[1]   Collective Correlation Factors In Random Non-Stoichiometric Intermetallic Compounds

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Abstract. In this paper Manning random alloy model has been extended to the binary nonstoichiometric intermetallic compound of the B2 structure. Two sub-lattices, that are dynamically independent in six-jump cycle (6JC) mechanism, are coupled together by taking into consideration the vacancy motion as a sequence of nearest neighbour jumps in random directions. The linear response expressions for the phenomenological transport coefficients are evaluated making use of the kinetic equation approach. The expressions for collective correlation factors are derived in terms of the equilibrium partial atomic concentrations and jump frequencies. Results are compared with Monte Carlo simulation results using the four-frequency model.

Introduction

Much of the interest in collective correlation factors has centered on the random alloy model because Manning [1] has provided far-reaching formalism for correlation effects which can also be made to give accurate expressions for the collective correlation factors [2]. The Manning relations are of special significance since they provide relationships between the phenomenological coefficients of non-equilibrium thermodynamics and the tracer diffusion coefficients, or, equivalently, relations between the collective correlation factors and the tracer correlation factors. Apart from the Manning formalism, there have been various other expressions derived for collective correlation factors. Sato, Ishikawa and Kikuchi [3] derived expressions for the collective correlation factors within the framework of the path probability method [4]. Qin and Murch [5] used a diffusion of probability approach for calculating the collective correlation factors using the cosine expansions of the collective correlation factors. Wang and Akbar [6] calculated phenomenological coefficients L_{ij} in the Ising alloy model taking B1 and B2 structures using the original path probability method of Sato [4]. Qin and Allnatt [7] have also used a matrix method for the calculation of the collective correlation factors via the collective cosines. In another approach Belova and Murch [8, 9] generalized the Manning [1] formulation to two or more sub-lattices of different compositions. The results when compared with simulated values were only in fair agreement. Belova and Murch [10, 11] then used the 6JC mechanism, first introduced by Elcock and McCombie [12] in the limit of perfect order, to calculate the phenomenological coefficients and the collective correlation factors. The results obtained with effective jump frequencies taken from Arita *et al.* [13] were found to be in very good agreement with simulation data at stoichiometry and in the asymptotic limit $(T \rightarrow 0)$. The 6JC mechanism, however, weakens when disorder is introduced either by temperature increase or by non-stoichiometry.

In the present paper, we have extended the random alloy model developed for tracer diffusion [14] to the calculation of phenomenological coefficients and collective correlation factors in a binary AB intermetallic compound taking the B2 structure. On account of non-stoichiometry, disorder arises by the presence of antistructural atoms on the host sub-lattices of A and B atoms. If we assume that initially a vacancy is on one of the sub-lattices (and perfect order conditions) then it will exchange its position with atoms on the other sub-lattice, resulting in an antistructural atom on the first sub-lattice. Hence, soon an ordered structure will result in a highly disordered one. The dynamics can be followed by the introduction of four frequencies [8]. Although the algebraic structure of the present calculations is similar to that of the tracer, the level of approximation is different. The expressions for the collective correlation factors are derived for both atomic components at small deviations from stoichiometry. The results are compared with Monte Carlo simulation data obtained with the four-frequency model, reduced to only two independent frequencies.

Transport Coefficients

We consider the B2-type AB intermetallic compound where 1 constitutes the home sub-lattice of B atoms and 2 is the home sub-lattice of A atoms. We assume that all sites of a given sub-lattice are energetically equivalent. There will be four frequencies with two different types of vacancies [8]; V_1 = vacancy on sublattice-1 only and V_2 = vacancy on sublattice-2 only. The four frequencies are $W_{A_1} \equiv W_A^{1 \rightarrow 2}$, the atom-vacancy exchange frequency when A atom is on sublattice-1 and vacancy on sublattice-2. Similarly, we define $W_{A_2} \equiv W_A^{2 \rightarrow 1}$, $W_{B_1} \equiv W_B^{1 \rightarrow 2}$ and $W_{B_2} \equiv W_B^{2 \rightarrow 1}$.

In a two-sublattice system, the phenomenological transport coefficients L_{ij} (i, j = A, B) can be expressed as [15]

$$L_{ij} = \sum_{\alpha, \beta} L_{i_\alpha j_\beta} \tag{1}$$

where α and β denote the sub-lattices 1 and 2. We now use a linear response approach [16] for the phenomenological coefficients $L_{i_\alpha j_\beta}$ and divide them into uncorrelated and correlated parts. The uncorrelated part $L_{ij}^{(0)}$ can be obtained as:

$$L_{ij}^{(0)} = \delta_{ij} \left(\frac{NZs^2}{6k_BT} \right) \left(C_{V_1} C_{i_2} W_{i_2} + C_{V_2} C_{i_1} W_{i_1} \right)$$

$$= \delta_{ij} \left(\frac{NZs^2}{3k_BT} \right) \left(C_{V_1} C_{i_2} W_{i_2} \right) \tag{2}$$

where we have used the detailed balance condition:

$$C_{V_i} C_{i_2} W_{i_2} = C_{V_2} C_{i_1} W_{i_1} \tag{3}$$

Here N is the number of sites per unit volume, Z is the co-ordination number in bcc lattice, **s** is the nearest neighbour jump distance, δ_{ij} is the Kronecker delta function and k_B and T have their usual meanings.

Further, the correlated parts of the phenomenological coefficients can be expressed as

$$L_{ij}^{(1)} = -\left(\frac{Ns^2}{3k_BT} \right) \sum_{\alpha, \beta} W_{i_\alpha} W_{j_\beta} \sum_{s, s_0} \left(\frac{\mathbf{s} \cdot \mathbf{s_0}}{\mathbf{s}^2} \right) \varphi_{V_{\alpha'} i_\alpha; V_{\beta'} j_\beta} (\mathbf{s} : \mathbf{s_0}) \tag{4}$$

Here $\alpha' \neq \alpha$, and $\beta' \neq \beta$. The ϕ functions are defined as

$$\varphi_{V_{\alpha'}i_{\alpha}:V_{\beta'}j_{\beta}}\left(\mathbf{s}.\mathbf{s_0}\right)=\int\limits_0^{\infty} dt \sum_{\lambda} \Psi_{V_{\alpha'}i_{\alpha}:V_{\beta'}j_{\beta}}.\left(\lambda,\lambda-\mathbf{s};\, t:\lambda_0,\lambda_0-\mathbf{s_0};\, t=0\right) \tag{5}$$

The function Ψ is the conditional probability of finding, at time t, the vacancy at site λ on the sublattice-α' and atom of species i at its nearest-neighbour site $(\lambda-\mathbf{s})$ on the other sublattice-α when initially the vacancy was at any site λ_0 on sublattice-β' and the atom of species j was at its nearest-neighbour site $(\lambda_0-\mathbf{s_0})$ on sublattice-β.

In the above we find that there are four kinds of ϕ functions for two values of i and j. Again each ϕ function will be of four kinds for different values of α and β. The number of these unknown ϕ functions can be reduced if we note that the nearest neighbour of a vacancy can be occupied by either A or B atoms, the total occupancy probability of which is unity. Thus the occupancy probability of A atoms in the definitions of Ψ functions can be expressed in terms of B atoms only. Substituting this into Equation 4 one finds that the terms involving φ functions that are independent of $\mathbf{s}$ or $\mathbf{s_0}$ or both vanish [17]. The final expression for the correlated part then becomes:

$$L_{ij}^{(1)}=(1-2\delta_{ij})\left(\frac{Ns^2}{3k_BT}\right)\sum_{\alpha,\beta} W_{i_{\alpha}}W_{j_{\beta}} \sum_{s,s_0}\left(\frac{\mathbf{s}.\mathbf{s_0}}{\mathbf{s}^2}\right)\varphi_{V_{\alpha'}B_{\alpha}:V_{\beta'}B_{\beta}}\left(\mathbf{s}:\mathbf{s_0}\right) \tag{6}$$

Now using the definition of Fourier transform:

$$\widetilde{\phi}(\mathbf{K}:\mathbf{s}^0)=\sum_{\mathbf{r}} e^{i\mathbf{K}.\mathbf{r}}\,\phi(\mathbf{r}:\mathbf{s}^0) \tag{7}$$

Equation (6) can be expressed as

$$L_{ij}^{(1)}=(1-2\delta_{ij})\left(\frac{NZs^2}{3k_BT}\right)\sum_{\alpha,\beta} W_{i_{\alpha}}W_{j_{\beta}}\, U_{\alpha\beta} \tag{8}$$

Here we have defined

$$U_{\alpha\beta}=8i\left(\frac{a}{2\pi}\right)^3 \int d^3K\, \mathrm{Sin}_x a\, \mathrm{Cos}_y a\, \mathrm{Cos}_z a\, \widetilde{\varphi}_{V_{\alpha'}B_{\alpha}:V_{\beta'}B_{\beta}}\left(\mathbf{K}:\mathbf{s_0}\right) \tag{9}$$

and used the symmetry of the integral to fix a particular value of $\mathbf{s}_0$, say $\mathbf{s_0}=\dfrac{a}{2}(\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}})$.

The collective correlation factors can be expressed as:

$$f_{ij}^{(j)}=1+\frac{L_{ij}^{(1)}}{L_{jj}^{(0)}} \tag{10}$$

The superscript in f will be omitted when i=j.

Kinetic Equations

The kinetic equation for $\Psi_{V_1B_2}\left(\lambda,\lambda-\mathbf{r}\right)$, the probability of finding a vacancy at time t at site λ on sublattice-1 and the atom of B kind at site $(\lambda-\mathbf{r})$ on sublattice-2 when the system was in a given initial state, can be written as:

$$\frac{d\Psi_{V_1B_2}\left(\lambda,\lambda-\mathbf{r}\right)}{dt}=\theta(\mathbf{r})\left[W_{B_1}\Psi_{V_2B_1}\left(\lambda-\mathbf{r},\lambda\right)-W_{B_2}\Psi_{V_1B_2}\left(\lambda,\ \lambda-\mathbf{r}\right)\right]$$
$$+\sum_{\mathbf{r'}\neq\mathbf{r}}\theta(\mathbf{r'})\sum_{p}\left[W_{p_1}\Psi_{V_2B_2p_1}\left(\lambda-\mathbf{r'},\ \lambda-\mathbf{r},\lambda\right)-W_{p_2}\Psi_{V_1B_2p_2}\left(\lambda,\ \lambda-\mathbf{r},\lambda-\mathbf{r'}\right)\right]$$

$$\tag{11}$$

Here p=A, B and $\theta(\mathbf{r})$ is a step function, which is unity when $\mathbf{r}=\mathbf{s}$ and zero otherwise. The kinetic equation relates the n-site probability function to the (n+1)-site probability functions, leading to a hierarchy of rate equations; the classification here is chosen according to the number of lattice sites, the occupancy of which is specified at time t. The problem is of finding workable and useful ways of truncating this hierarchy. In the present paper, we first expand the probability functions in terms

of the fluctuations of the atomic site occupancy variables (but not of the vacancy) about their mean values. Then we use the simplest decoupling approximation [18,19] and terminate the hierarchy by neglecting all terms of second order in these fluctuations. Further, we add and subtract terms with $\mathbf{r'} = \mathbf{r}$ in the summation over $\mathbf{r'}$. Then, by integrating with respect to t and taking the sum over λ on both sides of Equation 11, we soon have:

$$-\sum_{\lambda}\Psi_{V_1B_2}(\lambda,\lambda-\mathbf{r};t=0)=\theta(\mathbf{r})\left[\overline{W}_1\varphi_{V_2B_1}(-\mathbf{r})-\left(W_2-W_{V_2}\right)\varphi_{V_1B_2}(\mathbf{r})\right]$$

$$+\sum_{\mathbf{r'}}\theta(\mathbf{r'})\left[W_{V_1}\varphi_{V_2B_1}(\mathbf{r}-\mathbf{r'})-W_{V_2}\varphi_{V_1B_2}(\mathbf{r})\right] \tag{12}$$

Here

$$W_{V_1}=C_{A_i}W_{A_i}+C_{B_1}W_{B_1} \qquad ; l=1,2 \tag{13a}$$

is the vacancy escape frequency from the 1th sub-lattice and

$$W_1=C_{A_1}W_{B_1}+C_{B_1}W_{A_1} \qquad ; l=1,2 \tag{13b}$$

$$\overline{W}_1=C_{A_{l'}}W_{B_1}+C_{B_{l'}}W_{A_1} \qquad ; l' \neq 1 \tag{13c}$$

Now multiplying both sides of Equation 12 by $e^{i\mathbf{K.r}}$ and taking the sum over $\mathbf{r}$, we get

$$-\phi_{V_1\mathbf{B}_2}(\mathbf{K},t=0)=\overline{W}_1\left(\frac{a}{2\pi}\right)^3\int d^3\mathbf{K'}\tilde{\theta}(\mathbf{K}+\mathbf{K'})\tilde{\phi}_{V_2B_1}(\mathbf{K'})$$

$$-\left[W_2-W_{V_2}\right]\left(\frac{a}{2\pi}\right)^3\int d^3\mathbf{K'}\tilde{\theta}(\mathbf{K}-\mathbf{K'})\tilde{\varphi}_{V_1B_2}(\mathbf{K'})$$

$$+W_{V_1}\tilde{\theta}(\mathbf{K})\tilde{\varphi}_{V_2B_1}(\mathbf{K})-W_{V_2}Z\,\tilde{\varphi}_{V_1B_2}(\mathbf{K}) \tag{14a}$$

Here, we have defined:

$$\tilde{\varphi}_{V_1B_2}(\mathbf{K},t=0)=\sum_{\mathbf{r}}e^{i\mathbf{K.r}}\sum_{\lambda}\Psi_{V_1B_2}(\lambda,\lambda\text{-}\mathbf{r};t=0) \tag{15a}$$

$$\tilde{\theta}(\mathbf{K})=\sum_{\mathbf{r}}e^{i\mathbf{K.r}}\theta(\mathbf{r})=\sum_{\mathbf{s}}e^{i\mathbf{K.s}} \tag{15b}$$

Similarly, we can write the kinetic equation for the probability function $\Psi_{V_2B_1}(\lambda,\lambda-\mathbf{r})$ and proceed as above. The resulting equation in fact can be obtained from Equation 14a by interchanging of 1 and 2. We shall denote this equation as Equation 14b. From these two equations an appropriate generating function can be obtained if we first add Equations 14a and 14b and then subtract Equation 14b from Equation 14a. This results in two coupled integral equations for the unknown functions $\phi_{V_1B_2}$ and $\phi_{V_2B_1}$. As shown earlier by Chaturvedi and Allnatt [17] for the dumbbell mechanism, instead of solving the integral equation it is much more convenient to solve directly for the U functions, defined by means of Equation 9. Finally, using the symmetry properties of Brillouin zone integrals we derive two linear equations for the U's in terms of the static correlation functions, which in random alloy model can be trivially evaluated for a given initial state. Thus the equation that results from the addition of Equations 14a and 14b for the two initial configurations, *i.e.,* when vacancy is on sublattice-1 and a B atom at its nearest neighbour site on sublattice-2 and when vacancy on sublattice-2 with a B atom on sublattice-1, finally yields:

$$b_1U_{21}+b_2U_{11}=J\,C_{V_1}C_{B_2}C_{A_2} \tag{16a}$$

$$b_1U_{22}+b_2U_{12}=J\,C_{V_2}C_{B_1}C_{A_1} \tag{16b}$$

Here

$$b_1=W_{V_1}(1-J)+(W_1+\overline{W}_1)J \qquad ; l=1,2 \tag{17}$$

and

$$J=8\left(\frac{a}{2\pi}\right)^3\int d^3K\frac{\left[\text{Sin}K_xa\,\text{Cos}K_ya\,\text{Cos}K_za\right]^2}{\left[Z\pm\theta(K)\right]} \tag{18}$$

For the bcc lattice, the value of J turns out to be 0.15793.

Similarly, the equation that results from the subtraction of Equation 14b from Equation 14a finally yields:

$$d_2 U_{11} - d_1 U_{21} = J\, C_{V_1} C_{B_2} C_{A_2} \tag{19a}$$

$$d_2 U_{12} - d_1 U_{22} = -J\, C_{V_2} C_{B_1} C_{A_1} \tag{19b}$$

where

$$d_l = W_{V_l}\left(1 - J\right) + \left(W_l - \overline{W}_l\right) J \qquad ;\ l=1,2 \tag{20}$$

By solving Equations 16a, 16b, 19a and 19b, the U-functions can be obtained as

$$U_{11} = \left(\frac{d_1 + b_1}{b_1 d_2 + b_2 d_1}\right) J\, C_{V_1} C_{B_2} C_{A_2} \tag{21a}$$

$$U_{22} = \left(\frac{d_2 + b_2}{b_1 d_2 + b_2 d_1}\right) J\, C_{V_2} C_{B_1} C_{A_1} \tag{21b}$$

$$U_{12} = \left(\frac{d_1 - b_1}{b_1 d_2 + b_2 d_1}\right) J\, C_{V_2} C_{B_1} C_{A_1} \tag{21c}$$

$$U_{21} = \left(\frac{d_2 - b_2}{b_1 d_2 + b_2 d_1}\right) J\, C_{V_1} C_{B_2} C_{A_2} \tag{21d}$$

By using the detailed balance condition (Equation 3), it can be shown from Equations 21c and 21d that $U_{21} = U_{12}$. This gives $L_{AB} = L_{BA}$ showing that our formalism satisfies the Onsager reciprocity theorem. The final expressions for the collective correlation factors f_{AA} and $f_{AB}^{(A)}$ can be written as:

$$f_{AA} = 1 - \frac{J}{\left(b_1 d_2 + b_2 d_1\right)}\left[\left(\frac{W_{A_1}^2}{W_{A_2}}\right) C_{B_2}\left(d_1 + b_1\right) + \left(\frac{W_{A_2}^2}{W_{A_1}}\right) C_{B_1}\left(d_2 + b_2\right) + 2 W_{A_2} C_{B_1}\left(d_1 - b_1\right)\right]$$
$$\tag{22}$$

$$f_{AB}^{(A)} = \frac{J}{\left(b_1 d_2 + b_2 d_1\right)}\left[\left(\frac{W_{A_1}}{W_{A_2}}\right) W_{B_1} C_{B_2}\left(d_1 + b_1\right) + \left(\frac{W_{A_2}}{W_{A_1}}\right) W_{B_2} C_{B_1}\left(d_2 + b_2\right)\right.$$
$$\left. + \left(\frac{W_{A_1} W_{B_2} + W_{A_2} W_{B_1}}{W_{A_1}}\right) C_{B_1}\left(d_1 - b_1\right)\right] \tag{23}$$

The expressions for f_{BB} and $f_{AB}^{(B)}$ can be obtained from f_{AA} and $f_{AB}^{(A)}$ respectively by interchanging A and B.

Results and Discussion

The Monte Carlo computer simulations were carried out for the 'random alloy' sub-lattice model at and near the stoichiometric composition. The four jump frequencies were chosen as $W_{A_1} = W_{B_2} = 1$ and $W_{A_2} = W_{B_1} = \alpha$, where α is a parameter. The equilibrium composition of A-atoms, *i.e.*, C_A was varied from 0.45 to 0.5. The collective correlation factors $f_{AA}, f_{BB}, f_{AB}^{(A)}$ and $f_{AB}^{(B)}$ were obtained as a function of C_A for different values of $\alpha = 0.1$, 0.08 and 0.06.

The theoretical results of collective correlation factors are compared with Monte Carlo simulation data as a function of C_A for fixed values of $\alpha = 0.1$, 0.08 and 0.06 in Figures 1, 2 and 3 respectively. The results are in reasonably good agreement with the simulation data when the ratio of jump frequencies of structured and antistructured atoms is of the order of 10^{-1}. We note
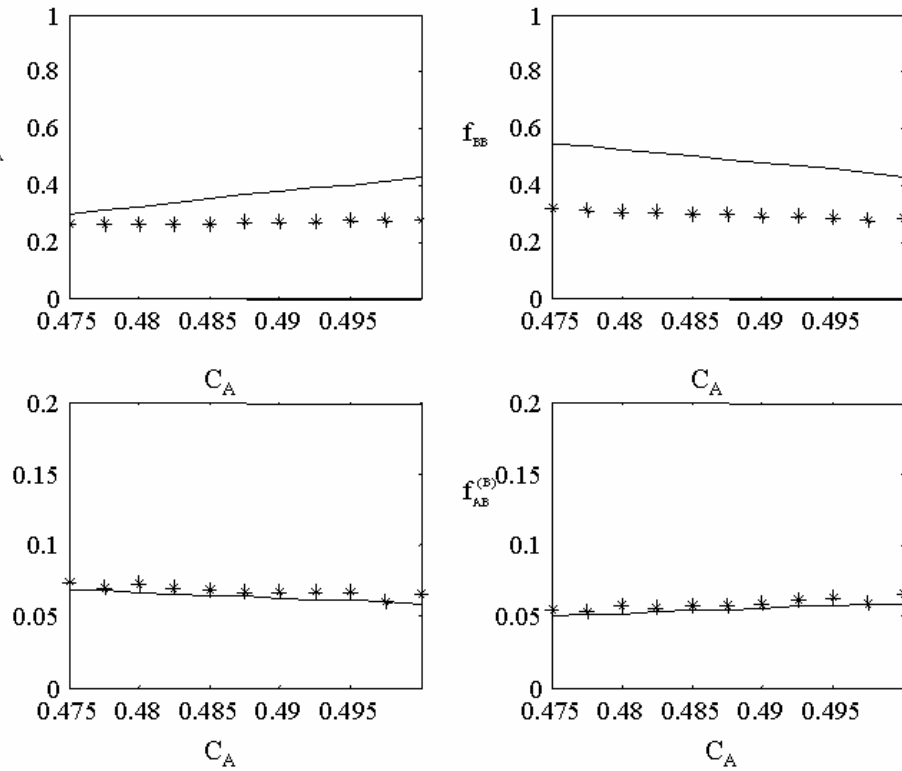
Figure 1. Collective correlation factors f_{AA}, f_{BB}, $f_{AB}^{(A)}$, $f_{AB}^{(B)}$ as functions of A-atom concentration C_A for $\alpha = 0.1$. Solid lines - calculated values, $*\,*\,*$ - simulation results.
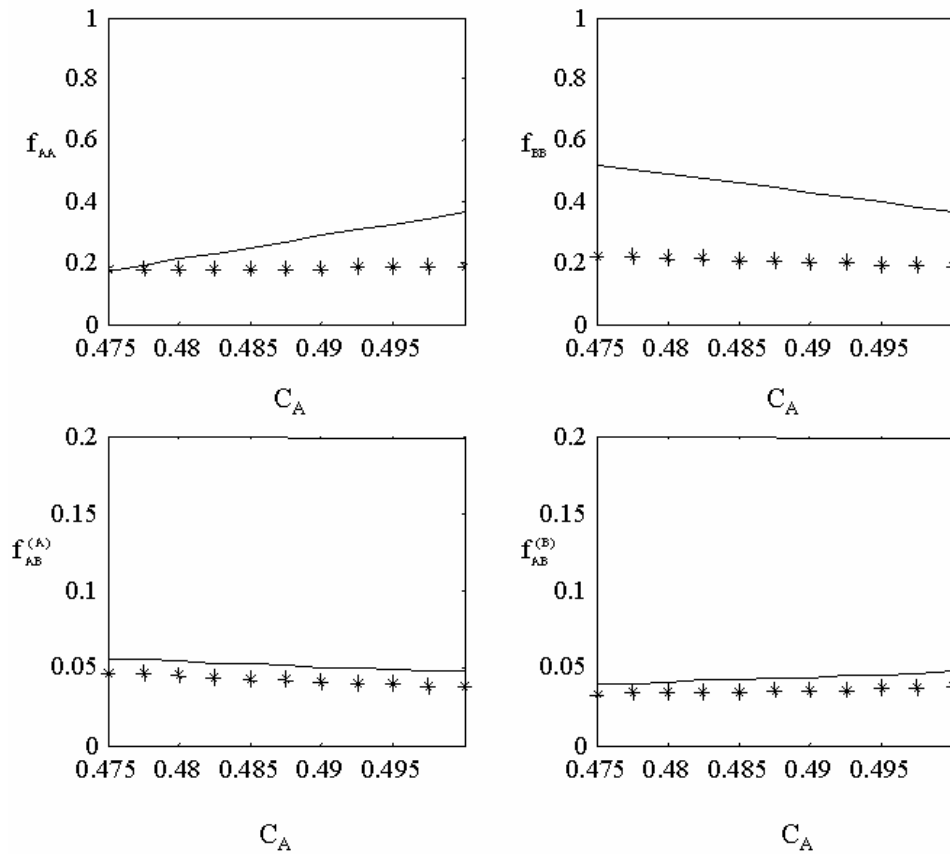

Figure 2. Collective correlation factors f_{AA}, f_{BB}, $f_{AB}^{(A)}$, $f_{AB}^{(B)}$ as a function of A-atom concentration C_A for $\alpha = 0.08$. Solid lines - calculated values, $*\,*\,*$ - simulation results.
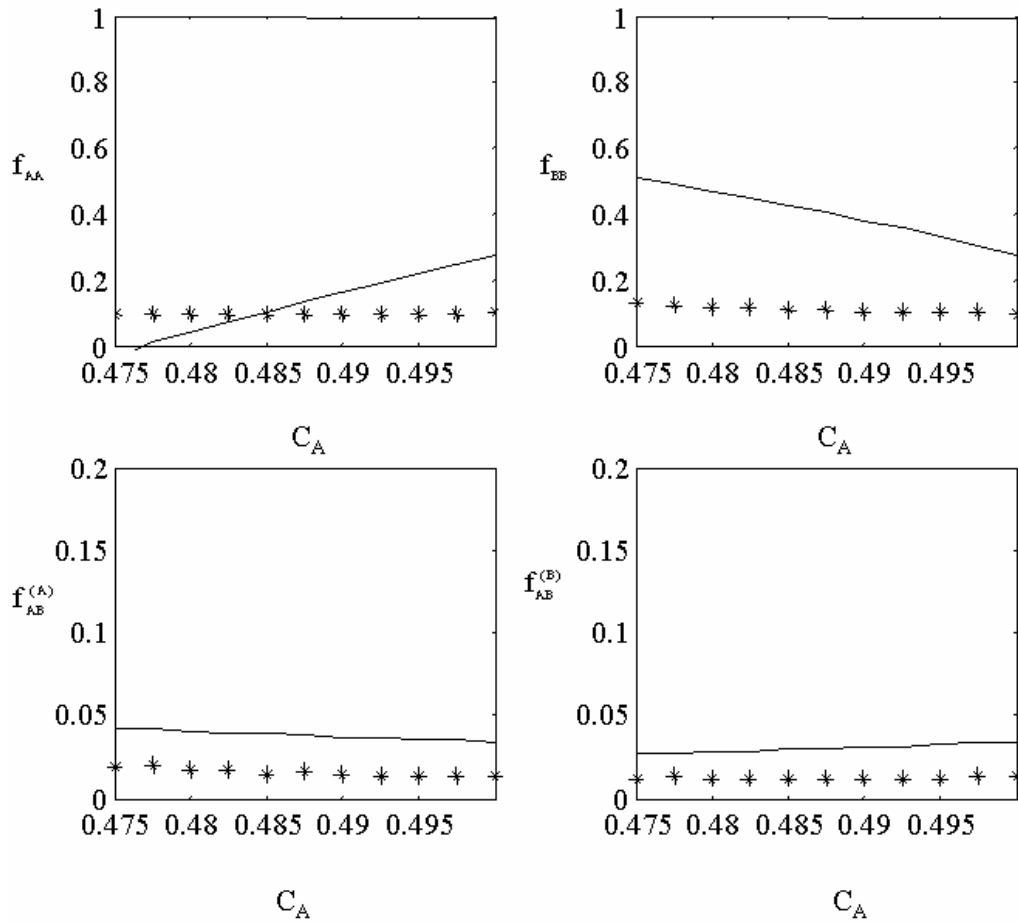
Figure 3. Collective correlation factors f_{AA}, f_{BB}, $f_{AB}^{(A)}$, $f_{AB}^{(B)}$ as functions of the A-atom concentration C_A for $\alpha = 0.06$. Solid lines - calculated values, * * * - simulation results.

that at the stoichiometric composition the results of f_{AA} and f_{BB} are equivalent. As C_A decreases the agreement of f_{AA} with the simulation results becomes better but this is not so for f_{BB}. This is due to the fact that as B atoms concentration increases, the vacancy can escape via a network of B atoms [8, 20]. The agreement of our results with computer simulation is much better for the cross correlation factors $f_{AB}^{(A)}$, $f_{AB}^{(B)}$ than for f_{AA}, f_{BB}. The results are in reasonably good agreement up to $\alpha = 0.08$.

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