Approximate expressions for the phenomenological coefficients of a binary alloy with short range order

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Abstract. Approximate expressions are derived for the phenomenological coefficients for vacancy-mechanism matter transport in a nearest-neighbour interaction lattice gas model of a concentrated binary alloy using the Kikuchi–Sato jump frequency model. These expressions are constructed from the leading coefficients (moments) in the Taylor series expansions in powers of time of the time correlation functions working within the Mori continued fraction representation. Numerical results are compared with earlier Monte Carlo simulations and with the predictions of the path probability method. Comparison with new Monte Carlo results shows that the approximate time correlation functions are good at short times but are too small at relatively long times.

1. Introduction

Within the framework of non-equilibrium thermodynamics the various matter transport properties of solids are all expressed in terms of the phenomenological coefficients, L_{ij}. Here, L_{ij} is the coefficient of proportionality between the flux of atom species i and the thermodynamic force on atom species j in the linear flux equations. Statistical mechanical theories are needed to obtain theoretical expressions for these L-coefficients for models whose parameters include both energies of interaction between atoms and between lattice defects and also jump frequencies of atomic jumps between sites in various local atom environments. Well established methods described by Allnatt and Lidiard (1993) are available for calculating the L-coefficients for simple models of dilute alloys with a variety of vacancy and interstitial defect transport mechanisms, but there is no comparable set of routine methods for models of concentrated alloys. There are, of course, useful approximate theories of the equilibrium properties of such alloys for the interacting lattice gas model with nearest-neighbour interactions between atoms. Kikuchi and Sato (1969, 1970, 1972) supplemented this equilibrium model with an *ansatz* for atom–vacancy exchange jump frequencies and calculated approximate expressions for the L-coefficients using the Kikuchi (1966) path probability method (PPM); a review of the later applications of this method has been given by Akbar (1992). A different approach has been the successful adaptation of ideas from the Manning (1968, 1971) theory of random alloys by Bakker (1976) and Stolwijk (1981) to calculations of the tracer diffusion coefficients of the Kikuchi–Sato model, but there appear to be no other kinetic theories of the non-tracer L-coefficients for this or any other parametrization of the jump frequencies. There are however Monte Carlo simulation results for the L-coefficients of the Kikuchi–Sato model for binary alloys with a very small vacancy content, mainly for the order–disorder case (Zhang *et al* 1989, Qin and Murch

1993) but also for the strictly regular solution case (Allnatt and Allnatt 1991). In this paper a new method is applied to the calculation of the L-coefficients of a concentrated alloy.

The route to be followed, which is suggested by extensive applications to transport in fluids (Boon and Yip 1980, Hansen and McDonald 1986, Heyes and Powles 1990, Tankeshwar and Pathak 1994), is the construction of the time correlation functions associated with the transport coefficients from their moments working within the framework of the Mori (1965) continued fraction formalism. Although we have been helped by our experience with applications of this method to the Manning random alloy model (Qin and Allnatt 1995) and to a two-sublattice generalization of that model (Qin *et al* 1997) we find the complexity of the interacting lattice gas model is much greater and a separate development is needed.

In section 2 we define the Kikuchi–Sato model of a concentrated alloy with vacancy transport and write the linear response formulae for the L-coefficients. In the next section we examine the coefficients (moments) of the Taylor series expansions in powers of time of the time correlation functions appearing in the L-coefficients. We introduce a superposition approximation for the equilibrium distribution functions appearing in the moments; it expresses them in terms of radial distribution functions. We also give approximate expressions for calculating the radial distribution functions. Expressions for the leading moments are found within these approximations assuming the absence of long range order. The construction of approximate expressions for the L-coefficients from the available moments within the Mori formalism is described in section 4. In the final section, 5, these results for the L-coefficients are compared with Monte Carlo simulation results and the PPM theory. Brief comments on further development of the method are also made.

2. Model and linear response formulae

We consider a cubic binary alloy with nearest-neighbour interaction energies E_{AA}, E_{BB} and E_{AB} between the atomic components A and B. There is a very small site fraction of vacancies. We adopt the Kikuchi–Sato approximation for the exchange frequency of an A atom with a vacant nearest-neighbour site when the lattice configuration preceding the jump is α:

$$w_\alpha^{(A)} = \nu_A \exp(-U_A^\dagger/kT) \exp\left(\sum_{j=A,B} z_\alpha^{(j)} E_{ij}/kT\right). \tag{1}$$

Here both ν_A, the frequency factor for A, and $U_A^\dagger$, the energy of the jumping atom in the saddle-point configuration, have been taken as independent of the initial and final configurations. The energy in the second exponential is that of the jumping atom at its site before the jump and $z_\alpha^{(j)}$ is the number of j atom nearest neighbours to the jumping atom before the jump. We can write the expression in the convenient form

$$w_\alpha^{(i)} = w_i^{(0)} \exp(-z_\alpha^{(\bar{i})} E_i/kT) \tag{2}$$

where $\bar{i} = A$ when $i = B$ and *vice versa*, and we define

$$E_i = E_{ii} - E_{i\bar{i}} \tag{3}$$

$$w_i^{(0)} = \nu_i \exp(-[U_i^\dagger - (z-1)E_{ii}]/kT) \tag{4}$$

where z is the coordination number of a site.

Our calculation starts from the general linear response formula (Allnatt and Lidiard 1993) for the phenomenological coefficient L_{ij} as the sum of two parts:

$$L_{ij} = L_{ij}^{(0)} + L_{ij}^{(1)}. \tag{5}$$

The uncorrelated part, $L_{ij}^{(0)}$, is defined by

$$L_{ij}^{(0)} = \frac{1}{6VkT} \sum_{\alpha,\beta} \boldsymbol{r}_{\beta\alpha}(i) \cdot \boldsymbol{r}_{\beta\alpha}(j) w_{\beta\alpha} p_\alpha \tag{6}$$

where p_α is the probability of finding the system in state (configuration) α at thermodynamic equilibrium, $w_{\beta\alpha}$ denotes the jump frequency for an atom jump that changes the state from α to β and $\boldsymbol{r}_{\beta\alpha}(j)$ is the sum of the vector displacements of all atoms of species j in this transition. The correlated part, $L_{ij}^{(1)}$, is defined by

$$L_{ij}^{(1)} = -\frac{1}{3VkT} \int_0^\infty \mathrm{d}t \, C_{ij}(t) \tag{7}$$

where

$$C_{ij}(t) = -\sum_{\alpha,\beta,\gamma,\delta} \boldsymbol{r}_{\delta\gamma}(i) \cdot w_{\delta\gamma} G_{\gamma\beta}(t) \boldsymbol{r}_{\beta\alpha}(j) w_{\beta\alpha} p_\alpha. \tag{8}$$

Here, $G_{\gamma\beta}(t)$ is the conditional probability that the system initially in state β will be in state γ after time t. The function $C_{ij}(t)$ can be written in the form of a time correlation function of stochastic velocities, see for example Qin *et al* (1995), but the form given here is more convenient for the present purposes.

3. Calculation of moments of the time correlation function

The Taylor expansion of the time correlation function about $t = 0$ will be written as

$$C_{ij}(t) = \sum_{n=0} \frac{t^n}{n!} C_{ij}^{(n)}. \tag{9}$$

As already described by Qin *et al* (1997), an expression for the nth moment, $C_{ij}^{(n)}$, can be found by substituting the formal power series expansion of the propagator $G_{\gamma\beta}(t)$ into (8); the result is

$$C_{ij}^{(n)} = -\sum_{\alpha,\beta,\gamma,\delta} \boldsymbol{r}_{\delta\gamma}(i) \cdot w_{\delta\gamma} |[\mathbf{W} - \mathbf{Y}]^n|_{\gamma\beta} \boldsymbol{r}_{\beta\alpha}(j) w_{\beta\alpha} p_\alpha \tag{10}$$

where $\mathbf{W}$ is a matrix with elements $W_{\gamma\beta} = w_{\gamma\beta}(1 - \delta_{\gamma,\beta})$, $\mathbf{Y}$ is a matrix with elements $Y_{\gamma\beta} = -\delta_{\gamma,\beta} w_{\gamma\gamma}$, $\delta_{\gamma,\beta}$ is a Kroenecker delta and

$$-w_{\gamma\gamma} = \sum_{\delta\neq\gamma} w_{\delta\gamma}. \tag{11}$$

Our approximation for the phenomenological coefficients in section 4 is based on a knowledge of the zeroth and first moments, plus the uncorrelated part $L_{ij}^{(0)}$. The calculation of these quantities will be illustrated for parts of the first moment.

3.1. Reduction of formal expressions

According to equation (10) the first moment can be written as a difference of contributions containing $W_{\gamma\beta}$ and $Y_{\gamma\beta}$ respectively:

$$C_{ij}^{(1)} = C_{ij}^{(1)}(\mathbf{W}) - C_{ij}^{(1)}(\mathbf{Y}). \tag{12}$$

In order to evaluate such expressions we introduce a notation for the positions of the particles in the different molecular states. The item particle is taken to include both atoms and vacancies. We define an occupancy variable $\rho_\beta^{(p)}(l)$ which is unity if there is a particle

of kind p at site l in state β and is zero otherwise. A typical jump frequency can then be written as

$$w_{\gamma\beta} = \sum_i \sum_{l,s} \rho_\gamma^{(v)}(l-s)\rho_\gamma^{(i)}(l)\rho_\beta^{(v)}(l)\rho_\beta^{(i)}(l-s)w_\beta^{(i)}(l-s) \tag{13}$$

where s denotes a nearest-neighbour vector. The first part of the first moment, defined through equations (10) and (12), can then be written as

$$-C_{ij}^{(1)}(\mathbf{W}) = \sum_{l,l_1,l_0} \sum_{s,s_1,s_0} \sum_k s \cdot (-s_0)\langle \rho^{(v)}(l-s)\rho^{(i)}(l)|\rho^{(v)}(l)\rho^{(i)}(l-s)w^{(i)}(l-s)$$
$$\times \rho^{(v)}(l_1-s_1)\rho^{(k)}(l_1)|\rho^{(v)}(l_1)\rho^{(k)}(l_1-s_1)w^{(k)}(l_1-s_1)\rho^{(v)}(l_0)$$
$$\times \rho^{(j)}(l_0-s_0)|\rho^{(v)}(l_0-s_0)\rho^{(j)}(l_0)w^{(j)}(l_0)\rangle. \tag{14}$$

The vertical lines separate different states and the angle brackets denotes an equilibrium average, for example

$$\langle D|C|B|A\rangle \equiv \sum_{\delta,\gamma,\beta,\alpha} D_\delta C_\gamma B_\beta A_\alpha p_\alpha \tag{15}$$

where we shall call $\alpha, \beta, \ldots$ the first, second, $\ldots$ states respectively. In (14) there are restrictions to be added to the various summations as well as some simplifications, as follows.

For a crystal of N sites with z nearest neighbours per site there are Nz possible choices of the sites l_0 and $l_0 - s_0$ of the j atom and its adjacent vacancy in the initial state; each of these contributes equally to the result. Since we consider only the limit of very dilute vacancies, it will be the same vacancy in all the jumps in (14) and inspection of the second state therefore shows that $l_1 = l_0$, and for the third state shows that $l = l_1 - s_1$. These considerations allow (14) to be written as

$$-C_{ij}^{(1)}(\mathbf{W}) = Nz \sum_{s,s_1} \sum_k s \cdot (-s_0)\langle \rho^{(v)}(l_0-s_1-s)$$
$$\times \rho^{(i)}(l_0-s_1)|\rho^{(i)}(l_0-s_1-s)w^{(i)}(l_0-s_1-s)\rho^{(v)}(l_0-s_1)$$
$$\times \rho^{(k)}(l_0)|\rho^{(k)}(l_0-s_1)w^{(k)}(l_0-s_1)\rho^{(v)}(l_0)$$
$$\times \rho^{(j)}(l_0-s_0)|\rho^{(v)}(l_0-s_0)\rho^{(j)}(l_0)w^{(j)}(l_0)\rangle. \tag{16}$$

The fact that the particles of different species must occupy different sites places limitations on the nearest-neighbour vectors in this equation. In the second state $s_1 = s_0$ contributes only if $k = j$. Furthermore, when $s_1 \neq s_0$ then $s = -s_1$ contributes only if $k = i$, and when $s_1 = s_0$ then $s = -s_0$ contributes only if $i = j$. The expression is therefore evaluated by splitting the summations into four parts:

$$\sum_k \sum_s \sum_{s_1} \rightarrow \sum_k \left\{ \sum_{s\neq -s_1} \sum_{s_1 \neq s_0} + \delta_{k,i} \sum_{s_1 \neq s_0} \delta_{s,-s_1} \right.$$
$$\left. + \delta_{k,j} \sum_{s\neq -s_0} \delta_{s_1,s_0} + \delta_{k,j}\delta_{i,j}\delta_{s_1,s_0}\delta_{s,-s_0} \right\}. \tag{17}$$

We take as an example the evaluation of the contribution to (16) of the second set of summations in (17):

$$Nz \sum_{s_1 \neq s_0} (-s_1) \cdot (-s_0)\langle \rho^{(i)}(l_0-s_1)\rho^{(v)}(l_0)|\rho^{(i)}(l_0)w^{(i)}(l_0)\rho^{(v)}(l_0-s_1)|\rho^{(i)}(l_0-s_1)$$
$$\times w^{(i)}(l_0-s_1)\rho^{(v)}(l_0)\rho^{(j)}(l_0-s_0)|\rho^{(v)}(l_0-s_0)\rho^{(j)}(l_0)w^{(j)}(l_0)\rangle. \tag{18}$$

It is clear that the occupancy variables of the three particles for the initial state in this contribution must be $\rho^{(i)}(l_0 - s_1)\rho^{(v)}(l_0 - s_0)\rho^{(j)}(l_0)$ and that the ensemble average in this expression can be conveniently written as a product of two averages:

$$\langle w^{(i)}(l_0)w^{(i)}(l_0 - s_1)w^{(j)}(l_0)/\rho^{(i)}(l_0 - s_1)\rho^{(v)}(l_0 - s_0)\rho^{(j)}(l_0)\rangle$$
$$\times \langle \rho^{(i)}(l_0 - s_1)\rho^{(v)}(l_0 - s_0)\rho^{(j)}(l_0)\rangle. \tag{19}$$

The second of these averages is the probability of finding a j atom, a vacancy and an i atom at the specified lattice sites. The first average is the mean value of the product of the jump frequencies for three successive atom exchanges with the vacancy (the first by the j atom from site l_0, the second of the i atom from site $l_0 - s_0$, the third of the i atom from site $l_0 - s_1$), conditional on the configuration before the first jump being that specified by the occupation variables after the slash.

A similar reduction can be made for all the contributions to $C_{ij}^{(1)}(\mathbf{W})$, (16), arising from the use of (17), as well as to the remaining part of the first moment, $C_{ij}^{(1)}(\mathbf{Y})$. In using the formal expression for the latter,

$$C_{ij}^{(1)}(\mathbf{Y}) = \sum_{\alpha,\beta,\gamma,\delta} r_{\gamma\beta}(i) \cdot w_{\gamma\beta} \left(\sum_{\delta \neq \beta} w_{\delta\beta} \right) r_{\beta\alpha}(j) w_{\beta\alpha} p_\alpha \tag{20}$$

it is important to remember that the result of a transition $\beta \to \delta$ in no way restricts the possible choices of the transitions $\beta \to \gamma$ out of state β.

3.2. Use of Kirkwood superposition approximation

Evaluation of the averages in such expressions requires a knowledge of distribution functions for the probabilities of finding groups of three or more particles in specified relative positions. In practice only expressions for the pair distribution functions at nearest-neighbour separations are readily available. We shall therefore use the Kirkwood superposition approximation to express each n-particle distribution function as a product of n site fractions (one for each particle) multiplied by a product of $n(n-1)/2$ pair correlation functions (one for each of the possible pairs from n particles). We also assume that the pair correlation functions differ from unity only at nearest-neighbour separations. For example, with these approximations the distribution function in equation (19) becomes

$$\langle \rho^{(i)}(l_0 - s_1)\rho^{(v)}(l_0 - s_0)\rho^{(j)}(l_0)\rangle = c_i c_v c_j g_{jv} g_{ji} \tag{21}$$

where g_{ji} is the pair correlation function for a j and an i atom at the nearest-neighbour separation and c_i and c_v are the site fractions of i atoms and vacancies, respectively.

Some care is needed in evaluating the average jump frequencies with the same approximation. We shall again use the contribution to $-C_{ij}^{(1)}(\mathbf{W})$ written in (18) as an example. For a simple cubic lattice inspection shows that only $s_1 = -s_0$ contributes to the sum and the contribution is therefore

$$-Nzs^2 c_i c_v c_j g_{jv} g_{ji} \langle w_{iij} \rangle \tag{22}$$

where

$$\langle w_{iij} \rangle \equiv \langle w^{(i)}(l_0)w^{(i)}(l_0 + s_0)w^{(j)}(l_0)/\rho^{(i)}(l_0 + s_0)\rho^{(v)}(l_0 - s_0)\rho^{(j)}(l_0)\rangle. \tag{23}$$

As shown in figure 1(a), it is convenient to draw a diagram of the lattice showing the sites occupied by the vacancy and jumping atoms in the initial configuration, i.e. before any jumps have occurred, marked by an open square and by open circles, respectively, and with the sites which are nearest neighbours to sites from which atoms make jumps marked

by filled circles; all other sites are indicated by small open circles and are referred to as unmarked sites. We recall that in the Kikuchi–Sato model a jump frequency depends on the energy of interaction of the jumping atom with its nearest neighbours, i.e. with atoms at black circle sites. The usual procedure at this point would be to imagine that we have first averaged over the occupancies of all unmarked sites leaving an expression for $\langle w_{iij} \rangle$ which is a sum over all possible occupancies of the black circle sites. The summand is a product of the jump frequencies and of the probability of finding a particular occupancy of black circle sites conditional on the presence of the jumping atoms and the vacancy at their sites in the initial configuration. However, if we calculated the corresponding contribution in $C_{ji}^{(1)}$ we would have an identical expression, except that there the initial configuration encountered would be the final configuration in $C_{ij}^{(1)}$ and the jumps would take place in the reverse order. Because of the principle of detailed balance ($w_{\alpha\beta} p_\beta = w_{\beta\alpha} p_\alpha$) the results would be identical if exact probabilities were available and, by doing this for all contributions, we would find $C_{ij}^{(1)} = C_{ji}^{(1)}$. Furthermore, application of detailed balance to the complete expression for L_{ij} shows that the Onsager reciprocal relation $L_{ij} = L_{ji}$ is valid. On the other hand, if we use approximate probabilities then these symmetries no longer necessarily hold, as can be verified by examples using the approximations proposed above. This difficulty can be avoided as follows. We first modify the diagram in $C_{ij}^{(1)}$ to include any additional black circles which would be appropriate if the jumps were carried out in reverse order, i.e. the order occurring in $C_{ji}^{(1)}$. In our example this gives figure 1(b). We again imagine
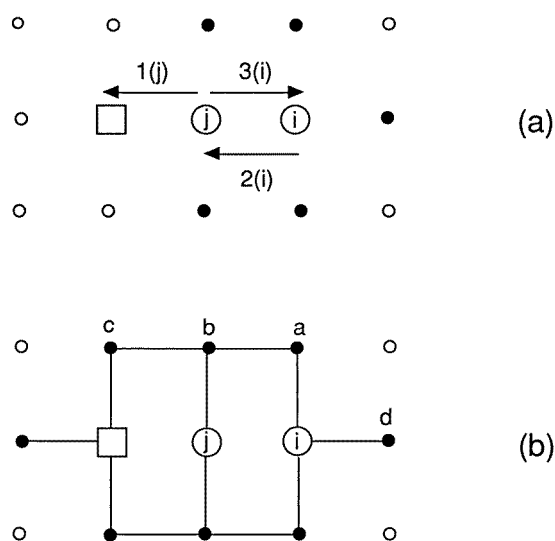
Figure 1. Schematic representations of $\langle w_{iij} \rangle$, (23). (a) A crystal plane containing the initial sites of atoms i and j (large open circles) and the vacancy (square). Lines indicate subsequent atom–vacancy exchanges; for example, the label 2(i) indicates that in the second jump atom i moves between the two sites connected by the line in the direction of the arrow. Atoms at sites which are black circles are nearest neighbours to the initial site of a jumping atom in one or more jumps; other sites are small open circles. A three dimensional diagram would show four more black circles (two nearest neighbours to the initial site of i and two nearest neighbours to the initial site of j) in a plane perpendicular to the present figure. (b) The same jump sequence as in (a) but with the additional black circles which are appropriate when the jumps are made in the reverse order. A line between two sites now signifies that a pair correlation function will appear in the expression for $\langle w_{iij} \rangle$. The letters a, b, c, d correspond to the usage in (24).

that we have averaged over unmarked sites and write the appropriate expression containing summations over the occupancies of black sites using the approximations for probability functions defined at the start of this subsection. This is facilitated by reference to the diagram where we have added lines for each pair correlation function, as in figure 1(b). The result is

$$\langle w_{iij} \rangle = (w_i^{(0)})^2 w_j^{(0)} \left(\frac{K_{ji} K_{ij}}{K_{jj} K_{ii}} \right) \left(\sum_{a,b,c} c_a c_b c_c g_{ia} g_{ab} g_{jb} g_{bc} g_{cv} \frac{K_{jb} K_{ia} K_{ib}}{K_{jj} K_{ii}^2} \right)^4$$

$$\times \left(\sum_d c_d g_{id} K_{id} / K_{ii} \right) \tag{24}$$

where

$$K_{ij} = \exp(E_{ij}/kT). \tag{25}$$

The diagram notation of figure 1 is also very convenient for the other terms.

3.3. Final expressions for the moments and for the uncorrelated part

The application of the methods of sections 3.1 and 3.2 is straightforward but lengthy and we therefore pass immediately to the final results. For the zeroth and first moments we find

$$C_{ij}^{(0)}/(Nzs^2 c_v c_j g_{jv}) = -c_i g_{ij} \langle w_{ij} \rangle_1 + \delta_{i,j} \langle w_{ii} \rangle_2 \tag{26}$$

$$C_{ij}^{(1)}/(Nzs^2 c_v c_j g_{jv}) = -c_i \sum_k c_k g_{ik} g_{jk} [\langle w_{ijk} \rangle_1 + 4(\langle w_{ijk} \rangle_2 - g_{iv} \langle w_{ijk} \rangle_3)]$$

$$+ c_i g_{ij} \left(\langle w_{iij} \rangle_4 + \langle w_{iij} \rangle_8 + \langle w_{ijj} \rangle_{11} + 4 \sum_k c_k g_{jk} \langle w_{ikj} \rangle_7 \right) + c_i g_{iv} \langle w_{ijj} \rangle_5$$

$$- \delta_{i,j} \left[\langle w_{iii} \rangle_6 + \langle w_{iii} \rangle_{12} + \sum_k c_k g_{jk} (4 \langle w_{kjj} \rangle_9 + \langle w_{kjj} \rangle_{10}) \right]. \tag{27}$$

The expression for the uncorrelated part of the phenomenological coefficient, evaluated by the same methods, is

$$L_{ij}^{(0)} = \delta_{i,j} Nzs^2 c_v c_j g_{jv} \langle w_j \rangle / (6VkT). \tag{28}$$

Expressions for the averages of products of jump frequencies in these equations are given in the appendix. Formulae in the appendix for the radial distribution functions in these expressions were derived in a manner consistent with that used in evaluating the moments, i.e. detailed balance and the extended Kirkwood superposition approximation were applied to atom–vacancy exchanges. The radial distribution function formulae turn out to be the same as those obtained by Kikuchi and Sato (1970) using the cluster variation method.

4. An approximation for the phenomenological coefficients

We shall use an adaptation of the Mori (1965) formalism to construct an approximation to the correlated parts of the *L*-coefficients. In the standard formulation Mori's method employs normalized time correlation functions $Y_{ij}(t)$ defined by the matrix equation

$$\mathbf{Y}(t) = \mathbf{C}(t) \mathbf{C}(0)^{-1} \tag{29}$$

where, for example, the matrix $\mathbf{C}(t)$ is, for a two component system,

$$\mathbf{C}(t) = \begin{bmatrix} C_{AA}(t) & C_{AB}(t) \\ C_{BA}(t) & C_{BB}(t) \end{bmatrix}. \tag{30}$$

A set of matrices $\mathbf{M}^{(n)}(t)$ where $n = 0, 1, 2, \ldots$ is introduced where $\mathbf{M}^{(0)}(t) = \mathbf{Y}(t)$ and the functions for $n > 0$ are called memory functions. The matrices satisfy a coupled set of equations of the form

$$\frac{\mathrm{d}\mathbf{M}^{(n)}(t)}{\mathrm{d}t} = -\mathbf{\Omega}^{(n)}\mathbf{M}^{(n)}(t) + \int_0^t \mathbf{M}^{(n+1)}(t - \tau)\mathbf{\Delta}^{2(n+1)}\mathbf{M}^{(n)}(\tau)\,\mathrm{d}\tau. \tag{31}$$

The functions $M_{ij}^{(n)}$, $\Omega_{ij}^{(n)}$ and $\Delta_{ij}^{2(n+1)}$ in the matrices can all be expressed as inner products of certain 'random force' functions as described by Qin and Allnatt (in preparation). Their derivation elaborates the differences between the Mori-type results referred to here, which are based on the discrete master equation, and those for Hamiltonian systems first described by Mori (1965). (One such difference is the necessary difference in sign preceding the integral in (31).) From the Laplace transform of (31) with $n = 0, 1, 2, \ldots$ successively one can construct a continued fraction expression

$$\begin{aligned}
\bar{\mathbf{Y}}(p) &= [p\mathbf{I} + \mathbf{\Omega}^{(0)} - \bar{\mathbf{M}}^{(1)}(p)\mathbf{\Delta}^{2(1)}]^{-1} \\
&= [p\mathbf{I} + \mathbf{\Omega}^{(0)} - \{p\mathbf{I} + \mathbf{\Omega}^{(1)} - \bar{\mathbf{M}}^{(2)}(p)\mathbf{\Delta}^{2(2)}\}^{-1}\mathbf{\Delta}^{2(1)}]^{-1} = \cdots .
\end{aligned} \tag{32}$$

Here $\mathbf{I}$ denotes the unit matrix and $\bar{F}(p)$ is the Laplace transform with respect to t of a function $F(t)$. We shall use the first approximation obtained by approximating $\bar{\mathbf{M}}^{(1)}(p)$ by zero in the first line of (32). From (31) $-\mathbf{\Omega}^{(0)}$ is equal to the first moment, $\mathbf{Y}^{(1)}$ of $\mathbf{Y}(t)$ and our approximation is therefore

$$\bar{\mathbf{Y}}(p) = [p\mathbf{I} - \mathbf{Y}^{(1)}]^{-1}. \tag{33}$$

Results for the correlated parts of the L-coefficients are usually reported in terms of dimensionless correlation functions defined as $f_{AA} = L_{AA}/L_{AA}^{(0)}$ and $f_{AB} = L_{AB}/L_{AA}^{(0)}$ plus similar relations with A and B interchanged. (The less convenient notation $f_{AB}^{(A)}$ is often used in the literature for our f_{AB}.) By use of (5), (7), (29) and (33) one obtains

$$\mathbf{f} = \mathbf{I} + \frac{1}{3VkT}(\mathbf{Y}^{(1)})^{-1}\mathbf{C}^{(0)}(\mathbf{L}^{(0)})^{-1}. \tag{34}$$

The elements of $\mathbf{Y}^{(1)} = \mathbf{C}^{(1)}(\mathbf{C}^{(0)})^{-1}$ and of $\mathbf{C}^{(0)}$ are readily found from (26) and (27), and the elements of $\mathbf{L}^{(0)}$ from (28). The resultant expressions for the elements of $\mathbf{f}$ are rather lengthy and will not be written out here.

The corresponding approximation for the time correlation functions is also of interest. For comparison with Monte Carlo data the functions normalized to unity at $t = 0$ are convenient:

$$N_{ij}(t) = C_{ij}(t)/C_{ij}(0) \qquad (i, j = A, B). \tag{35}$$

The normalized matrix $\mathbf{N}(t)$ is symmetric, unlike $\mathbf{Y}(t)$. One finds from (33) the result

$$N_{ij}(t) = (a_1 - a_2)^{-1}\{[a_1 + N_{ij}^{(1)} - \mathrm{Tr}(\mathbf{Y}^{(1)})]\,\mathrm{e}^{a_1 t} - [a_2 + N_{ij}^{(1)} - \mathrm{Tr}(\mathbf{Y}^{(1)})]\,\mathrm{e}^{a_2 t}\} \tag{36}$$

where $N_{ij}^{(1)}$ is the first moment of $N_{ij}(t)$, a_1 and a_2 are the roots of

$$a^2 + \mathrm{Tr}(\mathbf{Y}^{(1)})a + |\mathbf{Y}^{(1)}| = 0 \tag{37}$$

and $|\mathbf{Y}^{(1)}|$ denotes the determinant of $\mathbf{Y}^{(1)}$.

5. Comparison with simulation results

The correlation functions f_{ij} are determined by E/kT, where $E = E_{AA} + E_{BB} - 2E_{AB}$, and a further quantity which reflects the difference in strength of AA and BB interactions; the latter is usually taken as U defined by

$$U = \frac{E_{AA} - E_{BB}}{E}. \tag{38}$$

Our calculations assume the absence of long-range order and are therefore limited to temperatures above the order–disorder temperature which is at $E/kT_c = 0.887$ for the

(a)

(b)
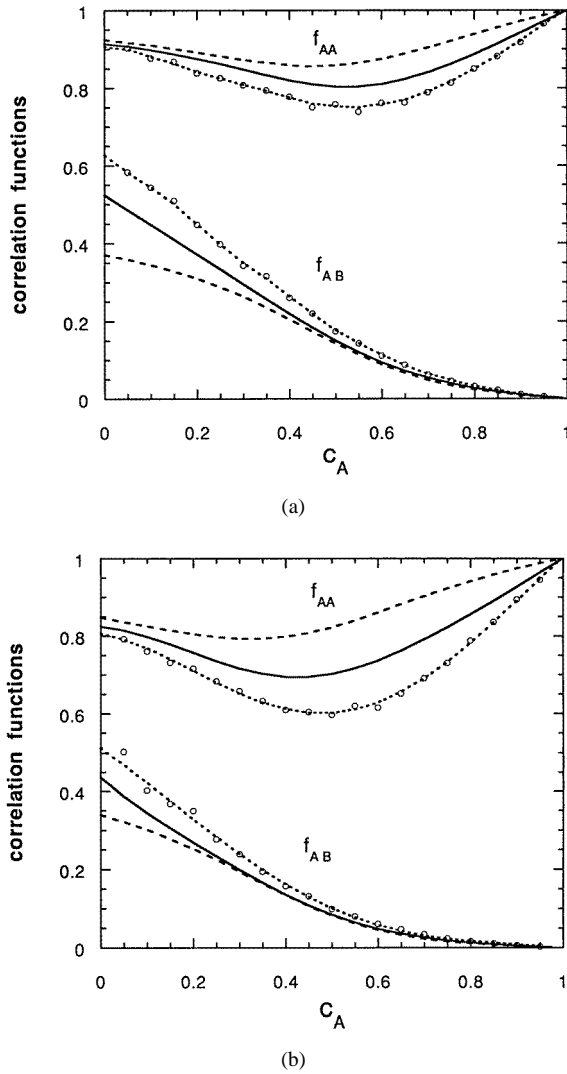
Figure 2. The correlation functions f_{ij} as functions of c_A, the site fraction of A, for $E/kT = 0.63$: —— the present approximation; - - - - the path probability theory, Wang and Akbar (1995); - - ○ - - simulation results, Zhang *et al* (1989), Qin and Murch (1993). (a) $U = 0$; (b) and (c) $U = 0.5$.

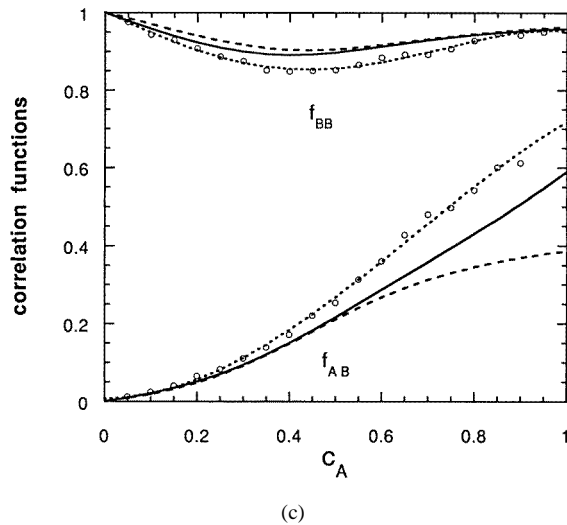(c)

Figure 2. (Continued)

simple cubic lattice. Monte Carlo simulations for the correlation functions as functions of composition at $E/kT = 0.63$ have been made for $U = 0$ by Zhang *et al* (1989) and for $U = 0.5$ by Qin and Murch (1993) with the simplifying model assumption that $v_i \exp(-U_i^{\dagger}/kT) = 1$ for $i = $ A, B in the expression for the jump frequency, (1). Our predictions are compared in figure 2 both with these Monte Carlo results and with the predictions of the pair approximation of the path probability method (PPM) given by Wang and Akbar (1995). For $U = 0$, figure 2(a), interchange of A and B labels gives results for the two other correlation functions. Our results for the diagonal correlation functions are superior to the PPM results in the middle of the concentration range where correlation effects (measured by the deviation of f_{ii} from unity) are largest; for the off-diagonal correlation functions (where correlation effects are to be measured by the deviation of f_{ij} from zero) they are again superior, particularly in the concentration ranges where the correlation functions are largest.

Qin *et al* (1995) have shown that for a binary random alloy the three normalized time correlation functions, $N_{ij}(t)$, must be exactly equal and that the approximation used here $(\bar{\mathbf{M}}^{(1)}(p) = 0)$ then expresses the single time correlation function as a single exponential decay in time. Comparison with Monte Carlo simulations showed that for the random alloy this approximation is good at small times but underestimates the time correlation function at long times. We have made a limited check on whether the same qualitative relationship between time dependence of the theoretical and simulated time correlation functions holds here. Monte Carlo simulations were made on a $20 \times 20 \times 20$ simple cubic lattice. An equilibrium system was first created by a grand canonical ensemble simulation as described by Murch (1982) starting from a random distribution of equal numbers of A and B atoms. The time correlation functions were then simulated by the method described by Qin *et al* (1995) for the random alloy; the only significant difference from the scheme they describe is that in each configuration the jump frequencies have to be calculated from the species of the neighbours of atoms adjacent to the jumping atom. The results in figure 3 for the equiatomic composition at the same temperature $E/kT = 0.63$ with $U = 0$ show that, once again, there is good agreement at small times but the theoretical values of the normalized
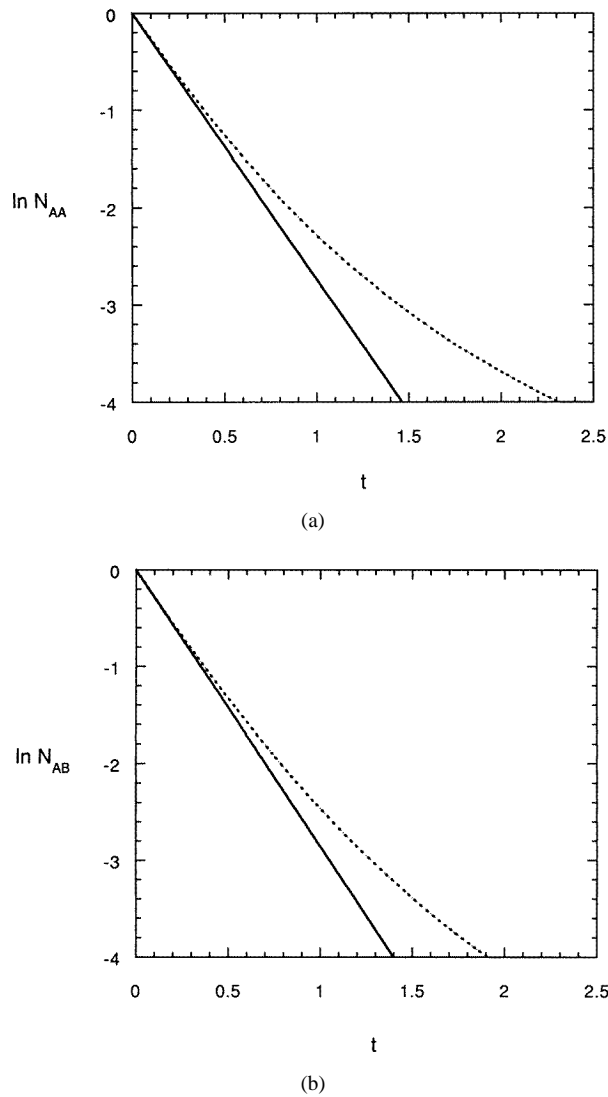
Figure 3. The logarithm of normalized time correlation functions $N_{ij}(t)$ as functions of time t for $c_A = 0.5$, $E/kT = 0.63$, $U = 0$: $\cdots\cdots$ Monte Carlo simulation; ——— present theory. (a) $N_{AA}(t)$, (b) $N_{AB}(t)$.

time correlation functions are too small in magnitude at long times. Results for $U = 0.5$ are very similar for all three correlation functions.

6. Concluding remarks

In this paper we have obtained approximate expressions for the time-dependent correlation contributions to the L-coefficients of a model of a binary alloy with short range order and the vacancy transport mechanism. These results were based on calculations of the zeroth and first moments of the time correlation functions and an approximation to the Mori continued

fraction. However, the method introduced for systematic enumeration of the contributions to the moments applies equally to higher moments and avoids the likelihood of omitting terms that accompanies other routes we have tried. An important feature of the method is that the Onsager reciprocal relations remain valid despite the use of the Kirkwood superposition approximation for equilibrium correlation functions.

Comparison with simulation results showed that our expressions for the L-coefficients are appreciably more accurate than the only other available expressions, which derive from the path probability formalism. The expressions are rather lengthy but we have not so far found convincing simplifying approximations. Because the moments are calculated exactly (within the Kirkwood superposition approximation) they can be used to check future approximate kinetic equation methods of evaluating the time correlation functions where physical approximations are more naturally introduced. Such theories will, in effect, make approximations to the moments we have calculated as well as making approximations to the higher moments not calculated here.

The results seem encouraging and we should comment briefly on the approximations made and their possible improvement. The least significant approximation is probably the use of the Kikuchi–Sato expressions for the nearest-neighbour radial distribution functions. Checks by Monte Carlo simulation indicate inaccuracies of up to 1–2% near the equiatomic composition which are not significant for present purposes. On the other hand estimates of the effect of using the Kirkwood superposition approximation for higher order distribution functions and the nearest-neighbour approximation are not easily made and would imply a substantial amount of simulation; at present any theory is likely to be forced to make this approximation in order to obtain useable results. The truncation approximation used in the Mori scheme is expected to be much more significant and two points arise in this context. In the first place further simulation data on the time correlation functions are needed to establish whether long time tails will be significant in modelling the time correlation functions over a wide range of conditions; such features are familiar for fluids, see for example Hansen and McDonald (1986). The Mori framework used here and the results for low order moments we have derived remain useful in such circumstances but would have to be supplemented by mode coupling ideas. The second question is whether higher moments of the time correlation functions are likely to become available. In additional work we have found that several hundred terms contribute to the second and third moments. This suggests that computer assisted symbolic calculation would be an essential feature if higher moments are to be incorporated, even if they are based on the Kirkwood superposition approximation.

Acknowledgment

Appendix

The averages of products of jump frequencies appearing in (26)–(28) can be written in terms of the following functions. The functions $F_p(n_p)$, $F_{pq}(n_p, n_q)$, $F_{pqr}(n_p, n_q, n_r)$, ..., where p, q, r, ... denote particle species, are defined with the aid of figure A1. We translate the diagram into a product containing (i) a factor g_{ab} for a full line between black circles labelled a and b, (ii) a factor $g_{pa} (K_{pa}/K_{pp})^{n_p}$ for a broken line between a white circle labelled p and a black circle labelled a (with the definition $K_{va} = 1$) and (iii) a factor of

$$F_p(n_p) \qquad F_{pq}(n_p,n_q) \qquad F_{pqr}(n_p,n_q,n_r)$$
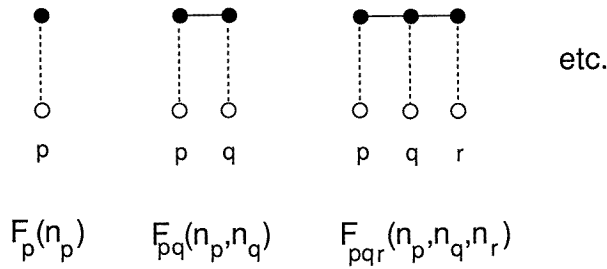
Figure A1. The graphical definition of the functions $F_p(n_p)$, $F_{pq}(n_p, n_q)$, $F_{pqr}(n_p, n_q, n)r)$, ... with the conventions introduced in the appendix.

c_a for a black circle labelled a. We sum the product over the atom species of each black circle, e.g. if there is a black circle labelled a we sum over $a =$ A, B. For example, we have

$$F_{pq}(n_p, n_q) = \sum_a \sum_b c_a c_b g_{ab} g_{pa} \left(\frac{K_{pa}}{K_{pp}}\right)^{n_p} g_{qb} \left(\frac{K_{qb}}{K_{qq}}\right)^{n_q}. \tag{A1}$$

We also define modified F-functions, such as $F_{pq[r]}(n_p, n_q, [n_r, m_r])$, in which one of the particles in the subscript is in square brackets and the corresponding symbol in the argument is replaced by a pair of labels in square brackets. In such a case we write the formula for the corresponding unmodified function (the n_r in square brackets here plays the role of n_r for the unmodified function) and then multiply the summand by an additional factor $(K_{ra'}/K_{rr})^{m_r}$, where a' is the species of the black circle which is connected by a broken line to the white circle of the particle immediately to the left of q in the subscript of F, e.g.

$$F_{pq[r]}(n_p, n_q, [n_r, m_r]) = \sum_{a,b,c} c_a c_b c_c g_{ab} g_{bc} g_{pa}$$
$$\times \left(\frac{K_{pa}}{K_{pp}}\right)^{n_p} g_{qb} \left(\frac{K_{qb}}{K_{qq}}\right)^{n_q} g_{rc} \left(\frac{K_{rc}}{K_{rr}}\right)^{n_r} \left(\frac{K_{rb}}{K_{rr}}\right)^{m_r}. \tag{A2}$$

We also define four additional functions by the equations

$$G_{pq} = \sum_a c_a g_{pa} K_{qa}/K_{qq}$$

$$G_{pq}(n_p, n_q) = \sum_a c_a g_{pa} g_{qa} \left(\frac{K_{pa}}{K_{pp}}\right)^{n_p} \left(\frac{K_{qa}}{K_{qq}}\right)^{n_q}$$

$$G_{pqr} = \sum_a c_a g_{pa} K_{pa} g_{qa} K_{ra}$$

$$G_{pqrs}(n_p, n_q, n_r, n_s) = \sum_{a,b,c,d} c_a c_b c_c c_d g_{ab} g_{bc} g_{cd} g_{ad} g_{pa}$$
$$\times \left(\frac{K_{pa}}{K_{pp}}\right)^{n_p} g_{qb} \left(\frac{K_{qb}}{K_{qq}}\right)^{n_q} g_{rc} \left(\frac{K_{rc}}{K_{rr}}\right)^{n_r} g_{sd} \left(\frac{K_{sd}}{K_{ss}}\right)^{n_s}. \tag{A3}$$

The expressions for the averages of products of jump frequencies in (26) and (27) are then

$$\langle w_{ij}\rangle_1 = w_i^{(0)} w_j^{(0)} F_i(1)[F_{vji}(0, 1, 1)]^4 K_{ji}/K_{jj}$$

$$\langle w_{ii}\rangle_2 = (w_i^{(0)})^2 F_i(1) G_{vi}[F_{v[i]}(0, [1, 1])]^4$$

$$\langle w_{ijk}\rangle_1 = w_i^{(0)} w_j^{(0)} w_k^{(0)} F_i(1)[F_{vjki}(0, 1, 1, 1)]^4 K_{jk} K_{ki}/(K_{jj} K_{kk})$$

$$\langle w_{ijk}\rangle_2 = w_i^{(0)} w_j^{(0)} w_k^{(0)} F_i(1)[F_{ki}(1, 1) F_{vj}(0, 1)]^3 G_{vk}(0, 1) G_{ji}(1, 1) K_{jk} K_{ki}/(K_{jj} K_{kk})$$

$$\langle w_{ijk} \rangle_3 = w_i^{(0)} w_j^{(0)} w_k^{(0)} F_{ik}(1,1) F_{jk}(1,1) F_{jv}(1,0) F_{iv}(1,0) [G_{ijkv}(1,1,1,0)]^2$$
$$\times K_{ij} K_{jk} K_{ki} / (K_{ii} K_{jj} K_{kk})$$

$$\langle w_{iij} \rangle_4 = (w_i^{(0)})^2 w_j^{(0)} F_i(1) [F_{vj[i]}(0,1,[1,1])]^4 K_{ji} K_{ij} / (K_{jj} K_{ii})$$

$$\langle w_{ijj} \rangle_5 = w_i^{(0)} (w_j^{(0)})^2 F_i(1) F_j(1) [F_{iv[j]}(1,0,[1,1])]^4 K_{ji} / K_{jj}$$

$$\langle w_{iii} \rangle_6 = (w_i^{(0)})^3 F_i(2) G_{vi} [F_{v[i]}(0,[2,1])]^4$$

$$\langle w_{ikj} \rangle_7 = w_i^{(0)} w_k^{(0)} w_j^{(0)} F_i(1) [F_k(1) F_{vji}(0,1,1)]^3 G_{ik}(1,1) G_{kv}(1,0) K_{jk} K_{ji} / K_{jj}^2$$

$$\langle w_{iij} \rangle_8 = (w_i^{(0)})^2 w_j^{(0)} F_i(2) [F_{vji}(0,1,2)]^4 K_{ji} / K_{jj}$$

$$\langle w_{kjj} \rangle_9 = w_k^{(0)} (w_j^{(0)})^2 F_k(1) G_{vj} F_{kj}(1,1) F_{v[j]}(0,[1,1]) [F_{v[j]k}(0,[1,1],1)]^2 G_{kvj} K_{jk} / K_{jj}$$

$$\langle w_{kjj} \rangle_{10} = w_k^{(0)} (w_j^{(0)})^2 F_k(1) G_{vj} [F_{v[j]k}(0,[1,1],1)]^4 K_{jk} / K_{jj}$$

$$\langle w_{ijj} \rangle_{11} = w_i^{(0)} (w_j^{(0)})^2 F_i(1) G_{vj} [F_{v[j]i}(0,[1,1],1)]^4 K_{ji} / K_{jj}$$

$$\langle w_{iii} \rangle_{12} = (w_i^{(0)})^3 F_i(1) F_i(2) [F_{v[j]}(0,[1,2])]^4. \tag{A4}$$

For (28) we also need

$$\langle w_j \rangle = w_j^{(0)} F_j(1) F_{vj}(0,1). \tag{A5}$$

Only three of the radial distribution functions needed in (A4) and (A5) are independent. Expressions for these are

$$g_{jj} = (c_j - c_{\bar{j}} + R) / [c_j (1+R)] \tag{A6}$$

$$g_{j\bar{j}} = 2/(1+R) \tag{A7}$$

$$g_{jv} = K_{jj}(c_j - c_{\bar{j}} + R) / \{c_j [K_{jj}(c_j - c_{\bar{j}} + R) + 2c_{\bar{j}} K_{j\bar{j}}]\} \tag{A8}$$

where

$$R^2 = (c_j - c_{\bar{j}})^2 + (4c_j c_{\bar{j}} K_{j\bar{j}}^2) / (K_{jj} K_{\overline{jj}}). \tag{A9}$$

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