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Collective and tracer diffusion kinetics in the ternary random alloy

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Abstract

In this study, collective and tracer diffusion kinetics is addressed for the ternary random alloy. A formal solution from the self-consistent theory of Moleko *et al* (Moleko L K, Allnatt A R and Allnatt E L 1989 *Phil. Mag. A* **59** 141) is derived for collective diffusion and compared with the corresponding solution for the binary random alloy. Tracer diffusion in the ternary alloy is treated from the perspective of a special case of the quaternary random alloy. Results from Monte Carlo calculations for tracer and collective correlation factors (for the bcc ternary random alloy) are found to be in excellent agreement with this self-consistent theory but in only semi-quantitative agreement with the earlier theory of Manning (Manning J R 1971 *Phys. Rev. B* **4** 1111).

1. Introduction

The random alloy model has long been useful for describing diffusion kinetics in concentrated disordered alloys. Introduced first by Manning (1968, 1971), the random alloy model requires that both the atomic components and the defect responsible for diffusion are randomly mixed. Taking diffusion of vacancies in the ternary random alloy as a specific example, the randomly mixed atomic components X_1 , X_2 , X_3 exchange with the vacancies at frequencies w_1 , w_2 and w_3 respectively and the vacancies are present in a vanishingly small concentration. Manning (1968, 1971) derived simple expressions for the tracer correlation factors in terms of the exchange frequencies. Related expressions were also developed for the tracer correlation factors in terms of the tracer diffusivities themselves. These latter expressions are a valuable alternative to obtaining the tracer correlation factors via analysis of the isotope effect.

Early Monte Carlo calculations for the binary random alloy implied that the Manning formalism for describing the tracer correlation factors was remarkably accurate over a wide range of exchange frequency ratios. But recent high-precision Monte Carlo work (Belova and Murch 2000a) has made it clear that much of this success was in fact illusory, coming as a result of specifying vacancy jump sequences that were much too short. There was in fact much

better agreement with the results of the formalism of Holdsworth and Elliott (1986) (hereon abbreviated to HE). That formalism used a method of decoupling a hierarchy of equations of motion. However, almost exact agreement over a very wide range of the ratios of exchange frequencies was obtained with the results from a self-consistent theory of Moleko *et al* (1989) (hereon abbreviated to MAA). This theory makes use of a hierarchy of kinetic equations for the time-dependent correlation functions from linear response theory. The decoupling approximation used by MAA is similar in spirit to that used by HE but is adapted to the different hierarchy of equations in the MAA theory.

The correlated parts of the Onsager phenomenological coefficients associated with atom components present in more than tracer amounts are often called collective correlation factors. Manning (1968, 1971) derived expressions for the collective correlation factors of a random alloy with an arbitrary number of atom components, but HE did not extend their formalism to address this problem. Equations determining the collective correlation factors for a random alloy with an arbitrary number of components were obtained with the MAA self-consistent theory but an explicit solution was given only for a binary alloy. The latter turned out to be equivalent to that obtained by Manning for this system (Belova and Murch 2000b). Recent results from high-precision Monte Carlo calculations for the binary random alloy are in excellent agreement with these expressions over a very wide range of the ratios of the exchange frequencies (Belova and Murch 2000b).

As a result of the findings summarized above and related ones addressing the vacancy wind effect (Belova and Murch 2001) and the isotope effect (Belova and Murch 2000c), it can be safely said that diffusion kinetics in the binary random alloy is very accurately described by MAA. This is no guarantee of course that similar success of this theory can be expected for alloys of more than two atomic components. In the present paper we address the collective and tracer correlation factors for the ternary random alloy. In section 2 we derive specific expressions for the ternary collective and tracer correlation factors based on the general equation (48) presented in MAA. In section 3 we describe high-precision Monte Carlo calculations of the collective and tracer correlation factors. This is followed in section 4 by a presentation and comparison of the results.

2. Theory

2.1. Collective correlation factors

First we consider the ternary system: (X_1, X_2, X_3) with atom–vacancy exchange frequencies w_1, w_2 and w_3 , atomic compositions c_1, c_2, c_3 and a vacancy site fraction c_v which is vanishingly small.

We follow the same notation as introduced in MAA, where the collective correlation factors $f_{ij}^{(j)}$ are expressed as

$$f_{ij}^{(j)} = \delta_{ij} - 2w_i U(VX_i : VX_j)(c_v c_j)^{-1} \quad (1)$$

where δ_{ij} is the Krönecker delta. The U -functions obey relations which ensure that the correlation functions are consistent with the Onsager reciprocal relations and with the sum rule for the random alloy (Moleko and Allnatt 1988). These relations are $U(VX_i : VX_j) = U(VX_j : VX_i)$ and

$$U(VX_1 : VX_j) + U(VX_2 : VX_j) + U(VX_3 : VX_j) = 0. \quad (2)$$

It follows that there are only three independent functions. We therefore introduce

$$\begin{aligned} g_1 &= U(VX_1 : VX_2) (=U(VX_2 : VX_1)), & g_2 &= U(VX_1 : VX_3) (=U(VX_3 : VX_1)), \\ g_3 &= U(VX_2 : VX_3) (=U(VX_3 : VX_2)). \end{aligned} \quad (3)$$

For the ternary random alloy, equation (1) will then take the forms

$$\begin{aligned} f_{11} &= 1 + 2w_1(g_1 + g_2)(c_v c_1)^{-1}; & f_{22} &= 1 + 2w_2(g_1 + g_3)(c_v c_2)^{-1}; \\ f_{33} &= 1 + 2w_3(g_2 + g_3)(c_v c_3)^{-1}; & f_{12}^{(1)} &= -2w_2 g_1 (c_v c_1)^{-1}; \\ f_{13}^{(1)} &= -2w_3 g_2 (c_v c_1)^{-1}; & f_{23}^{(2)} &= -2w_3 g_3 (c_v c_2)^{-1}; \\ f_{12}^{(2)} &= c_1 w_1 f_{12}^{(1)} (c_2 w_2)^{-1}; & f_{13}^{(3)} &= c_1 w_1 f_{13}^{(1)} (c_3 w_3)^{-1}; \\ f_{23}^{(3)} &= c_2 w_2 f_{23}^{(2)} (c_3 w_3)^{-1}. \end{aligned} \quad (4)$$

We assume that, in accord with all previous calculations for simple vacancy transport models, the phenomenological coefficients L_{ij} are all $O(c_v)$; we then find that all

$$(g_1, g_2, g_3) = O(c_v). \quad (5)$$

The general equation in MAA contains additional functions which have a skew symmetry property, $U(X_i X_j : V X_k) = -U(X_j X_i : V X_k)$, and are related to the earlier functions by

$$U(V X_i : V X_j) = -U(X_1 X_i : V X_j) - U(X_2 X_i : V X_j) - U(X_3 X_i : V X_j). \quad (6)$$

We introduce

$$y_1 = U(X_1 X_2 : V X_1), \quad y_2 = U(X_1 X_2 : V X_2), \quad y_3 = U(X_1 X_2 : V X_3). \quad (7)$$

It follows from equations (5) and (6) that

$$U(V X_1 : V X_1) = y_1 - U(X_3 X_1 : V X_1) = O(c_v). \quad (8)$$

Consistent with this result, we accept the approximation $U(X_3 X_1 : V X_1) \approx y_1$, with both functions independent of c_v . By means of analogous approximations for other functions of this type, we find

$$y_k = U(X_1 X_2 : V X_k) \approx U(X_2 X_3 : V X_k) \approx U(X_3 X_1 : V X_k) \quad \text{for } k = 1, 2, 3. \quad (9)$$

With these approximations and definitions in hand, we can write down a set of five equations for five unknown variables which can be chosen from the six $(g_1, g_2, g_3; y_1, y_2, y_3)$ in three ways with respect to the choice of the first jump. (For $U(V X_i : V X_k)$ and $U(X_i X_j : V X_k)$ the first jump is $V X_k$. Note also that in each MAA equation all the functions have the same first jump.) We can have $(g_1, g_2, g_3; y_1, y_2)$ as unknown variables (three equations for the first jump $V X_1$ and two equations for the first jump $V X_2$):

$$M_0 c_v y_1 (g - w_3 F_3) = c_1 c_2 c_v + c_2 (g_1 + g_2) (2w_1 + M_0 w_2 F_2) + c_1 g_1 (2w_2 + M_0 w_1 F_1); \quad (10)$$

$$M_0 c_v y_1 (g - w_1 F_1) = -c_3 g_1 (2w_2 + M_0 w_3 F_3) + c_2 g_2 (2w_3 + M_0 w_2 F_2); \quad (11)$$

$$M_0 c_v y_1 (-g + w_2 F_2) = c_1 c_3 c_v + c_3 (g_1 + g_2) (2w_1 + M_0 w_3 F_3) + c_1 g_2 (2w_3 + M_0 w_1 F_1); \quad (12)$$

$$M_0 c_v y_2 (-g + w_3 F_3) = c_1 c_2 c_v + c_2 g_1 (2w_1 + M_0 w_2 F_2) + c_1 (g_1 + g_3) (2w_2 + M_0 w_1 F_1); \quad (13)$$

$$M_0 c_v y_2 (-g + w_2 F_2) = -c_3 g_1 (2w_1 + M_0 w_3 F_3) + c_1 g_3 (2w_3 + M_0 w_1 F_1). \quad (14)$$

In the above equations we have used the following notation:

$$\begin{aligned} M_0 &= 2f_0(1 - f_0)^{-1}; & g &= w_1 f_{11} + w_2 f_{22} + w_3 f_{33}; \\ F_1 &= f_{11} + f_{12}^{(1)} + f_{13}^{(1)}; & F_2 &= f_{22} + f_{12}^{(2)} + f_{23}^{(2)}; & F_3 &= f_{33} + f_{13}^{(3)} + f_{23}^{(3)}, \end{aligned}$$

where f_0 is the geometric tracer correlation factor, which takes different values for different crystal structures (and mechanisms); see, for example, the classic review by Le Claire (1970). This system of equations (10)–(14) is a restatement for the ternary random alloy of the general equation (48) in MAA.

The functions g , F_1 , F_2 , F_3 can all be expressed in terms of g_1 , g_2 and g_3 as follows:

$$g = w_1 + w_2 + w_3 + 2(w_1^2(g_1 + g_2)(c_v c_1)^{-1} + w_2^2(g_1 + g_3)(c_v c_3)^{-1} + w_3^2(g_2 + g_3)(c_v c_3)^{-1}); \quad (15)$$

$$F_1 = 1 + 2(g_1(w_1 - w_2) + g_2(w_1 - w_3))(c_v c_1)^{-1}; \quad (16)$$

$$F_2 = 1 + 2(g_1(w_2 - w_1) + g_3(w_2 - w_3))(c_v c_2)^{-1}; \quad (17)$$

$$F_3 = 1 + 2(g_2(w_3 - w_1) + g_3(w_3 - w_2))(c_v c_3)^{-1}. \quad (18)$$

It was shown in Murch and Qin (1994) that F_1 has the meaning of the partial vacancy correlation factor f_v^1 (Manning 1968); similarly F_2 and F_3 correspond to f_v^2 and f_v^3 respectively.

We can see that in general the system of equations (10)–(14) is essentially nonlinear. We can treat the system as a linear one with the coefficients playing the role of parameters. Then we can derive the following very formal solution:

$$g_1 = -c_1 c_2 c_3 c_v (g - G) A (AB + AC + BC)^{-1}; \quad (19)$$

$$g_2 = -c_1 c_2 c_3 c_v (g - G) B (AB + AC + BC)^{-1}; \quad (20)$$

$$g_3 = -c_1 c_2 c_3 c_v (g - G) C (AB + AC + BC)^{-1}, \quad (21)$$

where

$$G = c_1 w_1 F_1 + c_2 w_2 F_2 + c_3 w_3 F_3; \quad (22)$$

$$A = M_0 (c_1 G - c_1 w_1 F_1) (c_2 G - c_2 w_2 F_2) + c_1 c_2 (g - G) (M_0 G + 2w_3); \quad (23)$$

$$B = M_0 (c_1 G - c_1 w_1 F_1) (c_3 G - c_3 w_3 F_3) + c_1 c_3 (g - G) (M_0 G + 2w_2); \quad (24)$$

$$C = M_0 (c_2 G - c_2 w_2 F_2) (c_3 G - c_3 w_3 F_3) + c_2 c_3 (g - G) (M_0 G + 2w_1). \quad (25)$$

These relations (equations (19)–(21)) should be compared with the corresponding solution in the case of the binary random alloy:

$$g_1 = -c_1 c_2 c_v (M_0 G + 2(w_1 c_2 + w_2 c_1))^{-1}, \quad (26)$$

which can be derived as a limit of the first relation (equation (19)) when $c_3 \rightarrow 0$. In this limit, $A = O(c_v)$, $B = O(c_3 c_v)$, $C = O(c_3 c_v)$. Then we have for g_1

$$g_1 = \lim_{c_3 \rightarrow 0} -c_1 c_2 c_v c_3 (g - G) (B + C)^{-1}, \quad (27)$$

from equations (24), (25) we have that

$$\begin{aligned} \lim_{c_3 \rightarrow 0} (B + C) c_3^{-1} &= \lim_{c_3 \rightarrow 0} ((c_1 + c_2) G - c_1 w_1 F_1 - c_2 w_2 F_2) (G - w_3 F_3) \\ &\quad + (g - G) (M_0 G + 2(w_1 c_2 + w_2 c_1)) \\ &= 0 + (g - G) (M_0 G + 2(w_1 c_2 + w_2 c_1)) \end{aligned} \quad (28)$$

which together with equation (27) gives the final expression (26).

In the case of the binary random alloy it was possible to use this solution directly for numerical calculations (Belova and Murch 2000b). Unfortunately, for the ternary random alloy, in general, the amount of calculation required by making use of the formal solution (equations (19)–(21)) is approximately equal to that required by making use of the original system of equations (10)–(14). This is because despite the clear structure of the solution equations (19)–(21), it still involves five unknown functions: A , B , C , g and G .

Manning's (1971) solution for the collective correlation factors for the ternary random alloy is as follows:

$$g_1^M = -c_v c_1 c_2 (H + 2w_3) (c_1 (H + 2w_2) (H + 2w_3) + c_2 (H + 2w_1) (H + 2w_3) + c_3 (H + 2w_1) (H + 2w_2))^{-1} \quad (29)$$

$$g_2^M = -c_v c_1 c_3 (H + 2w_2)(c_1(H + 2w_2)(H + 2w_3) + c_2(H + 2w_1)(H + 2w_3) + c_3(H + 2w_1)(H + 2w_2))^{-1} \quad (30)$$

$$g_3^M = -c_v c_2 c_3 (H + 2w_1)(c_1(H + 2w_2)(H + 2w_3) + c_2(H + 2w_1)(H + 2w_3) + c_3(H + 2w_1)(H + 2w_2))^{-1} \quad (31)$$

where H is a positive real solution to the equation

$$(M_0 + 2)(c_1 w_1 (H + 2w_2)(H + 2w_3) + c_2 w_2 (H + 2w_1)(H + 2w_3) + c_3 w_3 (H + 2w_1)(H + 2w_2)) = (H + 2w_1)(H + 2w_2)(H + 2w_3). \quad (32)$$

As a point of interest, if we neglect the first terms of the functions A , B and C (equations (23)–(25)) and use the relation $H = M_0 G$, then it is possible to show that the MAA equations (19)–(21) reduce to Manning's solution equations (29)–(32).

2.2. Tracer correlation factors

In order to address the tracer correlation factors for the ternary random alloy in the MAA formalism, we need to consider the quaternary random alloy system (X_1, X_2, X_3, X_4) with atom–vacancy exchange frequencies w_1, w_2, w_3 and w_4 and atomic compositions c_1, c_2, c_3 and c_4 and vanishingly small c_v . Then we can use the following expression for the tracer correlation factor f_i (and a similar method can be used in order to find f_2 and f_3):

$$f_i = \lim_{c_4 \rightarrow 0} f_{44}, \quad (33)$$

where the subscript i denotes the type of tracer atom (X_1, X_2 or X_3). We consider only the situation after the first jump $v - X_4$. Let us introduce functions h_1, h_2, h_3 similarly to the functions g_1, g_2 and g_3 (equation (3)):

$$h_1 = U(VX_1 : VX_4), \quad h_2 = U(VX_2 : VX_4), \quad h_3 = U(VX_3 : VX_4). \quad (34)$$

Now, we have that

$$h = U(VX_4 : VX_4) = -h_1 - h_2 - h_3, \quad (35)$$

together with

$$f_{44} = 1 - 2w_4 h (c_v c_4)^{-1}. \quad (36)$$

We will need additional functions of the type y_i (of equation (7) type):

$$y_4 = U(X_2 X_1 : VX_4), \quad y_5 = U(X_3 X_1 : VX_4), \quad y_6 = U(X_3 X_2 : VX_4). \quad (37)$$

Then, after making use of an asymptotical consideration with respect to the small quantity c_v (similar to that for the ternary random alloy case), we have that

$$\begin{aligned} U(X_1 X_4 : VX_4) &\approx y_4 + y_5; & U(X_2 X_4 : VX_4) &\approx -y_4 + y_6; \\ U(X_3 X_4 : VX_4) &\approx -y_5 - y_6. \end{aligned} \quad (38)$$

Now we are in a position to analyse the system of equations (48) in MAA. Together with the notation introduced above, we note that functions h_1, h_2 and h_3 are $O(c_v c_4)$. Then for the limit $c_4 \rightarrow 0$ we will have only three essential equations for the three unknowns $h, z_1 = y_4 + y_5$ and $z_2 = y_4 - y_6$:

$$\begin{aligned} M_0 c_v [z_1 (w_1 f_{11} + w_4 f_{44} - w_3 f_{13}^{(3)}) + z_2 (w_3 f_{13}^{(3)} - w_2 f_{12}^{(2)})] \\ + c_1 h (2w_4 + M_0 w_1 F_1) = c_1 c_4 c_v, \end{aligned} \quad (39)$$

$$\begin{aligned} M_0 c_v [z_1 (-w_3 f_{33} - w_4 f_{44} + w_1 f_{13}^{(1)}) + z_2 (w_3 f_{33} + w_4 f_{44} - w_2 f_{23}^{(2)})] \\ + c_3 h (2w_4 + M_0 w_3 F_3) = c_3 c_4 c_v, \end{aligned} \quad (40)$$

$$\begin{aligned} M_0 c_v [z_1 (w_1 f_{12}^{(1)} - w_3 f_{23}^{(3)}) + z_2 (-w_2 f_{22} - w_4 f_{44} + w_3 f_{23}^{(3)})] \\ + c_2 h (2w_4 + M_0 w_2 F_2) = c_2 c_4 c_v, \end{aligned} \quad (41)$$

where f_{44} is given by equation (32) and all the $f_{ij}^{(j)}$ and F_i are given by relations equations (4), (16)–(18). Therefore, the system of equations (10)–(14) (for the collective correlation quantities) needs to be solved first before one can solve the system of equations for the tracer correlation quantities.

It is clear that equations (39)–(41) can be used for all three tracer diffusion coefficients (separately): if $w_4 = w_1$, then the solution to the system gives the tracer correlation factor f_1 for the X_1 -tracers; if $w_4 = w_2$, then we obtain the tracer correlation factor f_2 for the X_2 -tracers; and if $w_4 = w_3$, then we obtain the tracer correlation factor f_3 for the X_3 -tracers.

Manning's (1971) solution for the tracer correlation effect for the ternary random alloy can be given as follows:

$$h^M = c_v c_4 (H + 2w_4)^{-1}, \quad (42)$$

where the H -function is a real positive solution to equation (31).

The systems of equations (10)–(14) and equations (39)–(41) for the case when $w_1 = w_2 = w_3 = w_4 = 1$ have the following trivial solutions:

$$\begin{aligned} g_1^0 &= -0.5c_v c_1 c_2 (1 - f_0); & g_2^0 &= -0.5c_v c_1 c_3 (1 - f_0); \\ g_3^0 &= -0.5c_v c_2 c_3 (1 - f_0); & h^0 &= 0.5c_v c_4 (1 - f_0); \\ y_i^0 &= 0, & & \text{for } i = 1, \dots, 6. \end{aligned} \quad (43)$$

It is suggested that these solutions are always used as a starting point in the usual procedure for the solving a system of nonlinear equations.

3. Monte Carlo simulation

In our Monte Carlo computer simulations we made direct use of the following equations for the collective correlation factors: (Allnatt 1982, Allnatt and Allnatt 1984):

$$f_{ii} = \langle \Delta \mathbf{R}_i^2 \rangle (\langle N_i \rangle a^2)^{-1}, \quad f_{ij}^{(i)} = \langle \Delta \mathbf{R}_i \Delta \mathbf{R}_j \rangle (\langle N_i \rangle a^2)^{-1}, \quad (44)$$

where $\Delta \mathbf{R}_i$ is the displacement of all atoms of species i in the system in time t , N_i is the total number of jumps of atoms of type i in time t and a is the jump distance. Details of this type of calculation can be found in Allnatt and Allnatt (1984) and Belova and Murch (2000b). General details of Monte Carlo simulations of diffusion kinetics can be found in the review by Murch (1984). The number of observations used in the present calculations was at least 20 000. Determining the number of jumps in each observation turned out not to be without difficulties. In the case of tracer diffusion in the binary random alloy it was found that at least 100 jumps per atom (of the slower species) were required for convergence (Belova and Murch 2000a). Failure to meet this requirement in early published Monte Carlo work resulted in the Manning formalism appearing to be (falsely) superior to the HE and MAA approaches, as mentioned in section 1. On the other hand, for collective diffusion in the binary alloy it was found that only several hundred atom jumps *in toto* per observation were required for convergence (Belova and Murch 2000b). In the ternary random alloy, we found that simply using several hundred jumps in each observation, as used for the binary random alloy, does *not* give converged results, though they do happen to agree quite closely with the Manning formalism. In order to get convergence one needs about 100 jumps *per atom* in each observation. The collected evidence therefore is that the Manning formalism is generally equivalent to short times in a simulation. In the binary random alloy case short times suffice because the Manning, HE and MAA approaches all give the same (very accurate) expressions for the collective correlation factors and convergence is obtained very quickly. This is not the case for the ternary random alloy. As a result, far more computational time is required for the ternary system compared with the binary.

To obtain the tracer correlation factors we made use of the well known equation

$$f_i = \langle \Delta r_i^2 \rangle (\langle n_i \rangle a^2)^{-1}, \quad (45)$$

where $\langle n_i \rangle$ is the average number of jumps of the atoms of type i and $\langle r_i^2 \rangle$ is the mean squared displacement of all the atoms of type i . For further details see Belova and Murch (2000a). We averaged over the equivalent of at least 20 000 atoms. As was found for tracer diffusion in the binary system, some 100 jumps for the slowest diffuser were required to obtain convergence of the tracer correlation factors.

4. Simulation results

For the ternary alloy we present a cross-section of results for the collective correlation factors. In figures 1, 2 we show as data points our Monte Carlo results for the collective correlation factors as functions of c_1 with $c_3 = 0.1, 0.3$ and 0.6 for the exchange frequency ratios $w_1/w_2 = 10.0$ and $w_1/w_3 = 0.1$. Corresponding results from Manning (1971) are shown as broken curves and from MAA (as described in this study) as solid curves. It is immediately clear that MAA results are consistently in excellent agreement with the Monte Carlo results whereas, in general, the results from Manning's formalism are only in semi-quantitative agreement. The off-diagonal collective correlation factors especially are seen often to be in poor agreement with Manning's theory. Further extensive Monte Carlo data at other compositions, not shown here for brevity, are in similar agreement with the self-consistent theory.

In figure 3 we show as data points corresponding Monte Carlo results for the tracer correlation factors as functions of c_1 with $c_3 = 0.1, 0.3$ and 0.6 for exchange frequency ratios $w_1/w_2 = 10.0$ and $w_1/w_3 = 0.1$. Results from Manning (1971) are shown as broken curves and those from MAA (as described in this study) as solid curves. Similar to the case for the collective correlation factors presented above, it is immediately clear that MAA results are in excellent agreement with the Monte Carlo results whereas the results from Manning's formalism remain only in semi-quantitative agreement. Again, further extensive Monte Carlo data, not shown here for brevity, are in similar agreement with MAA data.

Accordingly, it is quite clear that for the ternary random alloy the MAA formalism shows a similar level of agreement with Monte Carlo data as seen earlier for the binary random alloy and that the MAA one is definitely the formalism of choice for describing diffusion kinetics in those disordered binary and ternary alloy systems that can be reasonably described by the random alloy model.

5. Conclusions

In this study, collective and tracer diffusion kinetics has been addressed for the ternary random alloy. A formal solution from the MAA self-consistent theory has been derived for collective diffusion and compared with the corresponding solution for the binary random alloy. It was shown that the Manning (1971) result can be found from the MAA theory by neglecting certain terms in the expressions. Tracer diffusion in the ternary alloy was treated from the perspective of a special case of the MAA description of the quaternary random alloy. Results from Monte Carlo calculations for tracer and collective correlation factors (for the bcc ternary random alloy) were found to be in excellent agreement with the MAA theory but in only semi-quantitative agreement with the Manning (1971) theory.

Use of the MAA formalism to analyse experimental interdiffusion data is considerably more complicated than use of the Manning (1971) formalism. Use of both of these formalisms

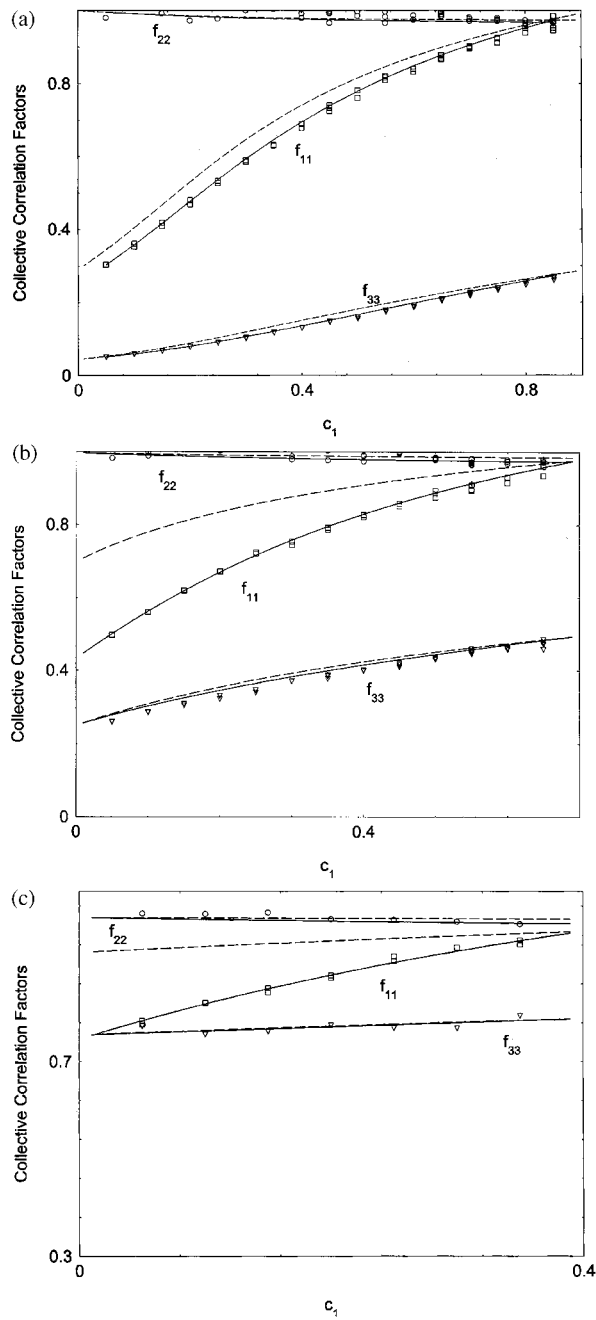


Figure 1. The diagonal collective correlation factors f_{11} , f_{22} and f_{33} as functions of c_1 at $w_1/w_2 = 10.0$ and $w_1/w_3 = 0.1$. (a) $c_3 = 0.1$; (b) $c_3 = 0.3$; and (c) $c_3 = 0.6$. Data points: Monte Carlo results; solid curves: MAA theory, equations (18)–(20); dashed curves: Manning (1971) theory, equations (28)–(30).

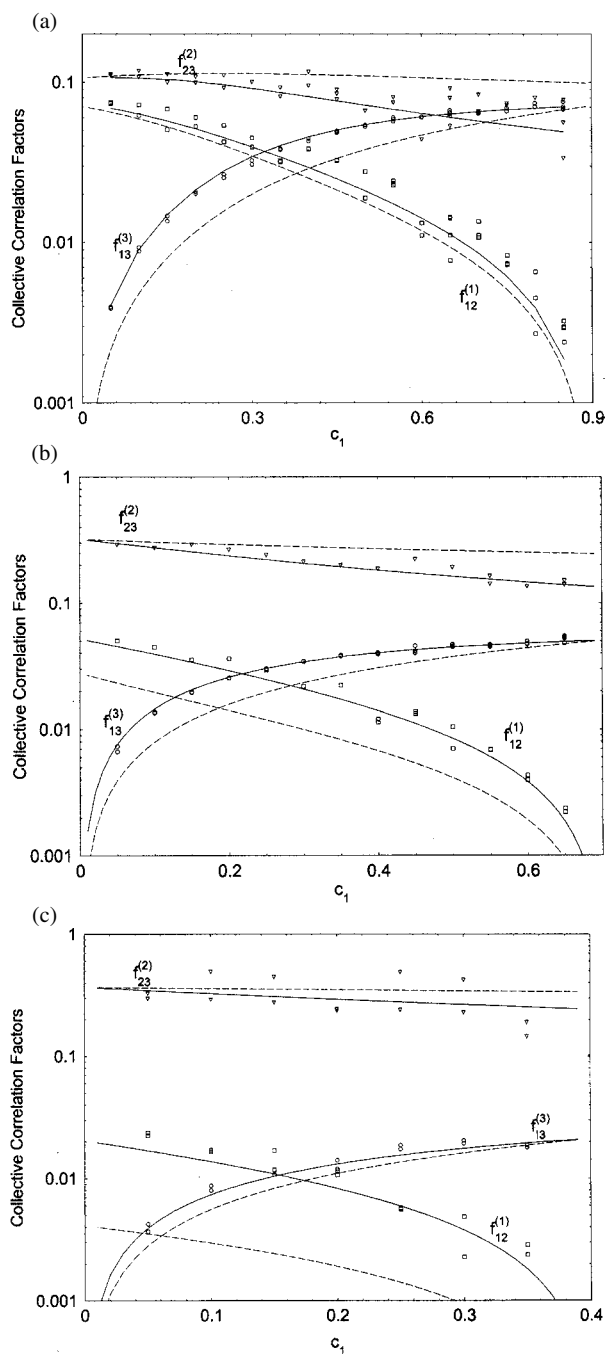


Figure 2. The off-diagonal collective correlation factors $f_{12}^{(1)}$, $f_{13}^{(3)}$ and $f_{23}^{(2)}$ as functions of c_1 at $w_1/w_2 = 10.0$ and $w_1/w_3 = 0.1$. (a) $c_3 = 0.1$; (b) $c_3 = 0.3$; and (c) $c_3 = 0.6$. Data points: Monte Carlo results; solid curves: MAA theory, equations (18)–(20); dashed curves: Manning (1971) theory, equations (28)–(30).

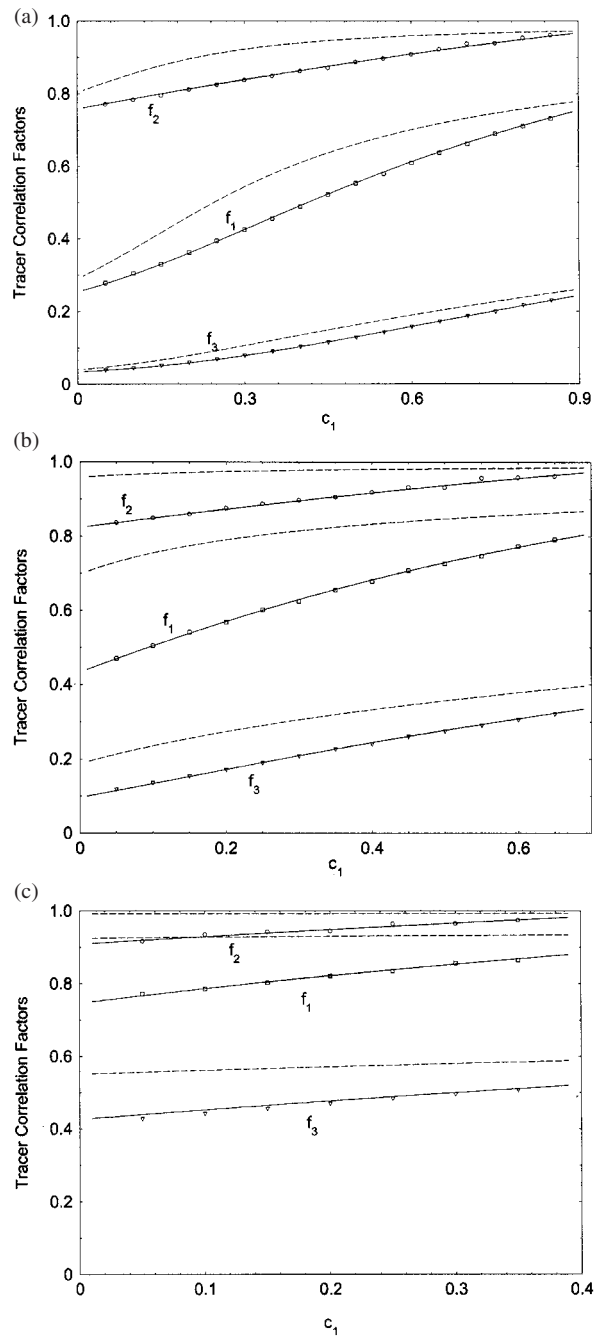


Figure 3. The tracer correlation factors f_1 , f_2 and f_3 as functions of c_1 at $w_1/w_2 = 10.0$ and $w_1/w_3 = 0.1$. (a) $c_3 = 0.1$; (b) $c_3 = 0.3$; and (c) $c_3 = 0.6$. Data points: Monte Carlo results; solid curves: MAA theory, equations (38)–(40); dashed curves: Manning (1971) theory, equations (41), (42).

to analyse interdiffusion data on the Fe–Ni–Cr system will be published shortly (Belova and Murch 2002).

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