

# Analytical description of the short-range order in alloys with many-body atomic interactions

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**Abstract.** Three simple analytical approximations are elaborated for calculation of the short-range order parameters and their Fourier transform in disordered binary alloys with many-body atomic interactions of arbitrary order and effective radius of action. Within all the approximations the account of non-pair atomic interactions is reduced to the replacement of the pair mixing potential by the effective concentration-dependent potential. From the form of such an effective potential it is concluded that the temperature–concentration phase diagram of an alloy with non-pair atomic interactions is asymmetrical with respect to the equiatomic composition and that the effect on the structural properties of the alloy of such interactions decreases with concentration decrease. These conclusions are justified by simulation within the Monte Carlo method. On the basis of the comparison with the simulation data, an approximation which demonstrates high numerical accuracy of results in a wide temperature–concentration interval is determined and it is shown that its accuracy increases with the increase of the effective radius of atomic interactions. We prove the general invariance of the statistical–thermodynamic properties of binary alloys with respect to a number of transformations which results in symmetry of the phase diagrams of alloys with respect to equiatomic composition in a particular case of the presence of nothing but concentration-independent pair atomic interactions.

## 1. Introduction

At the present time, it is well established that account of non-pair atomic interactions is crucial for adequate statistical–thermodynamic description of a great number of alloys. So, for example, it was shown [1–6] that widely experimentally observed asymmetry of the phase diagram of alloys with respect to the equiatomic composition may be caused by just the contribution from such interactions to formation of the structural and thermodynamic properties of the alloy†. Account of non-pair atomic interactions in the alloy was found to be necessary also for adequate theoretical description of the experimental data on critical indices [7] and for explanation of the stability of a number of ordered structures in alloys [8–12].

For a variety of alloys the considerable relative contribution from non-pair atomic interactions was calculated within the framework of the pseudopotential [13–17], generalized perturbation [18–23], Connolly–Williams [24–29] and direct configurational averaging [30–32] methods. The significant concentrational dependence of the *effective* pair potentials determined through the experimental data on short-range order (SRO) in alloys [33–38] also is indirect evidence of the possibility of a considerable contribution from such interactions

† The concentrational dependence of the atomic interactions is the second possible reason for such asymmetry.

to the alloy energy, because such dependence is a manifestation of the presence of non-pair atomic interactions in the alloy [18, 20, 25, 39] and/or of concentrational dependence of the atomic interactions.

Besides the above-mentioned contributions, the indirect elastic (strain-induced) interactions of impurity atoms caused by the relaxation of the elastic distortion fields may also be a contributor to non-pair atomic interactions [8, 40, 41]. The possibility of considerable contribution from non-pair atomic interactions of such a type to the alloy energy was established within the framework of the lattice statics method of Kanzaki–Krivoglaz [42, 43]. Often experimentally observed deviations from the Vegard law in the dependence of the crystal lattice parameters of the alloy on composition [44] are also indirect evidence of the presence of non-pair atomic interactions of elastic nature in alloys [45, 46].

Up to now, within the majority of elaborated analytical approximations for description of short-range order in alloys, the pair character of atomic interactions is assumed (for a review see [3, 4, 45–49]). A number of analytical approximations that fall outside the scope of this assumption take into consideration only a limited number of non-pair atomic interactions in the alloy (triplet [2, 50–53] or triplet and quadruplet [54] ones) and as a rule are found to be considerably complicated for application. Besides, evaluation of the numerical accuracy of these approximations was either not performed at all [2, 50–53] or yielded unsatisfactory results [54].

The approximations based on the cluster-variation method (CVM) [3, 4, 48, 55–59] proved to yield results of high numerical accuracy in the case of alloys with non-pair atomic interactions [6]. However, the increase of the effective radius of such interactions (being topical for description of actual alloys (see [49])) results in a considerable rise of the computational efforts within the framework of these approximations. Moreover, in the case of alloys for which the long-range strain-induced (elastic) atomic interactions are crucial for adequate statistical–thermodynamic description, the application of the CVM based approximations is conjectural in principle [3]. Besides, the analytical study of several phenomena (e.g., the diffuse intensity peak splitting [60, 61]) requires an application of the approximations whose form is different from that of the CVM based ones. Note that all the disadvantages listed in this paragraph may be also attributed to the widely used high-accuracy Monte Carlo method of simulation.

The aim of the present paper is to work out a simple but high-accuracy analytical approximation for description of short-range order in alloys that takes into consideration many-body atomic interactions of arbitrary order and effective radius of action. For this aim to be accomplished, the Krivoglaz approach [45, 47, 62] based on application of the thermodynamic fluctuation method within the mean-field approximation is successfully used.

## 2. Theory

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 can be written in the following form [63–65]

$$H = V_0 + \sum_{n=1}^N \frac{1}{n!} \sum_{R_1, R_2, \dots, R_n} V_{R_1, R_2, \dots, R_n}^{(n)} C_{R_1} C_{R_2} \dots C_{R_n} = V_0 + \sum_R V_R^{(1)} C_R + 1/2 \sum_{R_1, R_2} V_{R_1, R_2}^{(2)} C_{R_1} C_{R_2} + 1/6 \sum_{R_1, R_2, R_3} V_{R_1, R_2, R_3}^{(3)} C_{R_1} C_{R_2} C_{R_3} + \dots \quad (2.1)$$

In (2.1)  $V_0$  is the energy of ‘alloy’ in which all  $N$  sites are occupied by B-type atoms,

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

$\sum_R$  means the summation over all  $N$  sites of the crystal lattice and  $V_{R_1, R_2, \dots, R_n}^{(n)}$  is the mixing potential of  $n$ th order ( $n = 1, 2, \dots, N$ )

$$V_{R_1, R_2, \dots, R_n}^{(n)} = \sum_{s=n}^N \frac{1}{(s-n)!} \sum_{R_{n+1}, R_{n+2}, \dots, R_s} \sum_{l=0}^n \frac{(-1)^{n-l} n!}{l! (n-l)!} E_{\underbrace{AA \dots A}_{l} \underbrace{BB \dots B}_{n-l}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) \quad (2.3)$$

where  $E_{\alpha_1, \alpha_2, \dots, \alpha_s}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s)$  is the interaction energy of  $\alpha_1, \alpha_2, \dots, \alpha_s$ -type atoms situated respectively at  $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s$  sites of a crystal lattice. In appendix A the expressions for the mixing potentials from first to fourth orders inclusively are written explicitly.

Within the mean-field approximation, the expression for the free energy  $F$  of the alloy described by the Hamiltonian (2.1) is determined by the following expressions:

$$F = E - TS \quad (2.4)$$

$$E = \langle H \rangle = V_0 + \sum_{n=1}^N \frac{1}{n!} \sum_{R_1, R_2, \dots, R_n} V_{R_1, R_2, \dots, R_n}^{(n)} P_{R_1} P_{R_2} \dots P_{R_n} \quad (2.5)$$

$$S = -k_B \sum_R [P_R \ln P_R + (1 - P_R) \ln (1 - P_R)] \quad (2.6)$$

$$P_R = \langle C_R \rangle \quad (2.7)$$

where  $\langle \dots \rangle$  means the statistical average,  $T$  is the absolute temperature and  $k_B$  is the Boltzmann constant. For averaging in (2.5) the following mean-field approximation was used [66]

$$\langle C_{R_1} C_{R_2} \dots C_{R_n} \rangle = \langle P_{R_1} \rangle \langle P_{R_2} \rangle \dots \langle P_{R_n} \rangle \quad (2.8)$$

(at  $\mathbf{R}_i \neq \mathbf{R}_j$ , where  $i, j = 1, 2, \dots, n$ ). The expression (2.6) for the entropy  $S$  has the well known form [3, 4, 46, 48].

Within the thermodynamic fluctuation method [3, 45–47, 67], let us expand the function  $\delta P_R = P_R - c$  in the Fourier series

$$\delta P_R = \sum_k \delta P_k \exp(-i\mathbf{k} \cdot \mathbf{R}) \quad (2.9)$$

and choose  $\delta P_k$  corresponding to different  $\mathbf{k}$  as independent fluctuations (in (2.9) and below  $\sum_k$  means the summation over all points in the first Brillouin zone specified by the cyclic boundary conditions). Substituting  $P_R = c + \delta P_R$  into (2.4)–(2.6), introducing the Fourier transforms  $\delta P_k$  and  $\tilde{V}_{k_1, k_2, \dots, k_{n-1}}^{(n)}$  [63, 64]

$$\tilde{V}_{k_1, k_2, \dots, k_{n-1}}^{(n)} = \sum_{R_1, R_2, \dots, R_{n-1}} V_{R_1, R_2, \dots, R_{n-1}, 0}^{(n)} \exp\left(-i \sum_{l=1}^{n-1} \mathbf{k}_l \cdot \mathbf{R}_l\right) \quad (2.10a)$$

$$V_{R_1, R_2, \dots, R_n}^{(n)} = V_{0, R_2-R_1, R_3-R_1, \dots, R_n-R_1}^{(n)} = 1/N^{n-1} \sum_{k_2, k_3, \dots, k_n} \tilde{V}_{k_2, k_3, \dots, k_n}^{(n)} \times \exp\left[i \sum_{l=2}^n \mathbf{k}_l \cdot (\mathbf{R}_l - \mathbf{R}_1)\right] \quad (2.10b)$$

and expanding the obtained expression in the series in powers of  $\delta P_k$ , we obtain the following fluctuational change of the free energy

$$\delta F = k_B T / 2 \sum_{k_1, k_2} B_{k_1, k_2} \delta P_{k_1} \delta P_{k_2}^* \quad (2.11)$$

In (2.11) all terms that are proportional to the powers of  $\delta P_k$  greater than the second power are neglected and

$$B_{k_1, k_2} = N \delta_{k_1, k_2} [c(1-c)\beta_{k_1}]^{-1} \quad (2.12)$$

$$\beta_k = \left[ 1 + c(1-c) \tilde{V}_k^{eff} / (k_B T) \right]^{-1} \quad (2.13)$$

$$\tilde{V}_k^{eff} = \sum_{m=0}^{N-2} \frac{c^m}{m!} \tilde{V}_{k, \mathbf{0}, \mathbf{0}, \dots, \mathbf{0}}^{(2+m)} = \tilde{V}_k^{(2)} + c \tilde{V}_{k, \mathbf{0}}^{(3)} + c^2 / 2 \tilde{V}_{k, \mathbf{0}, \mathbf{0}}^{(4)} + \dots \quad (2.14)$$

$$\delta_{k_1, k_2} = \begin{cases} 1 & \text{if } k_1 = k_2 \\ 0 & \text{if } k_1 \neq k_2 \end{cases} \quad (2.15)$$

$c$  is the concentration of component A and it is taken into account that in the disordered state  $P_{\mathbf{R}} = c$  for any  $\mathbf{R}$ . From (2.11), following the general formalism of the thermodynamic fluctuation method, we have

$$\langle \delta P_{k_1} \delta P_{k_2}^* \rangle_{\text{fluct}} = [B_{k_1, k_2}]^{-1} = N^{-1} c(1-c) \delta_{k_1, k_2} \beta_{k_1} \quad (2.16)$$

where  $\langle \dots \rangle_{\text{fluct}}$  means the statistical average over the Gaussian distribution of the probabilities of fluctuations [67] and  $[\dots]^{-1}$  the inversion of the matrix in brackets. In the case of the disordered state of the alloy, the short-range order Warren–Cowley parameters  $\alpha_{\mathbf{R}}$  determined as the two-body correlation function divided by  $c(1-c)$

$$\alpha_{\mathbf{R}_1 - \mathbf{R}_2} = \frac{\langle C_{\mathbf{R}_1} C_{\mathbf{R}_2} \rangle - c^2}{c(1-c)} \quad (2.17)$$

are expressed in terms of the fluctuation averages in the following way

$$\alpha_{\mathbf{R}_1 - \mathbf{R}_2} = \frac{\langle P_{\mathbf{R}_1} P_{\mathbf{R}_2} \rangle_{\text{fluct}} - c^2}{c(1-c)} = \frac{\langle \delta P_{\mathbf{R}_1} \delta P_{\mathbf{R}_2} \rangle_{\text{fluct}}}{c(1-c)} \quad \text{at } \mathbf{R}_1 \neq \mathbf{R}_2. \quad (2.18)$$

In (2.18) it is taken into account that the probability  $\langle C_{\mathbf{R}_1} C_{\mathbf{R}_2} \rangle$  of simultaneously finding two A-type atoms at given sites  $\mathbf{R}_1$  and  $\mathbf{R}_2$  is determined by the expression  $\langle P_{\mathbf{R}_1} P_{\mathbf{R}_2} \rangle_{\text{fluct}}$  only at  $\mathbf{R}_1 \neq \mathbf{R}_2$ . Notice that the quantity  $\langle \delta P_{\mathbf{R}}^2 \rangle_{\text{fluct}}$  determines the square dispersion of the fluctuating quantity  $P_{\mathbf{R}}$  rather than the correlation function at  $\mathbf{R} = \mathbf{0}$ . Using (2.9), (2.16) and (2.18), we obtain

$$\alpha_{\mathbf{R}} = N^{-1} \sum_k \beta_k \exp(ik \cdot \mathbf{R}) \quad \text{at } \mathbf{R} \neq \mathbf{0}. \quad (2.19)$$

Then, for the Fourier transform  $\alpha_k$  of the SRO parameters

$$\alpha_k = \sum_{\mathbf{R}} \alpha_{\mathbf{R}} \exp(-ik \cdot \mathbf{R}) \quad (2.20)$$

taking into account the constraint [3, 4, 46, 48, 66, 68, 69]

$$\alpha_{\mathbf{R}=\mathbf{0}} = N^{-1} \sum_q \alpha_q = 1 \quad (2.21)$$

we have

$$\alpha_k = 1 - N^{-1} \sum_q \beta_q + \beta_k. \quad (2.22)$$

The summands before  $\beta_k$  in (2.22) ensure the constraint (2.21) is met. In analogy with the Krivoglaz–Clapp–Moss (KCM) formula [45, 47, 62, 68, 69], the expression (2.22) may be transformed as follows

$$\alpha_k = \beta_k \left[ N^{-1} \sum_q \beta_q \right]^{-1} \quad (2.23)$$

generalizing the KCM formula to the case of taking into account the many-body atomic interactions of arbitrary order. It is easy to show that the expression (2.23) coincides with that obtained by Taggart and Tahir-Kheli [2, 51] in the approximation linear in the quantity  $(k_B T)^{-1}$ , when the non-pair atomic interactions of higher than third order vanish.

Besides, in the spirit of the Brout approach [66] the expression (2.22) may be transformed to the following form

$$\alpha_k = \left[ 1 + \frac{c(1-c)}{k_B T} (\tilde{V}_k^{eff} + \mu) \right]^{-1} \quad (2.24)$$

by the replacement  $\tilde{V}_k^{eff} \rightarrow \tilde{V}_k^{eff} + \mu$  with the subsequent determination of  $\mu$  from

$$N^{-1} \sum_q \left[ 1 + \frac{c(1-c)}{k_B T} (\tilde{V}_q^{eff} + \mu) \right]^{-1} = 1 \quad (2.25)$$

because in this case all the summands before  $\beta_k$  in (2.22) cancel. The expressions (2.24) and (2.25) may be considered as a generalization of those obtained within the framework of the spherical model [66, 70–73] to the case of taking into account the many-body atomic interactions of arbitrary order.

Note that in [74], in the context of a modified thermodynamic perturbation theory within the grand canonical ensemble [49, 75], the expressions (2.13), (2.14) and (2.22) were obtained as zero-order approximations adopting the inverse temperature as a small parameter of expansion. When the inverse effective radius of atomic interactions plays the role of a small parameter of expansion, the expressions (2.24) and (2.25) are derived in a zero-order approximation.

From (2.13), (2.14) and (2.22)–(2.25) it follows that, within all the considered approximations, the account of non-pair atomic interactions is reduced (from the point of view of SRO calculation) to the replacement  $\tilde{V}_k^{(2)} \rightarrow \tilde{V}_k^{eff}$  to which in real space the replacement of the pair mixing potential by the effective concentration-dependent potential  $V_{R_1, R_2}^{eff}$

$$\begin{aligned} V_{R_1, R_2}^{eff} &= \sum_{m=0}^{N-2} \frac{c^m}{m!} \sum_{R'_1, R'_2, \dots, R'_m} V_{R_1, R_2, R'_1, R'_2, \dots, R'_m}^{(2+m)} = V_{R_1, R_2}^{(2)} \\ &+ c \sum_{R'_1} V_{R_1, R_2, R'_1}^{(3)} + \frac{c^2}{2} \sum_{R'_1, R'_2} V_{R_1, R_2, R'_1, R'_2}^{(4)} + \dots \end{aligned} \quad (2.26)$$

corresponds. The forms of  $\tilde{V}_k^{eff}$  and  $V_{R_1, R_2}^{eff}$  demonstrate that the relative effect of non-pair atomic interactions of the  $m$ th order ( $m > 2$ ) is proportional to  $c^{m-2}$  and, correspondingly, decreases on decrease of the concentration. This fact may be qualitatively explained through the approximate estimation of the contribution from the atomic interactions of  $m$ th order ( $m \geq 2$ ) by the quantity

$$\langle C_{R_1} C_{R_2} \dots C_{R_m} \rangle \approx \langle C_{R_1} \rangle \langle C_{R_2} \rangle \dots \langle C_{R_m} \rangle = c^m \quad (2.27)$$

which is equal to the probability of finding  $m$  A-type atoms in the nearest-neighbouring sites  $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_m$ . Just the decrease of the probabilities of finding non-pair clusters of A-type atoms results in the decrease of the relative effect of the non-pair atomic interactions on the statistical–thermodynamic properties of alloy at concentration decrease.

From the expressions (2.22)–(2.25), it follows that, within all three considered approximations, the values of the SRO parameters are not invariant to the replacement  $c \rightarrow (1 - c)$  in the presence of non-pair atomic interactions in the alloy. The same is true for the expression for the critical temperature  $T_c$  of the absolute instability of the disordered state determined by the following expressions

$$k_B T_c = -c(1 - c) \min_k \tilde{V}_k^{eff} = -c(1 - c) \tilde{V}_{\mathbf{k}_0}^{eff} \quad (2.28)$$

$$k_B T_c = \frac{c(1 - c)}{N^{-1} \sum_k \left( \tilde{V}_k^{eff} - \tilde{V}_{\mathbf{k}_0}^{eff} \right)^{-1}} \quad (2.29)$$

which results from the equation  $\beta_k^{-1} = 0$  within the framework of, respectively, the approximations (2.22), (2.23) and (2.24), (2.25) [66]†. From (2.28) and (2.29) it follows that, for an alloy with non-pair atomic interactions, the phase diagram is asymmetrical with respect to the equiatomic composition and that the instability wave vector  $\mathbf{k}_0$  is concentration dependent even in the case of concentration-independent atomic interactions. This asymmetry is discussed below in section 5 in detail.

### 3. Alternative forms of the function $\tilde{V}_k^{eff}$

There exist alternative forms for the Hamiltonian of the system under consideration to the expression (2.1) [18, 39, 76]:

$$H = J_0 + \sum_{n=1}^N \frac{1}{n!} \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n} J_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n}^{(n)} S_{\mathbf{R}_1} S_{\mathbf{R}_2} \dots S_{\mathbf{R}_n} = J_0 + \sum_{\mathbf{R}} J_{\mathbf{R}}^{(1)} S_{\mathbf{R}} + \frac{1}{2} \sum_{\mathbf{R}_1, \mathbf{R}_2} J_{\mathbf{R}_1, \mathbf{R}_2}^{(2)} S_{\mathbf{R}_1} S_{\mathbf{R}_2} + \frac{1}{6} \sum_{\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3} J_{\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3}^{(3)} S_{\mathbf{R}_1} S_{\mathbf{R}_2} S_{\mathbf{R}_3} + \dots \quad (3.1)$$

where

$$S_{\mathbf{R}} = \begin{cases} 1 & \text{if an A-type atom is at site } \mathbf{R} \\ -1 & \text{otherwise} \end{cases} \quad (3.2)$$

and also

$$H = \Phi_0 + \sum_{n=1}^N \frac{1}{n!} \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n} \Phi_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n}^{(n)} \Delta_{\mathbf{R}_1} \Delta_{\mathbf{R}_2} \dots \Delta_{\mathbf{R}_n} = \Phi_0 + \sum_{\mathbf{R}} \Phi_{\mathbf{R}}^{(1)} \Delta_{\mathbf{R}} + \frac{1}{2} \sum_{\mathbf{R}_1, \mathbf{R}_2} \Phi_{\mathbf{R}_1, \mathbf{R}_2}^{(2)} \Delta_{\mathbf{R}_1} \Delta_{\mathbf{R}_2} + \frac{1}{6} \sum_{\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3} \Phi_{\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3}^{(3)} \Delta_{\mathbf{R}_1} \Delta_{\mathbf{R}_2} \Delta_{\mathbf{R}_3} + \dots \quad (3.3)$$

where

$$\Delta_{\mathbf{R}} = C_{\mathbf{R}} - c. \quad (3.4)$$

In appendix B, one can find the expressions establishing a one-to-one correspondence not only among the potentials  $V_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n}^{(n)}$ ,  $J_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n}^{(n)}$  and  $\Phi_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n}^{(n)}$  but also among their

† The quantity  $T_c$ , determined in (2.28) and (2.29), characterizes the lowest (on the temperature scale) limit of applicability of the expressions (2.22), (2.23) and (2.24), (2.25), respectively.

Fourier transforms. With the help of those expressions, it is easy to derive the following expressions for the quantity  $\tilde{V}_k^{eff}$  determined by (2.14)

$$\tilde{V}_k^{eff} = 4 \sum_{m=0}^{N-2} \frac{(2c-1)^m}{m!} \tilde{J}_{k,0,0,\dots,0}^{(2+m)} = 4 \left[ \tilde{J}_k^{(2)} - (1-2c)\tilde{J}_{k,0}^{(3)} + \frac{(1-2c)^2}{2} \tilde{J}_{k,0,0}^{(4)} - \dots + \frac{(2c-1)^{N-2}}{(N-2)!} \tilde{J}_{k,0,0,\dots,0}^{(N)} \right] \quad (3.5)$$

$$\tilde{V}_k^{eff} = \tilde{\Phi}_k^{(2)} \quad (3.6)$$

through the Fourier transforms  $\tilde{J}_{k_1,k_2,\dots,k_{n-1}}^{(n)}$  and  $\tilde{\Phi}_{k_1,k_2,\dots,k_{n-1}}^{(n)}$  of the potentials  $J_{R_1,R_2,\dots,R_n}^{(n)}$  and  $\Phi_{R_1,R_2,\dots,R_n}^{(n)}$ , respectively, both determined in analogy with (2.10). From (3.5) and (3.6) it follows that SRO in the alloy is completely determined by the pair potentials  $J_{R_1,R_2}^{(2)}$  (at equiatomic composition  $c = 0.5$ ) or  $\Phi_{R_1,R_2}^{(2)}$  (at arbitrary composition) within the framework of all three approximations considered. It is notable that the expression (2.26) for the effective pair potential  $V_{R_1,R_2}^{eff}$  being expressed in terms of potentials  $J_{R_1,R_2,\dots,R_n}^{(n)}$  coincides with the corresponding expression obtained by Carlsson [25].

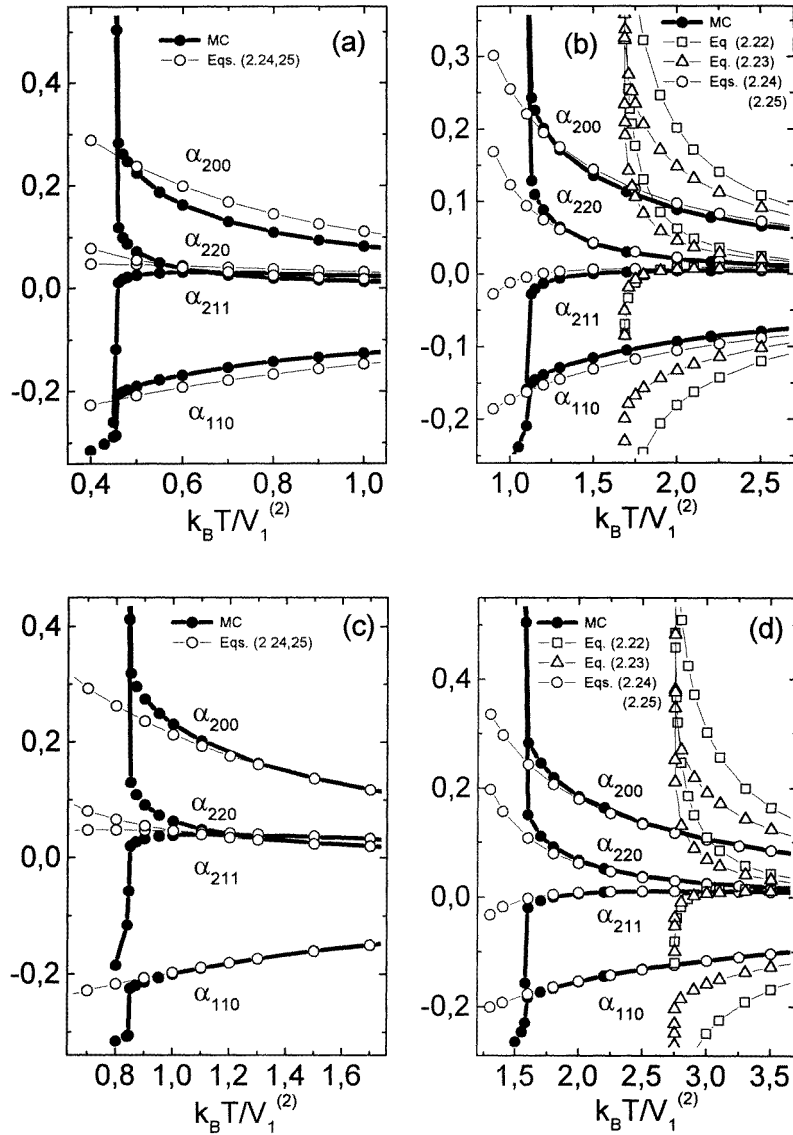
#### 4. Numerical accuracy of approximations

To study the numerical accuracy of the derived approximations, in figure 1(a)–(f) for a few model cases the dependences of the SRO parameters for the first four coordination shells of the f.c.c. crystal lattice on the reduced temperature that were calculated through the Monte Carlo simulations as well as by use of the expressions (2.22)–(2.25) are plotted. For each value of concentration  $c = 0.25, 0.50$  and  $0.75$ , the temperature interval  $[T_0, 2T_0]$  was considered, where  $T_0$  is the temperature of the order–disorder phase transition. Only pair (for one or two nearest coordination shells) and triplet (for the first coordination shell) interactions were taken into account. Such a choice of the values of the concentration and mixing potentials permits us to reveal the tendencies in the change of the numerical accuracy of approximations under a variation of both the concentration and effective radius of atomic interactions.

By the coordination shell for the mixing potential of  $n$ th order is implied the multitude of symmetry equivalent figures formed by  $n$  crystal lattice sites, one of which is situated at the origin. As a radius of such a coordination shell one may adopt, for example, the sum of lengths of all edges of the corresponding geometrical figure and classify the coordination shells by the value of this radius. Within such a classification, the triangles linking the nearest-neighbour sites form the first coordination shell for the triplet mixing potential in the f.c.c. crystal lattice. Note that in the case of the pair mixing potential, such generalized concepts of the coordination shell and its radius coincide with the generally accepted ones.

In simulations, the standard Monte Carlo method within the canonical ensemble under cyclic boundary conditions was applied [77]. The number of Monte Carlo (MC) steps (i.e. the interchanges of two randomly chosen atoms) both for the achievement of the equilibrium state and a subsequent averaging was not fixed but varied to obtain a relative error no more than 3%. To fulfil such a criterion, it was generally required to perform from 1000 to 20 000 MC steps per site. To eliminate the effect of boundary conditions, in each case the simulations were subsequently performed at increasing number of sites in a sample  $N = 20^3, 40^3, 80^3, \dots$ , until convergence (with increase of  $N$ ) of results was achieved with a relative error less than 3%.

In figure 1, the point of the phase transition corresponds to the abrupt change of the



**Figure 1.** The dependences of the SRO parameters for the first four coordination shells of the f.c.c. crystal lattice on the reduced temperature that were calculated through the Monte Carlo simulations as well as by use of the approximations (2.22), (2.23) and (2.24), (2.25) at  $V_1^{(2)} > 0$ ,  $V_1^{(3)} = 0.5 V_1^{(2)}$  and (a)  $c = 0.25$ ,  $V_2^{(2)} = 0$ ; (b)  $c = 0.25$ ,  $V_2^{(2)} = -0.5 V_1^{(2)}$ ; (c)  $c = 0.5$ ,  $V_2^{(2)} = 0$ ; (d)  $c = 0.5$ ,  $V_2^{(2)} = -0.5 V_1^{(2)}$ ; (e)  $c = 0.75$ ,  $V_2^{(2)} = 0$ ; (f)  $c = 0.75$ ,  $V_2^{(2)} = -0.5 V_1^{(2)}$ , where  $V_s^{(n)}$  is the value of the mixing potential of  $n$ th order for  $s$ th coordination shell.

temperature dependence of the SRO parameters obtained by the Monte Carlo method. The temperature  $T_c$  determined by (2.28) corresponds to the singularity of temperature dependence of the SRO parameters obtained by the use of approximations (2.22) and (2.23). In table 1, for each of the cases considered, one can find the values of the temperature  $T_0$  of

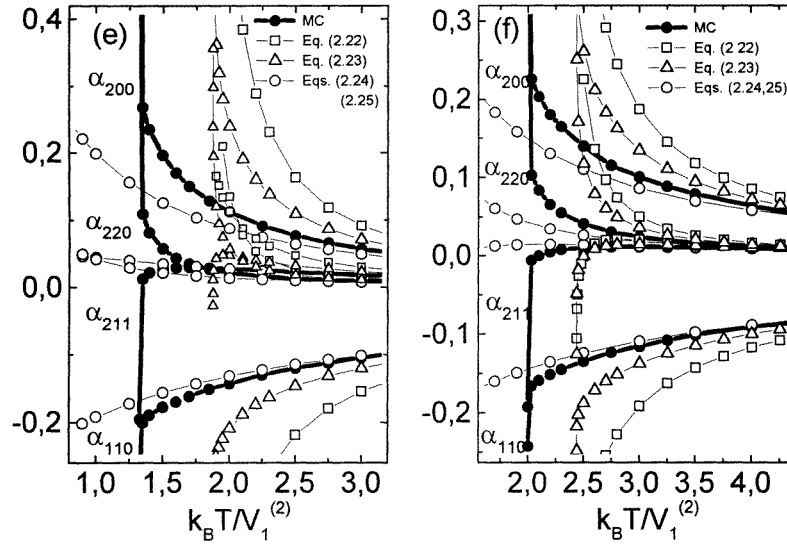


Figure 1. Continued.

order–disorder phase transition determined by the Monte Carlo method and of the critical temperature  $T_c$  calculated by the use of the expression (2.28) as well as the values of the temperature  $T'_0$  obtained by the Monte Carlo method in [49] for the same pair interactions but neglecting the non-pair ones. In two cases ( $c = 0.25, 0.50$  at  $V_2^{(2)} = 0$ ), we obtained  $T_c > 2T_0$  (see table 1) and therefore the dependences obtained by the use of the expressions (2.22) and (2.23) are not presented in the corresponding figure 1(a),(c).

**Table 1.** The values of the temperature  $T_0$  of order–disorder phase transition determined by the Monte Carlo method and of the critical temperature  $T_c$  calculated by the use of the expression (2.28) as well as the values of the temperature  $T'_0$  obtained by the Monte Carlo method in [49] for the same pair interactions but neglecting the non-pair ones for each of the cases presented in figure 1.

$c$	$V_2^{(2)}/V_1^{(2)}$	$k_B T_c/V_1^{(2)}$	$k_B T_0/V_1^{(2)}$	$k_B T'_0/V_1^{(2)}$	Figure 1
0.25	0	1.1250	0.458(2)	0.449(1)	(a)
	-0.5	1.6875	1.120(10)	1.095(5)	(b)
0.50	0	2.0000	0.848(2)	0.429(1)	(c)
	-0.5	2.7500	1.590(10)	1.140(10)	(d)
0.75	0	1.8750	1.340(10)	0.449(1)	(e)
	-0.5	2.4375	2.020(10)	1.095(5)	(f)

Accepting the results of the Monte Carlo simulations as a standard, on the basis of the data presented in figure 1(a)–(f) and in table 1, one may conclude the following. In all considered cases, the approximation (2.24), (2.25) demonstrates the high numerical accuracy of results in a wide temperature interval excluding the immediate vicinity of the phase transition temperature. The accuracy of this approximation considerably rises when the pair atomic interactions on the second coordination shell are taken into account (i.e. with an increase of the characteristic radius of atomic interactions) and/or when the concentration approaches the equiatomic value. The numerical accuracy of the approximations (2.22) and

(2.23) also rises when the pair atomic interactions on the second coordination shell are taken into account, but it is considerably lower than that of the approximation (2.24), (2.25) and decreases when the concentration moves away from the equiatomic value in all considered cases.

The comparison of the values  $T_0$  and  $T'_0$  presented in table 1 of the temperatures of the order–disorder phase transition determined by the Monte Carlo method taking and not taking into account the non-pair atomic interactions, respectively, justifies the above analytical conclusions about the asymmetry with respect to equiatomic composition of the  $T$ – $c$  phase diagram of an alloy with non-pair atomic interactions as well as about the decrease of the effect of such interactions on the structural properties of alloy when the concentration decreases. So, for example, from table 1 it follows that the relative changes of the phase transition temperature due to taking account of the triplet atomic interactions are 2.0, 97.7 and 198.4% at  $c = 0.25, 0.50$  and  $0.75$ , respectively, in the case of  $V_2^{(2)} = 0$ .

## 5. Discussion of the symmetry aspects

The studies within the framework of high-accuracy cluster-variation and Monte Carlo methods [1, 3, 6, 57] (see also section 4 of the present paper) revealed that the presence of non-pair (even concentration-independent) atomic interactions in binary alloy results in asymmetry of its  $T$ – $c$  phase diagram with respect to equiatomic composition. However, the symmetry aspects of such a phenomenon seem to have not found the deserved consideration and nothing more than one corresponding work [78] is familiar to us. The aim of the present section is the proof of the general invariance of the statistical–thermodynamic properties of binary alloys with respect to a number of transformations, which ensures the symmetry of the phase diagrams of alloys with respect to equiatomic composition in a particular case of the presence of nothing but concentration-independent pair atomic interactions in them.

The Hamiltonian (2.1) of a binary alloy may be rewritten in the following form [63]

$$H = \sum_{n=1}^N \frac{1}{n!} \sum_{\alpha_1, \alpha_2, \dots, \alpha_n = A}^B \sum_{R_1, R_2, \dots, R_n} E_{\alpha_1, \alpha_2, \dots, \alpha_n}^{(n)}(R_1, R_2, \dots, R_n) C_{R_1}^{\alpha_1} C_{R_2}^{\alpha_2} \dots C_{R_n}^{\alpha_n} \quad (5.1)$$

where

$$C_R^\alpha = \begin{cases} 1 & \text{if an } \alpha\text{-type atom is at site } R \\ 0 & \text{otherwise.} \end{cases} \quad (5.2)$$

From the comparison of (2.2) and (5.2), it is evident that  $C_R = C_R^A$ . Using the relationship

$$C_R^A + C_R^B = 1 \quad (5.3)$$

one may exclude either all the quantities  $C_R^B$  (as in (2.1)) or  $C_R^A$  from (5.1). As a result, we obtain, respectively,

$$H = V^{(0,A)} + \sum_{n=1}^N \frac{1}{n!} \sum_{R_1, R_2, \dots, R_n} V_{R_1, R_2, \dots, R_n}^{(n,A)} C_{R_1}^A C_{R_2}^A \dots C_{R_n}^A \quad (5.4)$$

and

$$H = V^{(0,B)} + \sum_{n=1}^N \frac{1}{n!} \sum_{R_1, R_2, \dots, R_n} V_{R_1, R_2, \dots, R_n}^{(n,B)} C_{R_1}^B C_{R_2}^B \dots C_{R_n}^B \quad (5.5)$$

where

$$V^{(0,A)} = V_0 \quad V_{R_1, R_2, \dots, R_n}^{(n,A)} = V_{R_1, R_2, \dots, R_n}^{(n)} \quad (5.6)$$

(see (2.1), (2.3)),  $V^{(0,B)}$  is the energy of an ‘alloy’ in which all sites are occupied by A-type atoms,

$$V_{R_1, R_2, \dots, R_n}^{(n,B)} = \sum_{s=n}^N \frac{1}{(s-n)!} \sum_{R_{n+1}, R_{n+2}, \dots, R_s} \sum_{l=0}^n \frac{(-1)^{n-l} n!}{l!(n-l)!} E_{\underbrace{BB \dots B}_{l} AA \dots A}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s). \quad (5.7)$$

Initial Hamiltonian (5.1) is invariant with respect to the exchange  $A \leftrightarrow B$ , because the designation of two sorts of atom by symbols A and B is an arbitrary procedure. From the expressions (5.4) and (5.5), it follows that any statistical–thermodynamic relationship characterizing the alloy with Hamiltonian (5.1) may be expressed in terms of either the quantities  $\{V_{R_1, R_2, \dots, R_n}^{(n,A)}, C_R^A\}$  or  $\{V_{R_1, R_2, \dots, R_n}^{(n,B)}, C_R^B\}$ . Since all the denoted statistical–thermodynamic relationships must possess the symmetry of the initial Hamiltonian, they, therefore, must be invariant with respect to the transformation

$$\begin{cases} V_{R_1, R_2, \dots, R_n}^{(n,A)} \leftrightarrow V_{R_1, R_2, \dots, R_n}^{(n,B)} \\ C_R^A \leftrightarrow C_R^B. \end{cases} \quad (5.8)$$

The invariance with respect to the transformation (5.8) is just the general symmetry of binary alloys described at the beginning of this section.

To study the consequences of the derived symmetry, for instance, let us consider two following statistical–thermodynamic relationships

$$\varphi(T_c, c, V_{R_1, R_2}^{(2,A)}, V_{R_1, R_2, R_3}^{(3,A)}, \dots) = 0 \quad (5.9)$$

$$\psi(\alpha_R, T, c, V_{R_1, R_2}^{(2,A)}, V_{R_1, R_2, R_3}^{(3,A)}, \dots) = 0 \quad (5.10)$$

which determine, respectively, the critical temperature  $T_c$  of the order–disorder phase transition and SRO parameters in the disordered state of alloy ( $\varphi$  and  $\psi$  are certain functionals). Note that the expressions (2.28), (2.29) and (2.22), (2.24) are the particular cases of (5.9) and (5.10), respectively. By the use of (5.3), it is easy to obtain that

$$\alpha_R^{AA} = \alpha_R^{BB} = \alpha_R \quad (5.11)$$

where

$$\alpha_{R_1-R_2}^{AA} = \frac{\langle C_{R_1}^A C_{R_2}^A \rangle - c_A^2}{c_A(1-c_A)} \quad \alpha_{R_1-R_2}^{BB} = \frac{\langle C_{R_1}^B C_{R_2}^B \rangle - c_B^2}{c_B(1-c_B)} \quad (5.12)$$

$$c_A = \langle C_R^A \rangle = c \quad c_B = \langle C_R^B \rangle = 1 - c \quad (5.13)$$

( $\alpha_{R_1-R_2}^{AA}$  and  $\alpha_{R_1-R_2}^{BB}$  are the SRO parameters of A- and B-type atoms, respectively). From the expressions (5.11)–(5.13), it follows that the invariance of the expressions (5.9) and (5.10) with respect to the transformation (5.8) leads to the invariance both of the critical temperature  $T_c$  and of the SRO parameters  $\alpha_R$  with respect to the following transformation

$$\begin{cases} V_{R_1, R_2, \dots, R_n}^{(n,A)} \leftrightarrow V_{R_1, R_2, \dots, R_n}^{(n,B)} & n > 2 \\ c \leftrightarrow (1 - c). \end{cases} \quad (5.14)$$

In a particular case of the absence of non-pair atomic interactions in the alloy, we have (see (5.6), (5.7), (A.2) and [63])

$$\begin{aligned} V_{R_1, R_2}^{(2,A)} &= V_{R_1, R_2}^{(2,B)} = E_{AA}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) - 2E_{AB}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) + E_{BB}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) \\ V_{R_1, R_2, \dots, R_n}^{(n,A)} &= V_{R_1, R_2, \dots, R_n}^{(n,B)} = 0 \quad (n > 2). \end{aligned} \quad (5.15)$$

Assuming also that pair atomic interactions are independent from concentration and substituting (5.15) into (5.14), we obtain that, in this case, both  $T_c$  and  $\alpha_R$  must be invariant with respect to the transformation

$$c \leftrightarrow (1 - c). \quad (5.16)$$

It is obvious that the asymmetry of the phase diagrams of binary alloys with respect to equiatomic composition in the case of the presence of non-pair concentration-independent atomic interactions (both odd and even orders) is attributable to the lack of reduction of the transformation (5.14) to (5.16) in this case.

One may prove that the expression (2.26) for  $V_{R_1, R_2}^{eff}$ , and, therefore, the expressions (2.22)–(2.25) for SRO parameters and (2.28), (2.29) for the critical temperature are invariant with respect to the transformation (5.14). So, for example, taking into account only pair and triplet atomic interactions, we obtain (using (5.6), (5.7), (A.2), (A.3) and a number of symmetry properties derived in [63])

$$\begin{aligned} V_{R_1, R_2}^{eff} &= V_{R_1, R_2}^{(2,A)} + c_A \sum_{R_3} V_{R_1, R_2, R_3}^{(3,A)} = E_{AA}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) - 2E_{AB}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) + E_{BB}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) \\ &+ \sum_{R_3} \left[ E_{AAB}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - 2E_{ABB}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) + E_{BBB}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \right] \\ &+ (1 - c_B) \sum_{R_3} \left[ E_{AAA}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - 3E_{AAB}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \right. \\ &\left. + 3E_{ABB}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - E_{BBB}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \right] = E_{AA}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) \\ &- 2E_{AB}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) + E_{BB}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) \\ &+ \sum_{R_3} \left[ E_{AAA}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - 2E_{AAB}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) + E_{ABB}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \right] \\ &+ c_B \sum_{R_3} \left[ E_{ABB}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - 3E_{AAB}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) + 3E_{AAB}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \right. \\ &\left. - E_{AAA}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \right] = V_{R_1, R_2}^{(2,B)} + c_B \sum_{R_3} V_{R_1, R_2, R_3}^{(3,B)}. \quad (5.17) \end{aligned}$$

It should be noticed that the invariance of the statistical–thermodynamic relationships with respect to the transformation (5.8) may be violated within the framework of *approximate* methods. So, for instance, the expressions for SRO parameters in alloys with pair atomic interactions, obtained both by the cluster–field method within the framework of the 4–2-cluster approximation [79] and within the low-concentration Krivoglaz approximation [49, 80] are not invariant with respect to the transformation (5.16) corresponding to this case. Or, for example, in the low-concentration approximation, one may reject the higher-order terms in the series (2.26) for  $\tilde{V}_k^{eff}$ , thus generally arriving at the violation of the invariance of the corresponding expressions (2.22)–(2.25), (2.28), (2.29) with respect to the transformation (5.8). However, the numerical accuracy of approximations preserving the initial symmetry of the Hamiltonian may be supposed (see, also, [49]) to be higher.

## 6. Conclusions

The above study of the numerical accuracy of the approximations elaborated in the present paper testifies that a comparatively simple analytical approximation (2.24), (2.25) may be recommended for description in a wide temperature interval of SRO parameters in actual

alloys for which the long-range [49] and many-body (see section 1) contributions to atomic interactions are typical. It is notable that, within the framework of this approximation, the effective radius of atomic interactions is not limited *a priori* (as, for instance, within the Monte Carlo and cluster-variation methods) since for corresponding calculations it is necessary to know the Fourier transforms of interatomic potentials. The obtained (see section 3 and appendix B) different forms of this approximation allow us to apply it along with such widely used methods as generalized perturbation Ducastelle–Gautier [18] and Connolly–Williams [24, 76] methods for calculation of interatomic potentials in alloy.

It is of interest also to use the approximation (2.24), (2.25) for evaluation of the relative contributions of the many-body atomic interactions through the study of experimental data on SRO in alloys [81]. The simple analytical form of this approximation permits us to use it for analytical study of such phenomena as the diffuse intensity peak splitting [60, 61]). The elaborated formalism concerning the lattice gas model itself may be also useful in fields other than alloy theory. For instance, owing to equivalence of the two-component lattice gas and Ising models [66], 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-dimension lattice systems, as well. The approximation advanced in the present work may be also useful in the investigations of fluids and amorphous materials within the framework of the lattice gas model [66].

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### Appendix A.

From (2.3), setting  $n = 1, 2, 3, 4$ , we obtain the following expressions for the mixing potentials from first to fourth orders, respectively

$$V_{\mathbf{R}}^{(1)} = E_{\mathbf{A}}^{(1)}(\mathbf{R}) - E_{\mathbf{B}}^{(1)}(\mathbf{R}) + \sum_{s=2}^N \frac{1}{(s-1)!} \sum_{\mathbf{R}_2, \mathbf{R}_3, \dots, \mathbf{R}_s} \left[ E_{\mathbf{ABB}\dots\mathbf{B}}^{(s)}(\mathbf{R}, \mathbf{R}_2, \dots, \mathbf{R}_s) - E_{\mathbf{BB}\dots\mathbf{B}}^{(s)}(\mathbf{R}, \mathbf{R}_2, \dots, \mathbf{R}_s) \right] \quad (\text{A.1})$$

$$V_{\mathbf{R}_1, \mathbf{R}_2}^{(2)} = E_{\mathbf{AA}}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) - 2E_{\mathbf{AB}}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) + E_{\mathbf{BB}}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) + \sum_{s=3}^N \frac{1}{(s-2)!} \sum_{\mathbf{R}_3, \mathbf{R}_4, \dots, \mathbf{R}_s} \left[ E_{\mathbf{AABB}\dots\mathbf{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) - 2E_{\mathbf{ABB}\dots\mathbf{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) + E_{\mathbf{BB}\dots\mathbf{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) \right] \quad (\text{A.2})$$

$$V_{\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3}^{(3)} = E_{\mathbf{AAA}}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - 3E_{\mathbf{AAB}}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) + 3E_{\mathbf{ABB}}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - E_{\mathbf{BBB}}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) + \sum_{s=4}^N \frac{1}{(s-3)!} \sum_{\mathbf{R}_4, \mathbf{R}_5, \dots, \mathbf{R}_s} \left[ E_{\mathbf{AAABB}\dots\mathbf{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) \right]$$

$$\begin{aligned}
& - 3E_{\text{AABB}\dots\text{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) + 3E_{\text{ABB}\dots\text{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) \\
& - E_{\text{BB}\dots\text{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) \Big] \tag{A.3}
\end{aligned}$$

$$\begin{aligned}
V_{\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4}^{(4)} &= E_{\text{AAAA}}^{(4)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4) - 4E_{\text{AAAB}}^{(4)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4) \\
&+ 6E_{\text{AABB}}^{(4)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4) - 4E_{\text{ABBB}}^{(4)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4) \\
&+ E_{\text{BBBB}}^{(4)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4) + \sum_{s=5}^N \frac{1}{(s-4)!} \sum_{\mathbf{R}_5, \mathbf{R}_6, \dots, \mathbf{R}_s} \\
&\times \left[ E_{\text{AAAAABB}\dots\text{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) - 4E_{\text{AAABB}\dots\text{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) \right. \\
&+ 6E_{\text{AABB}\dots\text{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) - 4E_{\text{ABB}\dots\text{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) \\
&\left. + E_{\text{BB}\dots\text{B}}^{(s)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_s) \right]. \tag{A.4}
\end{aligned}$$

## Appendix B.

Comparing the expressions (2.1) and (3.1) and using (2.2) and (3.2), it is easy to obtain a one-to-one correspondence not only between the potentials  $V_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n}^{(n)}$  and  $J_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n}^{(n)}$

$$\begin{aligned}
V_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n}^{(n)} &= 2^n \sum_{m=0}^{N-n} \frac{(-1)^m}{m!} \sum_{\mathbf{R}_{n+1}, \mathbf{R}_{n+2}, \dots, \mathbf{R}_{n+m}} J_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{n+m}}^{(n+m)} \\
&= 2^n \left[ J_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n}^{(n)} - \sum_{\mathbf{R}_{n+1}} J_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{n+1}}^{(n+1)} + \dots \right. \\
&\quad \left. + \frac{(-1)^{N-n}}{(N-n)!} \sum_{\mathbf{R}_{n+1}, \mathbf{R}_{n+2}, \dots, \mathbf{R}_N} J_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N}^{(N)} \right] \tag{B.1}
\end{aligned}$$

$$\begin{aligned}
J_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n}^{(n)} &= \sum_{m=0}^{N-n} \frac{1}{2^{n+m} m!} \sum_{\mathbf{R}_{n+1}, \mathbf{R}_{n+2}, \dots, \mathbf{R}_{n+m}} V_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{n+m}}^{(n+m)} \\
&= 2^{-n} \left[ V_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n}^{(n)} + \frac{1}{2} \sum_{\mathbf{R}_{n+1}} V_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{n+1}}^{(n+1)} + \dots \right. \\
&\quad \left. + \frac{2^{-(N-n)}}{(N-n)!} \sum_{\mathbf{R}_{n+1}, \mathbf{R}_{n+2}, \dots, \mathbf{R}_N} V_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N}^{(N)} \right] \tag{B.2}
\end{aligned}$$

but also between their Fourier transforms

$$\begin{aligned}
\tilde{V}_{\mathbf{k}_2, \mathbf{k}_3, \dots, \mathbf{k}_n}^{(n)} &= 2^n \sum_{m=0}^{N-n} \frac{(-1)^m}{m!} \tilde{J}_{\mathbf{k}_2, \mathbf{k}_3, \dots, \mathbf{k}_n, \mathbf{0}, \dots, \mathbf{0}}^{(n+m)} \\
&= 2^n \left[ \tilde{J}_{\mathbf{k}_2, \mathbf{k}_3, \dots, \mathbf{k}_n}^{(n)} - \tilde{J}_{\mathbf{k}_2, \mathbf{k}_3, \dots, \mathbf{k}_n, \mathbf{0}}^{(n+1)} + \dots + \frac{(-1)^{N-n}}{(N-n)!} \tilde{J}_{\mathbf{k}_2, \mathbf{k}_3, \dots, \mathbf{k}_n, \mathbf{0}, \dots, \mathbf{0}}^{(N)} \right] \tag{B.3}
\end{aligned}$$

$$\begin{aligned}
\tilde{J}_{\mathbf{k}_2, \mathbf{k}_3, \dots, \mathbf{k}_n}^{(n)} &= \sum_{m=0}^{N-n} \frac{1}{2^{n+m} m!} \tilde{V}_{\mathbf{k}_2, \mathbf{k}_3, \dots, \mathbf{k}_n, \mathbf{0}, \dots, \mathbf{0}}^{(n+m)} \\
&= 2^{-n} \left[ \tilde{V}_{\mathbf{k}_2, \mathbf{k}_3, \dots, \mathbf{k}_n}^{(n)} + \frac{1}{2} \tilde{V}_{\mathbf{k}_2, \mathbf{k}_3, \dots, \mathbf{k}_n, \mathbf{0}}^{(n+1)} + \dots + \frac{2^{-(N-n)}}{(N-n)!} \tilde{V}_{\mathbf{k}_2, \mathbf{k}_3, \dots, \mathbf{k}_n, \mathbf{0}, \dots, \mathbf{0}}^{(N)} \right] \tag{B.4}
\end{aligned}$$

where the Fourier transform  $\tilde{J}_{k_1, k_2, \dots, k_{n-1}}^{(n)}$  of the potential  $J_{R_1, R_2, \dots, R_n}^{(n)}$  is determined in analogy with (2.10).

Comparing the expressions (2.1) and (3.3) and using (2.2) and (3.4), we obtain the following analytical relationships between the potentials  $V_{R_1, R_2, \dots, R_n}^{(n)}$  and  $\Phi_{R_1, R_2, \dots, R_n}^{(n)}$  and between their Fourier transforms

$$\begin{aligned} \Phi_{R_1, R_2, \dots, R_n}^{(n)} &= \sum_{m=0}^{N-n} \frac{c^m}{m!} \sum_{R_{n+1}, R_{n+2}, \dots, R_{n+m}} V_{R_1, R_2, \dots, R_{n+m}}^{(n+m)} \\ &= V_{R_1, R_2, \dots, R_n}^{(n)} + c \sum_{R_{n+1}} V_{R_1, R_2, \dots, R_{n+1}}^{(n+1)} + c^2/2 \sum_{R_{n+1}, R_{n+2}} V_{R_1, R_2, \dots, R_{n+2}}^{(n+2)} + \dots \end{aligned} \quad (\text{B.5})$$

$$\begin{aligned} \tilde{\Phi}_{k_2, k_3, \dots, k_n}^{(n)} &= \sum_{m=0}^{N-2} \frac{c^m}{m!} \tilde{V}_{k_2, k_3, \dots, k_n, 0, 0, \dots, 0}^{(n+m)} \\ &= V_{k_2, k_3, \dots, k_n}^{(n)} + c V_{k_2, k_3, \dots, k_n, 0}^{(n+1)} + c^2/2 V_{k_2, k_3, \dots, k_n, 0, 0}^{(n+2)} + \dots \end{aligned} \quad (\text{B.6})$$

$$\begin{aligned} V_{R_1, R_2, \dots, R_n}^{(n)} &= \sum_{m=0}^{N-n} \frac{(-c)^m}{m!} \sum_{R_{n+1}, R_{n+2}, \dots, R_{n+m}} \Phi_{R_1, R_2, \dots, R_{n+m}}^{(n+m)} \\ &= \Phi_{R_1, R_2, \dots, R_n}^{(n)} - c \sum_{R_{n+1}} \Phi_{R_1, R_2, \dots, R_{n+1}}^{(n+1)} + c^2/2 \sum_{R_{n+1}, R_{n+2}} \Phi_{R_1, R_2, \dots, R_{n+2}}^{(n+2)} + \dots \end{aligned} \quad (\text{B.7})$$

$$\begin{aligned} \tilde{V}_{k_2, k_3, \dots, k_n}^{(n)} &= \sum_{m=0}^{N-2} \frac{(-c)^m}{m!} \tilde{\Phi}_{k_2, k_3, \dots, k_n, 0, 0, \dots, 0}^{(n+m)} \\ &= \tilde{\Phi}_{k_2, k_3, \dots, k_n}^{(n)} - c \tilde{\Phi}_{k_2, k_3, \dots, k_n, 0}^{(n+1)} + c^2/2 \tilde{\Phi}_{k_2, k_3, \dots, k_n, 0, 0}^{(n+2)} + \dots \end{aligned} \quad (\text{B.8})$$

where the Fourier transform  $\tilde{\Phi}_{k_1, k_2, \dots, k_{n-1}}^{(n)}$  of the potential  $\Phi_{R_1, R_2, \dots, R_n}^{(n)}$  is determined in analogy with (2.10).

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