha_{\mathbf{k}} = \beta_{\text{zero}}(\mathbf{k}). \quad (7.8)$$

8. Thermodynamic fluctuation method within the ring approximation

Within the ring approximation, applying the thermodynamic fluctuation method to Ω_{ring} (5.2) in much the same way as in section 7, we obtain

$$\alpha_{\mathbf{k}} = 1 - N^{-1} \sum_{\mathbf{q}} \beta_{\text{ring}}(\mathbf{q}) + \beta_{\text{ring}}(\mathbf{k}) \quad (8.1)$$

where

$$\begin{aligned} [\beta_{\text{ring}}(\mathbf{k})]^{-1} &= 1 + \frac{c(1-c)}{k_{\text{B}}T} \tilde{W}_{\mathbf{k}} - \frac{c(1-c)}{k_{\text{B}}T} N^{-1} \\ &\times \sum_{\mathbf{q}} \tilde{W}_{\mathbf{q}} \left[1 + \frac{c(1-c)}{k_{\text{B}}T} \tilde{W}_{\mathbf{q}} \right]^{-1} - \frac{c(1-c)(1-2c)^2}{2(k_{\text{B}}T)^2} N^{-1} \\ &\times \sum_{\mathbf{q}} \tilde{W}_{\mathbf{q}} \tilde{W}_{\mathbf{k}-\mathbf{q}} \left[1 + \frac{c(1-c)}{k_{\text{B}}T} \tilde{W}_{\mathbf{q}} \right]^{-1} \left[1 + \frac{c(1-c)}{k_{\text{B}}T} \tilde{W}_{\mathbf{k}-\mathbf{q}} \right]^{-1}. \end{aligned} \quad (8.2)$$

Comparing (7.6) with (8.1), one can assume that, within the ring approximation, the equation for calculation of μ has the following form, similar to (7.7),

$$N^{-1} \sum_{\mathbf{k}} \beta_{\text{ring}}(\mathbf{k}) = 1. \quad (8.3)$$

Substituting (8.3) into (8.1), we obtain

$$\alpha_{\mathbf{k}} = \beta_{\text{ring}}(\mathbf{k}). \quad (8.4)$$

Notice that, most likely, the rigorous proof of the validity of (8.3) may be performed by the calculation of the higher order additive $\Delta\Omega'$ to Ω_{ring} that ensures the derivation of the expression (8.3) within the method of differentiation with respect to potential and by the subsequent substitution of $\Omega_{\text{ring}} + \Delta\Omega'$ into (2.15). Unfortunately, we failed to obtain the quantity $\Delta\Omega'$. However, as an indirect proof of the validity of (8.3), on the one hand, one may accept the high numerical accuracy of the results obtained by the use of (8.4) in [52]. On the other hand, both (8.3) and (8.4) *continuously* transform into the corresponding expressions (7.7) and (7.8) (rigorously obtained within the zero approximation), when the high-order corrections to Ω_{zero} may be neglected. This is the case of sufficiently high temperatures and/or of a long-range character of atomic interactions [52].

The expressions (8.3) and (8.4) can be presented in the following equivalent form [53]

$$\begin{aligned} \alpha_{\mathbf{k}} &= [I + \tilde{W}_{\mathbf{k}}^{\text{eff}} c(1-c)/(k_{\text{B}}T)]^{-1} \\ N^{-1} \sum_{\mathbf{q}} [I + \tilde{W}_{\mathbf{q}}^{\text{eff}} c(1-c)/(k_{\text{B}}T)]^{-1} &= 1 \end{aligned} \quad (8.5)$$

where

$$I = N^{-1} \sum_q [1 + \tilde{W}_q c(1-c)/(k_B T)]^{-1}$$

$$\tilde{W}_k^{\text{eff}} = \tilde{W}_k - \frac{(1-2c)^2}{2k_B T} N^{-1} \sum_q \tilde{W}_q \tilde{W}_{k-q} \left[1 + \frac{c(1-c)}{k_B T} \tilde{W}_q\right]^{-1} \left[1 + \frac{c(1-c)}{k_B T} \tilde{W}_{k-q}\right]^{-1}. \quad (8.6)$$

Notice that on the basis of the results obtained in this as well as in two previous sections, one can conclude that the thermodynamic fluctuation method is preferable to the method of differentiation with respect to potential at calculation of the SRO parameters. Really, being applied within the same approximation, the fluctuation method yields the expression for correlation function whose accuracy is higher than that of the differentiation method (compare (6.3) with (7.8) and (6.7) with (8.4)).

9. High-temperature approximations

The classification of terms in the cumulant expansion (3.1) is possible not only by the powers of z^{-1} (see section 4) but also by the powers of $(k_B T)^{-1}$ [34]. It is evident that at sufficiently high temperatures, the terms that are proportional to the least powers of $(k_B T)^{-1}$ mainly contribute to (3.1). The approximation derived taking into account only the terms proportional to the powers of $(k_B T)^{-1}$ less than or equal to n in the cumulant expansion will be called the high-temperature approximation of the n th order. From (3.1), it follows that any term corresponding to the cumulant of the n th order is proportional to $(k_B T)^{n-1}$. Therefore, to obtain the high-temperature approximation of the n th order, one should take account of all cumulants up to the $(n+1)$ th order inclusive.

Let us consider the high-temperature approximations of the zeroth, first and second orders. From (3.1), it follows that the general expression for the grand thermodynamic potential $\Omega_{\text{HT}}^{(n)}$ corresponding to the high-temperature approximation of the n th order ($n = 0, 1, 2$) can be presented as follows

$$\Omega_{\text{HT}}^{(n)} = \sum_{i=0}^n \Omega^{(i)} - k_B T \ln \Delta \Gamma \quad (9.1)$$

where

$$\begin{aligned} \Omega^{(0)} &= \Omega_0 + M_1(X) = \Omega_0 + 1/2 \sum_{R_1, R_2} W_{R_1-R_2} P_{R_1} P_{R_2} + W_{R=0} \sum_R P_R (1 - P_R)/2 \\ &= \Omega_0 + N\mu c/2 + 1/2 \sum_{R_1, R_2} V_{R_1-R_2} P_{R_1} P_{R_2} \\ \Omega^{(1)} &= -M_2(X)/(2k_B T) = -1/(4k_B T) \sum_{R_1, R_2} (W_{R_1-R_2})^2 P_{R_1} (1 - P_{R_1}) P_{R_2} (1 - P_{R_2}) \\ \Omega^{(2)} &= \frac{M_2(X)}{6(k_B T)^2} = [12(k_B T)^2]^{-1} \sum_{R_1, R_2} (W_{R_1-R_2})^3 P_{R_1} (1 - P_{R_1}) P_{R_2} (1 - P_{R_2}) \\ &\quad \times (1 - 2P_{R_1})(1 - 2P_{R_2}) + [6(k_B T)^2]^{-1} \\ &\quad \times \sum_{R_1, R_2, R_3} W_{R_1-R_2} W_{R_2-R_3} W_{R_3-R_1} P_{R_1} (1 - P_{R_1}) \\ &\quad \times P_{R_2} (1 - P_{R_2}) P_{R_3} (1 - P_{R_3}). \end{aligned} \quad (9.2)$$

Note that the expressions (9.2) were obtained on the basis of the corresponding diagram expressions (3.13) by the use of the diagram technique rules described in section 3.

It should be emphasized that the high-temperature approximation of the zeroth order ($n = 0$ in (9.1)) corresponds to the well known mean-field approximation rather than the zero approximation advanced in section 4. Setting $\mu = 0$ in (9.1) at $n = 1, 2$, we arrive at the corresponding expressions for the high-temperature approximations obtained by Badalyan and Khachatryan [3, 35, 54] in the context of the thermodynamic perturbation theory within the *canonical* ensemble.

In the case of the disordered state of the alloy (see (4.2)), we have

$$\Omega_{\text{HT}}^{(n)}|_{P_R=c} = N \left\{ \sum_{i=0}^n \omega^{(i)} + k_B T [c \ln c + (1-c) \ln(1-c)] \right\} \quad (9.3)$$

where

$$\begin{aligned} \omega^{(0)} &= \nu_0 - \mu_B + c(\mu + c\tilde{V}_{k=0})/2 \\ \omega^{(1)} &= -[c(1-c)]^2 N^{-1} \sum_k (\tilde{W}_k)^2 / (4k_B T) \\ \omega^{(2)} &= [6(k_B T)^2]^{-1} \left\{ [c(1-c)(1-2c)]^2 N^{-2} \sum_{k_1, k_2} \tilde{W}_{k_1} \tilde{W}_{k_2} \tilde{W}_{k_1+k_2} / 2 \right. \\ &\quad \left. + [c(1-c)]^3 N^{-1} \sum_k (\tilde{W}_k)^3 \right\}. \end{aligned} \quad (9.4)$$

Applying the thermodynamic fluctuation method to $\Omega_{\text{HT}}^{(n)}$ determined by (9.1) and (9.2), in the same way as in sections 7, 8, we obtain the following expressions for the Fourier transform of the SRO parameters within the high-temperature approximation of the n th order ($n = 0, 1, 2$):

$$\begin{aligned} \alpha_k &= \left[1 + \sum_{i=0}^n \tilde{W}_k^{(i)} c(1-c) / (k_B T) \right]^{-1} \\ N^{-1} \sum_q \left[1 + \sum_{i=0}^n \tilde{W}_q^{(i)} (1-c) / (k_B T) \right]^{-1} &= 1 \end{aligned} \quad (9.5)$$

where

$$\begin{aligned} \tilde{W}_k^{(0)} &= \tilde{V}_k \\ \tilde{W}_k^{(1)} &= (k_B T)^{-1} \left\{ c(1-c) N^{-1} \sum_q (\tilde{W}_q)^2 - (1-2c)^2 \sum_q \tilde{W}_q \tilde{W}_{k-q} / 2 \right\} \\ \tilde{W}_k^{(2)} &= (k_B T)^{-2} \left\{ c(1-c)(1-2c)^2 \left[N^{-1} \sum_q (\tilde{W}_q)^2 \tilde{W}_{k-q} - N^{-2} \sum_{q_1, q_2} \tilde{W}_{q_1} \tilde{W}_{q_2} \tilde{W}_{q_1+q_2} \right] \right. \\ &\quad \left. + [1-6c(1-c)]^2 N^{-2} \sum_{q_1, q_2} \tilde{W}_{q_1} \tilde{W}_{q_2} \tilde{W}_{k-q_1-q_2} / 6 \right. \\ &\quad \left. - [c(1-c)]^2 N^{-1} \sum_q (\tilde{W}_q)^3 \right\}. \end{aligned} \quad (9.6)$$

The expression corresponding to the high-temperature approximation of zeroth order ($n = 0$ in (9.5)) is identical to the Krivoglaz [1, 2, 7] approximation. In another particular case, setting $\mu = 0$ in (9.5) and (9.6) at $n = 2$, we arrive at the corresponding expression for

the high-temperature approximation obtained by Semenovskaya [9] in the context of the thermodynamic perturbation theory within the *canonical* ensemble.

Note that, in the case of short-range interatomic potentials, the following easy to derive expressions are helpful for the calculations of the integrals entering (9.4) and (9.6):

$$N^{p-1} \sum_{k_1, k_2, \dots, k_p} \tilde{W}_{k_1} \tilde{W}_{k_2} \dots \tilde{W}_{k_p} \delta_{k, \sum_{i=1}^p k_i} = \sum_{\mathbf{R}} (W_{\mathbf{R}})^p \exp(-i\mathbf{k} \cdot \mathbf{R}) \quad (9.7)$$

where $p = 2, 3, \dots$

10. Chain approximation

As already noted in section 4, Brout [24] proved that the contribution to the cumulant expansion from the terms corresponding to unlinked and/or reducible diagrams is negligible as compared to the contribution of the other terms. Alternatively, ignoring this statement and using exclusively the Brout classification of terms in the cumulant expansion by the powers of z^{-1} , one should conclude that the chain-type diagrams



(for which $p = n + 1$ (see sections 3 and 4)) mainly contribute to the cumulant expansion at large z , because they all are proportional to the least, zeroth power of the quantity z^{-1} . Thus, it is reasonable to obtain the expressions for the SRO parameters within the corresponding chain approximation (taking into account only the chain-type diagrams in the cumulant expansion) and to compare their numerical accuracy with that of the zero and ring approximations. The first goal will be achieved below in this section, and the second one in the second part of the present work [52].

Within the chain approximation, the expression for the grand thermodynamic potential Ω_{chain} can be presented in the following form

$$\Omega_{\text{chain}} = \Omega_0 - k_B T \ln \Delta \Gamma + \Delta \Omega_{\text{chain}} \quad (10.1)$$

where

$$\Delta \Omega_{\text{chain}} = 1/2 \sum_{n=1}^{\infty} (-k_B T)^{-n+1} \times \sum_{R_1, R_2, \dots, R_{n+1}} W_{R_1-R_2} W_{R_2-R_3} \dots W_{R_n-R_{n+1}} P_{R_1} \times P_{R_2} (1 - P_{R_2}) P_{R_3} (1 - P_{R_3}) \dots P_{R_n} (1 - P_{R_n}) P_{R_{n+1}}. \quad (10.2)$$

Note that in (10.2), at the transition from the diagram form to the analytical one, the diagram technique rules described in section 3 were used, taking account of the following equality

$$S_{\text{chain}} = p!/2$$

obtained by means of (3.12). In the case of the disordered state of the alloy (see (4.2)), we have

$$\Delta \Omega_{\text{chain}}|_{P_R=c} = N c^2 \tilde{W}_{k=0} [1 + \tilde{W}_{k=0} c (1 - c) / (k_B T)]^{-1} / 2. \quad (10.3)$$

Applying the thermodynamic fluctuation method to Ω_{chain} , in the same way as in the derivation of (9.5) and (9.6), we obtain the following expressions for calculation of the Fourier transform of the SRO parameters

$$\alpha_{\mathbf{k}} = [1 + \tilde{W}_{\mathbf{k}}^{\text{eff}} c (1 - c) / (k_B T)]^{-1} \quad (10.4)$$

$$N^{-1} \sum_{\mathbf{q}} [1 + \tilde{W}_{\mathbf{q}}^{\text{eff}} c (1 - c) / (k_B T)]^{-1} = 1$$

where

$$\tilde{W}_k^{\text{eff}} = \frac{\tilde{W}_k + c^2[(\tilde{W}_{k=0})^2 + \tilde{W}_k \tilde{W}_{k=0}(2 + c\tilde{W}_{k=0}/(k_B T))]/(k_B T)}{[1 + \tilde{W}_{k=0}c(1 - c)/(k_B T)]^2 [1 + \tilde{W}_k c(1 - c)/(k_B T)]}. \quad (10.5)$$

11. Low-concentration approximation

In the case of small concentrations, only the terms proportional to the lowest powers of concentration mainly contribute into the cumulant expansion, and the quantity P_R should be chosen (see (4.2)) as a small parameter of expansion. According to the diagram technique rules presented in section 3, the quantity P_R enters the cumulant expansion exclusively through the quantities $M_n^0(\mathbf{R})$. From (3.3) and (3.5), it follows that, for any given $n = 1, 2, \dots$, the expansion of the quantity $M_n^0(\mathbf{R})$ in the series in powers of P_R starts with the first power. Therefore, taking into account that the multiplier $M_n^0(\mathbf{R})$ (with some $n = 1, 2, \dots$) is matched up to every site of the diagram in the cumulant expansion, one may conclude that the expansion of the analytical expression corresponding to an arbitrary diagram with p sites in the series in powers of P_R begins with the p th power. Thus, to derive the expression for the cumulant expansion with an accuracy of the p th power of the quantities P_R ($p = 0, 1, \dots$), one should take account of only the diagrams with the number of sites no more than p .

In particular, summing up the contributions from all linked irreducible diagrams with one and two sites, we obtain the following expression for the grand thermodynamic potential with an accuracy of the second power of the quantities P_R

$$\Omega_{\text{LC}} = \Omega_0 - k_B T \ln \Delta \Gamma + \text{diagram} + \text{diagram} \quad (11.1)$$

where

$$\text{diagram} = \text{diagram} + \text{diagram} + \text{diagram} + \text{diagram} + \dots \quad (11.2)$$

and Ω_0 and $\ln \Delta \Gamma$ are determined in (2.9) and (2.12), respectively. According to the diagram technique rules presented in section 3, we obtain (with an accuracy of the square of P_R)

$$\begin{aligned} \text{diagram} &= \frac{\mu}{2} \sum_R P_R (1 - P_R) \\ \text{diagram} &= k_B T / 2 \sum_{R_1, R_2} P_{R_1} P_{R_2} [1 - \exp(-W_{R_1 - R_2} / (k_B T))]. \end{aligned} \quad (11.3)$$

Applying the thermodynamic fluctuation method to the expression (11.1), in the same way as in sections 7 and 8, we obtain

$$\begin{aligned} \alpha_k &= \{1 + c(1 - c)[1 - \exp(-\mu/(k_B T)) - \mu/(k_B T) + \tilde{f}_k]\}^{-1} \\ N^{-1} \sum_q \alpha_q &= 1 \end{aligned} \quad (11.4)$$

where

$$\tilde{f}_k = \sum_R [1 - \exp(-V_R / (k_B T))] \exp(-ik \cdot \mathbf{R}). \quad (11.5)$$

It is notable that, passing in the expressions (11.1) and (11.4) to the case of the canonical ensemble (i.e. setting $\mu = 0$ —see section 2), we arrive to the corresponding expressions for the low-concentration approximation derived by Krivoglaz [1, 2, 7, 55].

12. Conclusions

In the present work, in the framework of a modified thermodynamic perturbation theory within the grand canonical ensemble, by the use of the thermodynamic fluctuation method, in addition to the well known spherical model approximation, a number of new analytical approximations for calculations of the grand thermodynamic potential as well as of the SRO parameters and their Fourier transform in disordered binary alloys with a Bravais crystal lattice were developed. An alloy was considered in the framework of the lattice gas model with pair atomic interactions of an arbitrary effective radius of action, and the inverse effective number of atoms interacting with one fixed atom, inverse temperature and concentration of the impurity component were used as small parameters of expansion. It was established that the thermodynamic fluctuation method permits us to obtain more accurate results on the SRO parameters than the conventionally used method of differentiation with respect to potential.

It seems to be important to reveal the temperature–concentration intervals of the correct applicability of the developed approximations and to compare the numerical accuracies of these approximations in the cases of actual alloys and the simplest model systems for which the necessary information concerning atomic interactions is available. It is significant also to ascertain what choice of small parameter of expansion in the thermodynamic perturbation theory within the considered formalism is the best in respect to the rate of convergence of a corresponding expansion. Both problems are solved in the second part of the present work [52] (see also [56, 57]).

Notice that the approach advanced in the present work may be also used for the derivation of subsequent approximations within the thermodynamic perturbation theory. Besides, it seems to be advisable to extend this approach to the case of a multicomponent alloy with a complex crystal lattice as well as to the case of an alloy with nonpair atomic interactions [58, 59] and/or with a long-range order. Owing to the equivalence of the two-component lattice gas and Ising models [27, 60], the obtained results may be also used in research on magnetics. The absence of *a priori* assumptions about the space dimensionality of a crystal lattice in the developed formalism permits us readily to apply it in investigations of low-dimensional lattice systems, as well. The approximations elaborated in the present work may be also useful in the investigations of fluids and amorphous materials within the framework of the lattice gas model.

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Appendix

To generalize the diagram technique rules as well as the expression for the combinatorial factor K to the case of the presence of diagrams with loops in the cumulant expansion (see section 3), let us consider the cumulant $M_n(X)$ of any given order n . In the expression (3.3) for such a cumulant, the term $\langle X^n \rangle$ is always present and corresponds to the choice

$m_i = \delta_{i,n}$ for any i in the sum in (3.3). This term can be written in the following form

$$\begin{aligned} \langle X^n \rangle &= \left\langle \left(1/2 \sum_{\mathbf{R}_1, \mathbf{R}_2} W_{\mathbf{R}_1 - \mathbf{R}_2} C_{\mathbf{R}_1} C_{\mathbf{R}_2} \right)^n \right\rangle = \left\langle \left(1/2 \sum_{i=1}^N \sum_{j=1}^N W_{\mathbf{R}_i - \mathbf{R}_j} C_{\mathbf{R}_i} C_{\mathbf{R}_j} \right)^n \right\rangle \\ &= \left\langle \left(\sum_{i>j=1}^N W_{\mathbf{R}_i - \mathbf{R}_j} C_{\mathbf{R}_i} C_{\mathbf{R}_j} + 1/2 \sum_{i=1}^N W_{\mathbf{R}=0} C_{\mathbf{R}_i} \right)^n \right\rangle \end{aligned} \quad (\text{A.1})$$

where the summations are carried out over all sites of a crystal lattice numbered by $1, 2, \dots, N$. Transforming (A.1) as follows

$$\langle X^n \rangle = n! \sum_{\{m_{ij}, n_i\}=0} \left\langle \prod_{i>j=1}^N \left[\frac{(W_{\mathbf{R}_i - \mathbf{R}_j} C_{\mathbf{R}_i} C_{\mathbf{R}_j})^{m_{ij}}}{m_{ij}!} \right] \prod_{i=1}^N \left[\frac{(W_{\mathbf{R}=0} C_{\mathbf{R}_i})^{n_i}}{2^{n_i} n_i!} \right] \right\rangle \quad (\text{A.2})$$

$$\left(\sum_{i>j=1}^n m_{ij} + \sum_{i=1}^n n_i = n \right)$$

and, then, grouping together the terms that correspond to topologically equivalent diagrams, we obtain

$$\begin{aligned} \langle X^n \rangle &= \sum_{\text{Diagram}} \frac{S}{p!} n! \left(\prod_{i>j=1}^N [m_{ij}!] \prod_{i=1}^N [n_i! 2^{n_i}] \right)^{-1} \\ &\times \sum_{\mathbf{R}_1 \neq \mathbf{R}_2 \neq \dots \neq \mathbf{R}_p} \left[\prod W_{\mathbf{R}_i - \mathbf{R}_j} \right] \left\langle \prod C_{\mathbf{R}_i} \right\rangle \end{aligned} \quad (\text{A.3})$$

where

$$\begin{aligned} \left[\prod W_{\mathbf{R}_i - \mathbf{R}_j} \right] &= \prod_{i>j=1}^p [W_{\mathbf{R}_i - \mathbf{R}_j}]^{m_{ij}} \prod_{i=1}^p [W_{\mathbf{R}=0}]^{n_i} \\ \left\langle \prod C_{\mathbf{R}_i} \right\rangle &= \left\langle \prod_{i>j=1}^p [C_{\mathbf{R}_i} C_{\mathbf{R}_j}]^{m_{ij}} \prod_{i=1}^p [C_{\mathbf{R}_i}]^{n_i} \right\rangle = \left\langle \prod_{i=1}^p (C_{\mathbf{R}_i})^{l_i} \right\rangle. \end{aligned} \quad (\text{A.4})$$

In (A.3) and (A.4) \sum_{Diagram} means the summation over all topologically nonequivalent diagrams; the vertices of a diagram are numbered by $1, 2, \dots, p$; the summations on the vectors $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_p$ are carried out over all N crystal lattice sites; S is the number of nonequivalent ways of distribution of p unequal fixed indices through the p vertices of a given diagram (see (3.12)); m_{ij} is the number of lines linking two different vertices i and j ; n_i is the number of loops corresponding to the vertex i and l_i is the total number of lines entering the vertex i .

Horwitz and Callen [36] proved that the transition in consideration

$$\langle X^n \rangle \rightarrow M_n(X)$$

is equivalent to the simultaneous performance of the two following changes

$$\left\langle \prod_{i=1}^p (C_{\mathbf{R}_i})^{l_i} \right\rangle \rightarrow \prod_{i=1}^p M_{l_i}^0(\mathbf{R}_i) \sum_{\mathbf{R}_1 \neq \mathbf{R}_2 \neq \dots \neq \mathbf{R}_p} \rightarrow \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_p}.$$

Performing these changes in (A.3) and (A.4) we obtain

$$M_n(X) = \sum_{\text{Diagram}} \tilde{K} \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_p} \prod_{i>j=1}^p [W_{\mathbf{R}_i - \mathbf{R}_j}]^{m_{ij}} \prod_{i=1}^p [(W_{\mathbf{R}=0})^{n_i} M_{l_i}^0(\mathbf{R}_i)] \quad (\text{A.5})$$

where

$$\tilde{K} = \frac{S}{p!} n! \left(\prod_{i>j=1}^N [m_{ij}!] \prod_{i=1}^N [n_i! 2^{n_i}] \right)^{-1}. \quad (\text{A.6})$$

Taking into account that $M_n(X)$ enters the expansion (3.1) with the corresponding coefficient, we have

$$K = \tilde{K} (-k_B T)^{1-n} / n! \quad (\text{A.7})$$

from where, by the use of (A.6), we arrive at the desired expression (3.11).

From the expression (A.5), it follows that the diagram technique rules quoted in section 3 still stand in the case of the presence of diagrams with loops in a diagram expansion, as long as the expression (3.11) is used for calculation of the combinatorial factor K . Note that the expression (3.11) is also valid for diagrams without loops, i.e. when $n_i = 0$ for any $i = 1, 2, \dots, p$.

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