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A High Accuracy Diffusion Kinetics Formalism for Random Multicomponent Alloys: Application to High Entropy Alloys

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Abstract

In this paper, a new, lighter, version of the highly accurate Moleko, Allnatt and Allnatt formalism for describing both tracer (self) and collective diffusion kinetics in multicomponent random alloys is presented. Verification of the resulting expressions is performed by means of kinetic Monte Carlo simulation. The accuracy of the new formalism is much higher than that of the combined Manning and Holdsworth and Elliott formalism discussed recently. Using this formalism the possible range of the tracer diffusion ratio of the highest to the lowest atomic component is examined for equiatomic (or near equiatomic) binary, ternary, quaternary and quinary alloys. It is shown that in the random alloy model, the correlation effect is the highest with a reduction of the fastest tracer diffusion by 40-55%, when moving from two pure metals to their equiatomic binary alloy. By adding the third component (with an intermediate mobility) this effect can be further increased with a possible total reduction of the fastest tracer diffusion by up to 70% (depending on the combinations of mobilities), while adding the fourth component brings this reduction up to 80% and with a possible maximum of up to 85% reduction for the 5-component alloy (again depending on the combinations of mobilities). But the slowest diffusing components are not affected by this. This suggests that kinetics arguments alone are not enough for explaining the sluggish diffusion observed of all atomic components in (equiatomic) high entropy alloys.

Introduction

Diffusion quantities can be categorized as either being characteristic of an individual atom (tracer) or characteristic of a species of atoms (collective). The former is accessible in tracer diffusion experiments whilst the latter is accessible in interdiffusion experiments.

The main collective diffusion parameters are the Onsager phenomenological transport coefficients. In [1] it was shown how the correlated part of these coefficients, the diagonal and off-diagonal collective correlation factors, can be defined. The principal tracer diffusion quantity, the tracer diffusion coefficient, can be formally defined as a limiting case, with a vanishingly small tracer content, of the corresponding diagonal Onsager phenomenological coefficient (Eq. 14 below). The correlated part of the tracer diffusion coefficient is called the tracer correlation factor. Whilst the Onsager phenomenological coefficients are very difficult to measure explicitly, the tracer diffusion coefficients can be measured using a number of techniques as presented, for example, in [2-10].

Theories of diffusion kinetics in random alloys are usually based on atom-vacancy exchange frequencies that can, in principle, be related to the atomic interaction energies and are usually assumed to be some average over possible local configurations around an atom. In an n -component alloy with n independent diffusion quantities available, it should be possible to solve an appropriate theory of diffusion kinetics in order to find the full set of average atom-vacancy exchange frequencies. The main assumption is that a particular diffusion mechanism is operating. In crystalline materials it is well-accepted of course that the vacancy mechanism is operating.

In [11] a brief historic overview of the development of various theories of diffusion kinetics in random alloys with vacancy mechanism was presented. The majority of those theories lack accuracy especially for the fastest component which is also the most correlated (lowest tracer correlation factor). Only one theory, that derived by Moleko, Allnatt and Allnatt (MAA) [12], provides a high accuracy, which was later confirmed by means of precision kinetic Monte Carlo simulations [13,14]. The main obstacle for using the MAA theory in the case of multicomponent alloys is its great complexity. It is almost impossible to push this theory beyond 3-component systems.

In the present paper, we present a much 'lighter' version (here called MAA-light) of the MAA theory. It nonetheless remains much more complex than the combined Manning [15] and Holdsworth and Elliott (HE) [16] theory that was recently suggested [11]. The principal advantage of MAA-light, however, is in its very accurate predictions of the correlation factors for the fastest atomic component. These correlation factors are usually small. This is rather more valuable for analysis of diffusion processes than obtaining highly

accurate correlation factors that are usually close to unity for the slowest diffusing atoms. Furthermore, MAA-light is a self-consistent theory in the sense that both collective and tracer correlation factors are calculated using the same system of equations. It should be pointed out that for quinary and higher alloys MAA-light will require application of iterative numerical methods and therefore rather more computational effort will be needed compared with the approach described in [11].

In addition, in the present paper, we apply MAA-light to analyze the possible slowing down of the diffusion kinetics of multicomponent alloys with up to five components. This is done in the following way. We first consider hypothetically pure metals, the fastest and the slowest ones in the alloy. We assume that their tracer diffusion coefficient differ by an order of magnitude. Then we consider them being put together into an equiatomic binary alloy. The ratio of their tracer diffusion coefficients will be significantly reduced. By adding a third, fourth and fifth component with intermediate tracer diffusion coefficients and keeping equiatomic compositions (as in high entropy alloys) the ratio of the fastest tracer diffusion coefficient to the slowest one will be further reduced. In the present paper, this effect is analyzed in detail.

Finally, in the present paper, the MAA-light random alloy approach is applied to the case of the CoCrMn_{0.5}FeNi high entropy alloy. It is found that for the fastest atomic components, Mn and Cr, the corresponding tracer correlation factors contribute about 4% of the total activation energy. For the intermediate Co and Fe components there is no detectable contribution from the tracer correlation factor to the total activation energy, whereas for the slowest atomic component, Ni, a small negative contribution of about 0.6% was found to the total activation energy.

1. MAA-light theory

Let us consider a random alloy of n atomic species, labelled $i = A, B, \dots, N$. The collective correlation functions $f_{ij}^{(i)}$ ($f_{\underline{u}}^{(i)}$ is used for the diagonal collective correlation factors $f_{\underline{u}}$) are to be calculated using the following relations that were derived originally in MAA [12]:

$$f_{ij}^{(i)} = \delta_{ij} - (2w_j / c_v c_i) h_{vi:vj} \quad (1)$$

where δ_{ij} is the Kronecker delta, c_i , c_v are the compositions of an atomic component i and vacancies v , w_i is the frequency of the vacancy exchange with an atom of type i . In MAA [12] the functions $h_{vi:vj}$ were derived on the basis of linear response theory and the use of time correlation functions. They satisfy the exact relations:

$$\sum_{i=1}^n h_{vi:vj} = 0, \quad (2)$$

which, by Eq. 1, are equivalent to the Sum-rule in the random alloy that was derived in [17]:

$$\sum_{i=1}^n \frac{f_{ij}^{(j)} w_j}{w_i} = 1 \quad (3)$$

Approximate kinetic equations in [12] lead to equations for $h_{vi:vj}$ which turn out to contain new functions $h_{ik:vj}$ (k is an atom species). The central result in MAA is an approximate equation (Equation 48 in [12]), from which all the h functions can, in principle, be found. Unfortunately its structure makes it very difficult to use for the case of alloys with more than three atomic components. In the following sections, a lighter version of the MAA formalism is developed and presented in a way that can be easily used for calculations. (Please note that we have deposited all the suitable matrices $[a_{ij}]$, suitable for solving diffusion kinetics in up to $n = 5$ atomic component alloys, $[a_{ij}]_{(15 \times 15)}$, into a supplementary material folder together with a working Mathematica[®] program for solving the equations for a 5-component alloy.)

1.1 MAA-light central result

Equation 48 in MAA [12] has the following form:

$$M_0 c_v \sum_k w_k \left[f_{kl}^{(k)} h_{ik:vj} - f_{ki}^{(k)} h_{lk:vj} \right] = t^{-1} h_{il:vj}^0$$

$$- c_l \left[2w_i + M_0 w_l \sum_k f_{lk}^{(l)} \right] h_{vi:vj} + c_i \left[2w_l + M_0 w_i \sum_k f_{ik}^{(i)} \right] h_{vl:vj}$$

where $h_{il:vj}^0$ can be calculated using special relations that are simple and are given in [12].

The above equation in [12] is replaced by:

$$\sum_k a_{ik} h_{vk:vj} = b_{ij} \quad i < j; \quad i, j, k = A, B, \dots, N; \quad (4)$$

where

$$a_{ik} = -\frac{(M_0 c_i w_i F_i + 2c_i w_k)}{c_v M_0 (w_i F_i + w_k F_k)} \quad i \neq k \quad (5a)$$

$$a_{ii} = 1 - \sum_{k \neq i} a_{ki} \quad (5b)$$

$$b_{ij} = -\frac{c_i c_j}{M_0 (w_i F_i + w_j F_j)} \quad \text{for } i \neq j, \quad (6a)$$

$$b_{ii} = -\sum_{j \neq i} b_{ij} \quad (6b)$$

and $M_0 = 2f_0 / (1 - f_0)$, where f_0 is the geometric tracer correlation factor for the lattice and

$$F_j = \sum_i f_{ij}^{(j)} \quad (7)$$

When solving Eqs. 4 it should be noted that the h functions obey the Sum-rule, Eq. 2, together with being symmetric with respect to their subscripts:

$$h_{vi:vj} = h_{vj:vi} \quad (8)$$

For a n -component alloy we will then consider $n(n-1)/2$ equations for the same number of unknown $h_{vi:vj}$ functions. Note that unlike Equation 48 of [12], no $h_{ik:vj}$ functions appear in Eq. 4.

The way to proceed is to first eliminate $h_{vj:vj}$ by using the Sum-rule, Eq. 2. This gives:

$$\sum_{k \neq j} (a_{ik} - a_{ij}) h_{vk:vj} = b_{ij} \quad (9)$$

For each particular choice of j there are n such equations of which $(n - 1)$ are independent; we will take the $(j - 1)$ independent equations to be the ones with $i < j, j > 1$ and $i < n$.

1.2 Case of a low vacancy composition

When the vacancy composition is very small ($c_v \rightarrow 0$), as is usually the case in real alloys, the above equations should be re-arranged to make them suitable for computations.

First, we introduce

$$a'_{ik} = a_{ik} c_v = -\frac{(M_0 c_i w_i F_i + 2c_i w_k)}{M_0 (w_i F_i + w_k F_k)} \quad (10)$$

and then, multiplying Eq. 5b by c_v , we have that at the limit $c_v \rightarrow 0$:

$$a'_{ii} = -\sum_{k \neq i} a'_{ki} \quad (11)$$

Next, we introduce

$$h'_{vi:vj} = h_{vj:vj} / c_v \quad (12)$$

which then allows us to re-write Eqs. 1 as:

$$f_{ij}^{(i)} = \delta_{ij} - (2w_j / c_i) h'_{vi:vj} \quad (13)$$

Note that Eqs. 4, 9 remain the same, with a'_{ik} , $h'_{vi:vj}$ simply replacing a_{ik} , $h_{vi:vj}$.

1.3 Solution for the tracer correlation factor

The formal definition of the tracer correlation factor will be used in this section and it can be described as follows. We introduce $(n + 1)^{\text{st}}$ atomic species that will represent the tracer atoms of one of the main atomic component, its composition c_{n+1} will be treated as vanishingly small, namely $c_{n+1} \rightarrow 0$. We will need to keep all $(n+1)n/2$ equations in modified Eq. (4). But some of the terms in those equations can be dropped taking into account the smallness of some quantities. For example, $b_{i(n+1)}$ and $b_{(n+1)i}$ are small as well as $a'_{(n+1)i}$ and $h'_{vi:v(n+1)}$. The formal definition of the tracer correlation factor [18] can be then employed as ($w_{n+1} = w_i$):

$$f_i = \lim_{c_{n+1} \rightarrow 0} f_{(n+1)(n+1)}^{(n+1)} = 1 - (2w_i / c_{n+1}) h'_{v(n+1):v(n+1)} \quad (14)$$

When applied to the matrix Eq. (4) when re-written for the low vacancy case is:

$$\sum_k a'_{ik} h'_{vk:vj} = b_{ij} \quad i < j; \quad i, j, k = 1, 2, \dots, n+1 \quad (15)$$

The following compact expression for the tracer correlation factor f_i can be obtained:

$$f_i = 1 - \frac{2w_i (\sum_{j \neq i} b''_{jn+1}) / c_i}{\sum_{j \neq i} a''_{jn+1}}, \quad i, j = 1, 2, \dots, n \quad (16)$$

where we need to use the following modifications to functions b_{in+1} and a'_{jn+1} : instead of

F_i we will use f_i , such as:

$$b''_{jn+1} = -\frac{c_j}{M_0(w_i f_i + w_j F_j)}, \quad a''_{jn+1} = -\frac{(M_0 c_j w_j f_j + 2c_j w_i)}{M_0(w_i f_i + w_j F_j)} \quad (17)$$

The reason for this correction is explained in Appendix below by making comparison with the derivation of the tracer correlation relations in the original MAA formalism [12]. The form of relations (Eqs. 16, 17) dictates that the collective correlation factors must be calculated first by solving a set of $(n+1)n/2$ linear equations, Eq. 9, in the following form:

$$\sum_{k \neq j} (a'_{ik} - a'_{ij}) h'_{vk:vj} = b_{ij}, \quad i, j, k = 1, 2, \dots, n+1 \quad (18)$$

Next, the relations (Eqs. 16,17) can be solved. Both sets of equations for the case of multicomponent alloys can easily be solved using iterative method. In addition, Eqs. 18 can be solved analytically for up to the quinary alloy when using appropriate symbolic algebra software (Mathematica[®] and similar). The starting values for this method can be used as the solution to the hypothetical case when all the exchange frequencies are equal. For the functions $h'_{vi:vj}$ the starting values are:

$$h'_{vi:vj}{}^{(0)} = -\frac{c_i c_j}{M_0 + 2} \quad (19)$$

and for all the tracer correlation functions the starting value is f_0 .

2. Binary alloy result

2.1 Collective correlation factors

For a binary alloy consisting of species A and B, the form for the collective correlation factors is just the same as in MAA,

$$f_{AA} = 1 - \frac{2c_B w_A}{\Omega}, \quad f_{AB}^{(A)} = \frac{2c_B w_B}{\Omega}, \text{ etc.}, \quad (20)$$

with the following definition of Ω :

$$\Omega = M_0 c_v (w_A F_A + w_B F_B) + M_0 (c_A w_A F_A + c_B w_B F_B) + 2(c_A w_B + c_B w_A), \quad (21a)$$

which is the same as MAA for $c_v \rightarrow 0$ but differs for $c_v \neq 0$. For $c_v \rightarrow 0$ we have, as in MAA,

$$\Omega = H + 2(c_A w_B + c_B w_A) \quad (21b)$$

where H in terms of jump frequencies is given in [14]. The loss of accuracy is similar to that for the tracer result in the following section.

2.2 Tracer correlation factors

We take $c_v \rightarrow 0$ everywhere in this section. Eq. 9 becomes two equations for an alloy of three components (A, B, C); we put component C as the tracer and take the limit $c_C \rightarrow 0$. The result is:

$$f_C = 1 - \frac{2w_C(c_A\Lambda_{CB} + c_B\Lambda_{CA})}{c_A\Lambda_{CB}(M_0w_A F_A + 2w_C) + c_B\Lambda_{CA}(M_0w_B F_B + 2w_C)} \quad (22)$$

where

$$\Lambda_{ij} = w_i F_i + w_j F_j \quad (23)$$

For an (A, B) alloy with C being a tracer of B, Eq. 22 gives the tracer correlation factor as

$$f_B = \frac{H_B}{2w_B + H_B} \quad (24)$$

where

$$H_B = M_0 w_B \frac{(f_B(c_A w_A F_A + c_B w_B F_B) + w_A F_A F_B)}{w_B f_B + c_A w_B F_B + c_B w_A F_A} \quad (25)$$

Finally, following [13], we substitute from Eq. 7, 20, 21b and simplify a little to obtain

$$H_B = \frac{H w_B (M_0 w f_B + w_A (2 + M_0)) + 2 M_0 w_A w_B^2 f_B}{2(f_B w_B w' + w_A w_B) + H(w' + f_B w_B)} \quad (26)$$

where

$$w = c_A w_A + c_B w_B \quad (27)$$

$$w' = c_A w_B + c_B w_A \quad (28)$$

Figure 1 shows, for the face centered cubic lattice, f_B vs c_B for $w_A/w_B = 0.001, 0.1, 10, 1000$. Red is MAA-light and blue is MAA.

3. Multicomponent alloys

To further test the present formalism we performed a series of Monte Carlo (MC) simulations for 3, 4 and 5-component alloys. For the details of our MC simulations see, for example, [11]. In all cases, the agreement between the MC results and MAA-light

approach is similar to the binary alloy: the diagonal collective correlation factors agree very well, the off-diagonal correlation factors agree to a good degree with an overall agreement that can be rated as very good, see Figs. 2 a,b (ternary alloy) and 3 a,b, (quaternary alloy) and Table 1 (quinary alloy) the tracer correlation factors for the fastest atoms are all in excellent agreement with MC results and slight deviations can be observed for the slowest diffusion atoms, see Figs. 2c, d and e (ternary alloy), 3c (quaternary alloy) and Table 1 (quinary alloy). The excellent agreement with Monte Carlo simulated tracer correlation factors for the fastest atoms (MAA-light) is much more valuable than the excellent agreement for the slowest atoms (Holdsworth and Elliott [16]) for the purposes of an in-depth diffusion kinetics analysis in multicomponent alloys. In summary, it can be concluded that the current formalism gives a much better accuracy than the combined Manning and HE approach proposed in [11]. However, from a practical point of view, application of the present formalism requires rather more computational effort compared to [11].

4. Applications of MAA-light formalism

4.1 Decrease of atomic mobilities due to the tracer correlation factors in multicomponent alloys

In recent years, there has been growing interest in multicomponent metallic alloy with equiatomic or near equiatomic compositions [19-26]. These alloys are now called high entropy alloys (HEAs) as their stability at higher temperatures is apparently dictated by the resulting high entropy term in the expression for the free energy. At low temperatures, where the entropy term must decrease, their continued stability is proposed to be due to sluggish diffusion. In [27] a study of the diffusion mobilities in $\text{CoCrMn}_{0.5}\text{FeNi}$ alloy was presented together with a comprehensive comparison with the corresponding mobilities in the pure metal and binary and ternary alloys (where experimental data is available). One of the possible reasons for the sluggish diffusion is a result of diffusion kinetics, specifically, tracer correlation effects.

In this section, we propose that tracer correlation effects in any alloy (as opposed to the pure element metal) would produce the effect of the slowing down of the apparent mobilities (given by the tracer diffusion coefficients) of some (but not all) of the atomic

components. With all other parameters as equal as practically possible, the increase of the total number of the atomic components in an alloy will decrease the highest tracer diffusion coefficients, and, consequently, their ratios to the slowest. The degree to which this decrease happens will depend on a number of factors. The correlation effect for the fastest atoms will always be the greatest, thus resulting in the largest decrease of the diffusion efficiency. For the slowest atoms, the correlation factor will be very close to unity resulting in little change in the diffusion efficiency and, consequently, mobility. All of the other atoms will have their correlation factors stacked in-between according to their place in the mobility hierarchy.

The tracer correlation effect on the diffusion mobilities in the multicomponent alloys can be analyzed in the following way. First, let us assume that the exchange frequency for the fastest component w_A and the exchange frequency of the slowest component w_N differ by some factor, say 10 (100). If they both were in the pure element metals their respective tracer correlation factors would be equal.

But, simply putting these metals into an equi-atomic binary alloy will always make the tracer correlation factor for the fastest atoms lower than the tracer correlation factor for the slowest atoms. This will result in the decrease of the ratio of the tracer diffusion coefficients (highest to the lowest – let us call this ratio as **R**). This will be equal to approximately half of the ratio of their exchange frequencies, in our case about 6.0 (45). In this process, the slowest tracer diffusion coefficient will remain almost the same while the fastest tracer diffusion coefficient will be reduced by about half. If we consider now the situation with three pure elements present with the ratio of the exchange frequencies for the fastest and the slowest being the same, 10 (100); putting them together into a ternary alloy will further reduce the **R** ratio down to as low as about 5.0 (25). The exact extent will, of course, depend on the all intermediate atomic component exchange frequencies. If these components (one intermediate for the case of ternary alloy, two intermediate for the case of quaternary alloys etc.) are close to the fastest one then adding them to the alloy (equi-atomic) will not change the **R** ratio very much. On the other hand, if these components are close to the slowest one, then adding them to the alloy will significantly reduce the **R** ratio. These types of scenarios were simulated with the use of the MAA-light formalism presented here. Results of the calculations are shown in Figure 4 a) and b). The ratios of the intermediate exchange

frequencies in the 4 and 5-component alloys were kept in the following fashion: for the 4-component alloy (ABCD) $w_B = 2.0w_C$ with w_B varying between $0.5w_A$ to $2.0w_D$. Ratio of $w_A/w_D = 10$ in a) and 100 in b); for the 5-component alloy (ABCDE) $w_B = 2.0w_C = 4.0w_D$ with w_B varying between $0.5w_A$ to $4.0w_E$. Again $w_A/w_E = 10$ in a) and 100 in b). It is clear that there is always some reduction in the \mathbf{R} ratio when another atomic component is added. This reduction could be as low as a factor of 0.15 (or 85% reduction) for the case of 5-component alloy; 0.20 (or 80% reduction) for the case of 4-component alloy; 0.30 (or 70% reduction) for the case of 3-component alloy; 0.45 (or 55% reduction) for the case of binary alloy.

It should be noted here that in the above consideration, all the reductions in mobilities are possible only for the components that are not the slowest ones. For the slowest atomic mobility there will not be a detectable change in mobility that is kinetically caused by additional atomic components.

4.2 Estimation of the tracer correlation factors and associated energies in CoCrMn_{0.5}FeNi alloy

As was mentioned above, in [27] an experimental investigation of the intrinsic diffusion coefficients in CoCrMn_{0.5}FeNi alloy was performed using quasi-binary diffusion couples with composition difference between 12 and 22 at%. The resulting diffusion coefficients were assumed to coincide with tracer (self) diffusion coefficients in this alloy and found to be almost constant, independent on composition, at a given temperature. Furthermore, the experiments were carried out at different temperatures and Arrhenius parameters for all diffusion coefficients were obtained. In this section, we apply MAA-light to these alloys at two temperatures, 1200K and 1300K using tracer diffusion coefficients from the experiments in [27] as the input and find corresponding sets of the exchange frequencies and tracer correlation factors. The iterative numerical process was set up in the following way. The first approximation was that all the tracer correlation factors were equal to unity and the scaled exchange frequencies were then obtained as the ratios of the tracer diffusion coefficients to the highest, D_{Mn} . With this set of exchange frequencies, the tracer correlation factors were calculated and corrected scaled exchange frequencies were used as the next iteration input. The iterations were stopped when the

tracer correlation factors calculated for the next iteration differ from the previous iterations by not more than 0.001. It was found that this iterative process converges quite quickly, requiring 8 iterations for the fastest diffusing atoms (Mn), 4 iterations for Cr, and 3 iterations for Fe, Co and Ni. The resulting sets of tracer correlation factors are presented in Fig. 5 as functions of $1/T$.

The energy associated with the tracer correlation factors for Mn and Cr are 10.9 kJ/mol and 12.0 kJ/mol respectively which is about 4% of their total activation energies [27]. The tracer correlation factors for Fe and Co are both almost constant, independent of temperature. Whereas the tracer correlation factor for Ni has a very small negative energy of -1.8 kJ/mol which is about 0.6% of total Ni activation energy. These results are consistent with the conclusions in Section 4.2 that not all atomic components are significantly slowed down in a multicomponent alloy. In the case of CrCoMn_{0.5}FeNi only Mn and Cr have some detectable reductions in their mobilities. In Figure 6 we presented uncorrelated parts of the diffusion coefficients in this alloy (thick dashed lines). Total diffusion coefficients are shown by thin dashed lines.

Summary

In this paper, a light version of Moleko, Allnatt and Allnatt formalism has been introduced and its origin explained. It was shown by means of computer simulations that the resulting expressions give very high accuracy values for the tracer correlation factors for the fastest diffusing atoms and deviate slightly for the slowest diffusing atoms.

Overall, the accuracy of this formalism is much higher than that of the combined Manning and Holdsworth and Elliott formalism. Using this formalism we examined the possible range of the tracer diffusion ratio of the highest to lowest atomic component for equiatomic binary, ternary, quaternary and quinary alloys. It was shown that, in the random alloy model, the kinetic (correlation) effect is the highest with the reduction of the fastest tracer diffusion by about 40-55%, when going from two pure metals (with different mobilities) to their equiatomic binary alloy. By adding the third component (with intermediate mobility) this effect can be further increased with possible total reduction of the fastest tracer diffusion by up to 70% (depending on the mobilities combinations), while adding the fourth component brings this reduction up to 80% with the possible maximum

of up to 85% reduction for the 5-component alloys (again depending on the mobilities combinations). But the slowest diffusion is not affected in this exercise. This means that a kinetics argument alone is not enough to explain the sluggish diffusion of all atomic components observed in high entropy alloys.

Appendix. Relationship of Eq. 4 (MAA-light) to Eq. 48 (MAA) [12]

Eq. 4 can be written down by taking the form of Eq. 48 in MAA [12] (the very first equation in section 1.1 above) and making two kinds of substitutions to the left-hand side only:

- (i) drop all off-diagonal correlation functions, i.e. $f_{kj}^{(j)} = \mathbf{0}$ for all $k \neq j$.
- (ii) replace all diagonal correlation functions f_{ii} by F_i (where F_i is exactly as defined in Eq. 7).

A consistent set of approximations that leads to the MAA-light can be presented in the following way.

In [12] equations for the various h functions are obtained from approximate solutions of kinetic equations of certain time correlation functions (tcfs) denoted by ψ . A key quantity is $\psi_{ij}(l, m; t)$, which is a tcf proportional to the probability that sites l and m are occupied respectively by atoms of species i and j at time t , conditional on a certain initial condition. The exact expression for the time derivative of this quantity (its ‘kinetic equation’) contains similar tcfs which, however, specify the occupancies of three particular sites, for example $\psi_{ijv}(l, m, n; t)$ which is proportional to the probability that sites l , m , and n are occupied respectively by an atom of species i , an atom of species j , and a vacancy v . (This is Eq. 47 of [12], but note, for example, that in their notation our $\psi_{ij}(l, m; t)$ would be denoted $\psi_{im}(ij; t)$, and so on.) There is of course a hierarchy of ψ -functions concerned with the occupancies of 1, 2, 3, sites which we refer to as one-site, two-site, three-site, ... functions; the kinetic equation for an n -site ψ -function contains contributions from $(n+1)$ -site ψ functions and can only be solved by making an approximation for these contributions in terms of n -site ψ -functions.

To solve their kinetic equation MAA followed a procedure modelled on that used originally by Holdsworth and Elliott [16] in a similar context. They noted that the kinetic

equation for a one-site function $\psi_i(l)$ similarly contains contributions from two-site functions, but here we know that the one-site equation in the limit of microscopically long times and long wavelengths must reduce to the macroscopic diffusion equation for atom species i . This places a restriction on the form of the two-site contributions to the kinetic equation for $\psi_i(l)$ in this limit and it is assumed that this can be a useful approximation at all times and wavelengths. The result is Eq. 30 of [12]; in the present notation this is:

$$w_j \sum_n \theta(l, n) [\psi_{N\Delta v}(n, l) - \psi_{N\Delta v}(l, n)] = -w_j \sum_k \left(\frac{f_{jk}^{(j)} c_j}{c_k} - \delta_{jk} \right) \times$$

$$\sum_n \theta(l, n) \{ c_v [\psi_{\Delta k}(l) - \psi_{\Delta k}(n)] - c_k [\psi_{\Delta v}(l) - \psi_{\Delta v}(n)] \}$$
(A1)

where $\theta(l, n)$ is unity if sites l and n are nearest-neighbours and zero otherwise, and the $f_{jk}^{(j)}$ are the correlation functions introduced in Eq. 1. (n.b. A subscript Δk in an ψ -function, as for example $\psi_{\Delta k}(l)$, means that this ψ is proportional to the probability of a *fluctuation* of the occupancy by species k of the site l from the equilibrium probability c_k that it would be so occupied.) It is now assumed that if we insert in each ψ -function appearing in this equation an additional fluctuation Δi at some nearby site m then the resultant equation,

$$w_j \sum_{n \neq m} \theta(l, n) [\psi_{N\Delta v \Delta i}(n, l, m) - \psi_{N\Delta v \Delta i}(l, n, m)] = -w_j \sum_k \left(\frac{f_{jk}^{(j)} c_j}{c_k} - \delta_{jk} \right) \times$$

$$\sum_{n \neq m} \theta(l, n) \{ c_v [\psi_{\Delta k \Delta i}(l, m) - \psi_{\Delta k \Delta i}(n, m)] - c_k [\psi_{\Delta v \Delta i}(l, m) - \psi_{\Delta v \Delta i}(n, m)] \}$$
(A2)

will also be a useful approximation. The left-hand side is of exactly the form of a typical contribution of three-site functions to the kinetic equation for two-site functions in MAA; the right-hand side provides an approximation for this contribution in terms of two-site functions. Using this approximation leads to the central result of MAA, their Equation 48 in [12].

It is possible that a simpler structure than MAA might result if, instead of using the kinetic equation for an atomic species to suggest a relation between one- and two-site functions, Eq. (A1), one used the corresponding result from the kinetic equation for the

vacancy species. On the other hand, this equation, replacing Eq. (A1), follows much quicker by just summing Eq. (A1) over atom species j . Either way, the equation replacing Eq. (A1) is then:

$$\begin{aligned} \sum_j w_j \sum_n \theta(l, n) [\psi_{\Delta v}(n, l) - \psi_{\Delta v}(l, n)] = \\ - \sum_n \theta(l, n) \sum_j w_j (F_j - 1) \{ c_j [\psi_{\Delta v}(n) - \psi_{\Delta v}(l)] + c_v [\psi_{\Delta v}(l) - \psi_{\Delta v}(n)] \} \end{aligned} \quad (\text{A3})$$

and, as before, it can be assumed that if we insert in each ψ -function appearing in this equation an additional fluctuation Δi at some nearby site m then the resultant equation connecting 3-site and 2-site ψ -functions will still be a useful approximation. However, this resultant equation contains a summation over species j on both sides and is only useable if we make the additional assumption that a useful relation still holds if we simply drop the summations over species j everywhere in Eq. (A3). If this is done, then an equation replacing MAA Equation (48) in [12] can be found and, from it, the MAA-light result, Eq. (4), quickly follows.

Acknowledgments

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Table 1. MAA light comparison with Monte Carlo simulation for the quinary system (ABCDE) with $w_a=1.0, w_b=0.2, w_c=0.04, w_d=0.008, w_e=0.0016$ and equiatomic composition.

	$e_i^{D_0(\text{Darken})}$ %	$e_i^{D_0(\text{Manning+HE})}$ %	$e_i^{D_0(\text{MAA-light})}$ %	$e_i^{Q(\text{Darken})}$ %	$e_i^{Q(\text{Manning+HE})}$ %	$e_i^{Q(\text{MAA-light})}$ %
Cr	9	13	1	0.78	0.99	0.29
Mn	0.6	11	10	0.18	0.44	0.35
Fe	16	25	22	0.25	0.61	0.41
Co	22	17	33	0.5	0.1	0.87
Ni	38	100	16	2	3	1.6

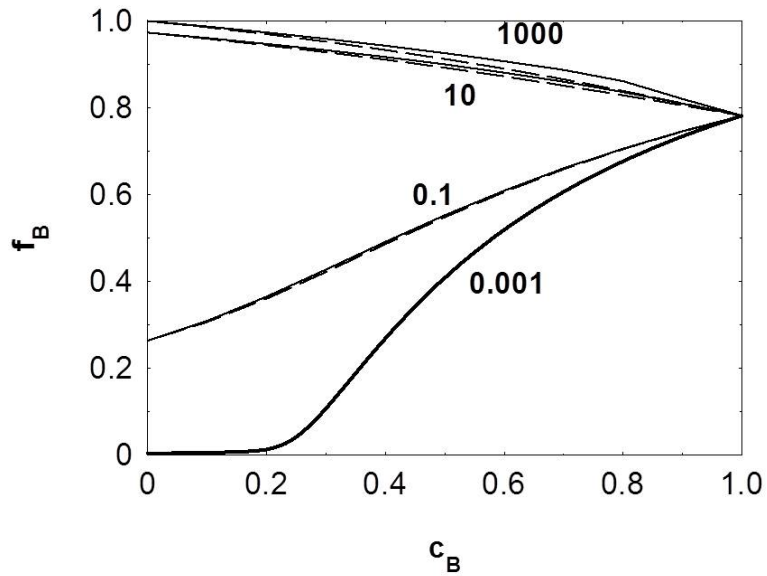


Figure 1. Tracer correlation factor f_B as a function of composition for different values of ratio w_A/w_B (marks at the lines). Dashed lines – MAA, solid lines – MAA-light.

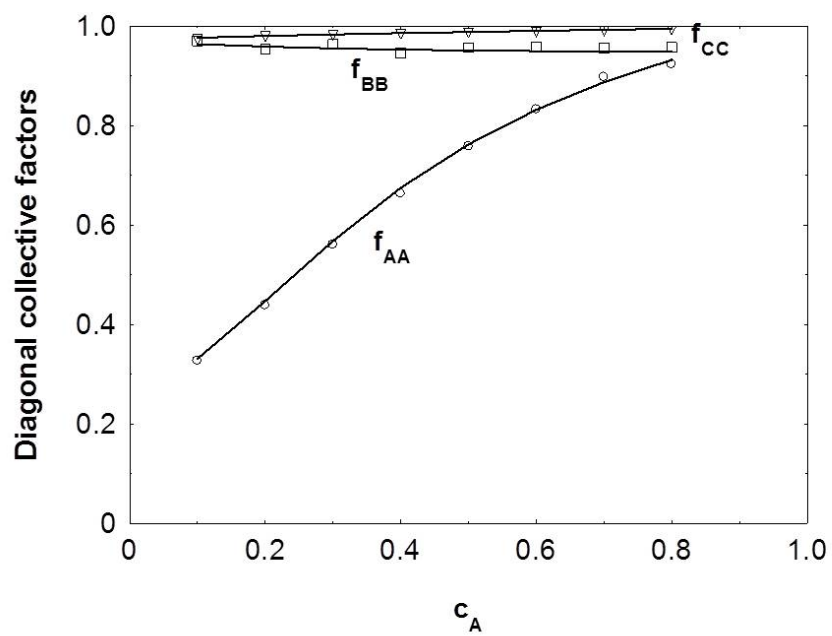


Figure 2a.

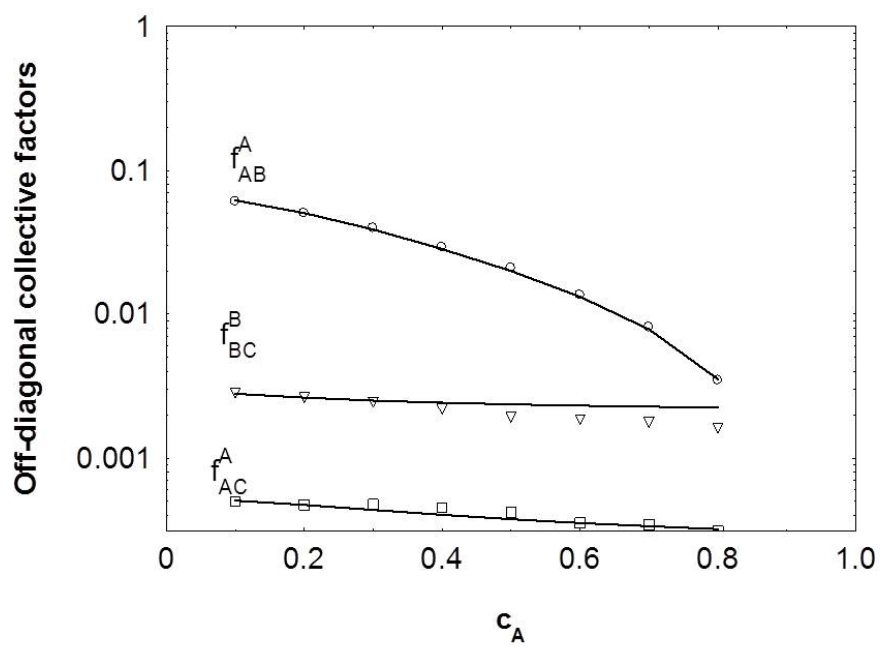


Figure 2b.

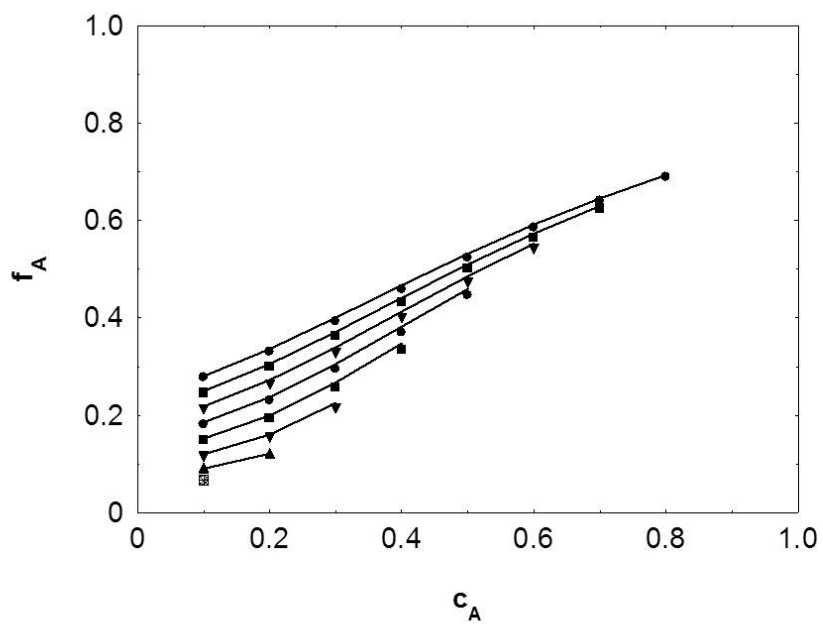


Figure 2c.

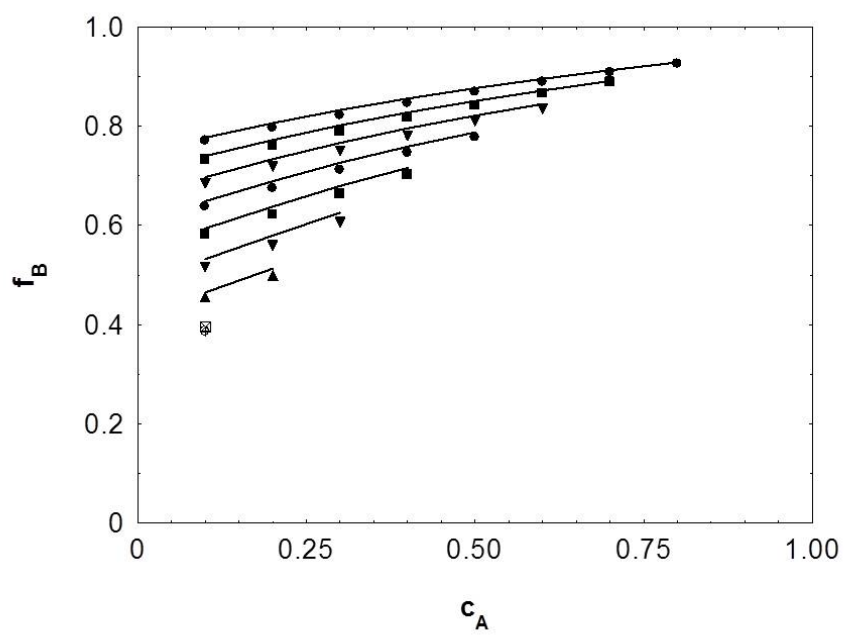


Figure 2d.

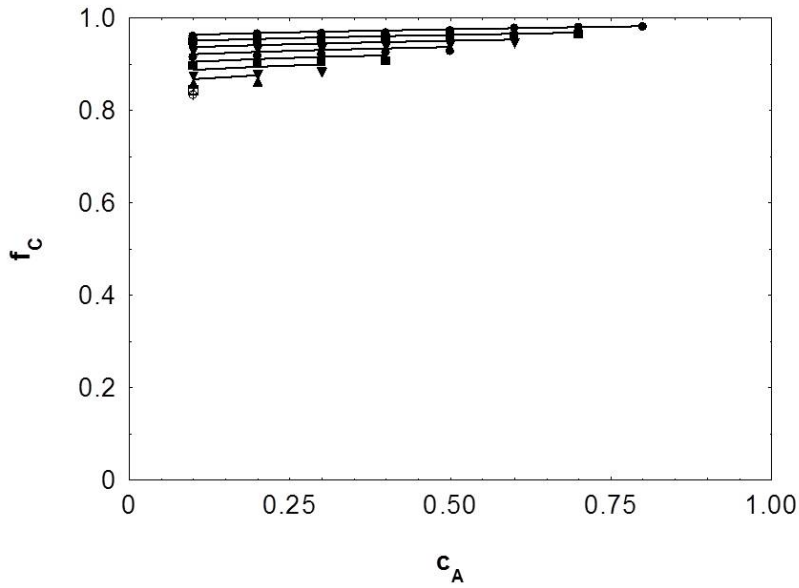


Figure 2e. Diagonal collective correlation factors a), and off-diagonal collective correlation factors b), Tracer correlation factors f_A c), f_B d), f_C e), as function of c_A for ternary (ABC) alloy with $w_B = 0.1w_A$, $w_C = 0.01w_A$. Symbols represent results of MC simulation and lines represent results of application of MAA-light. In a) and b) $c_C = 0.1$. In c), d) and e) lines and symbols corresponds to $c_C = 0.1$ (the top line), ..., 0.8 (bottom symbol).

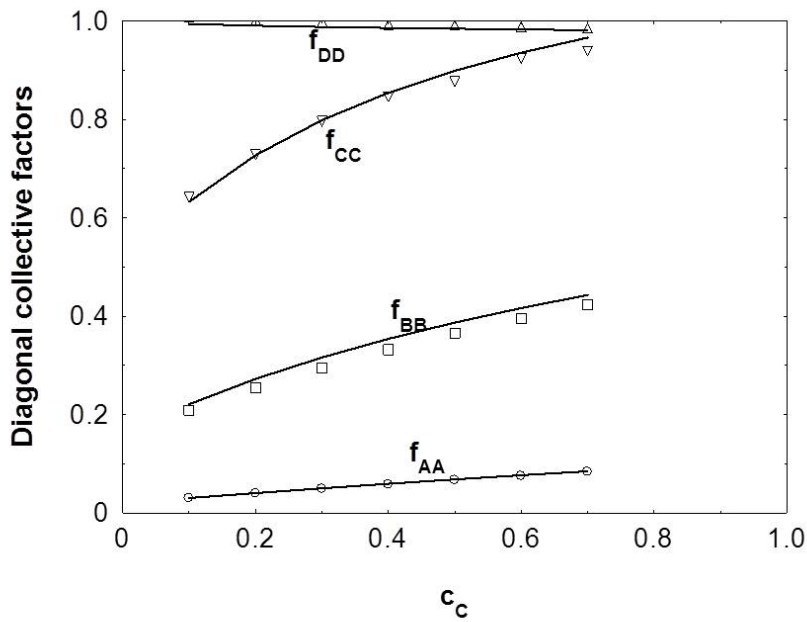


Figure 3a.

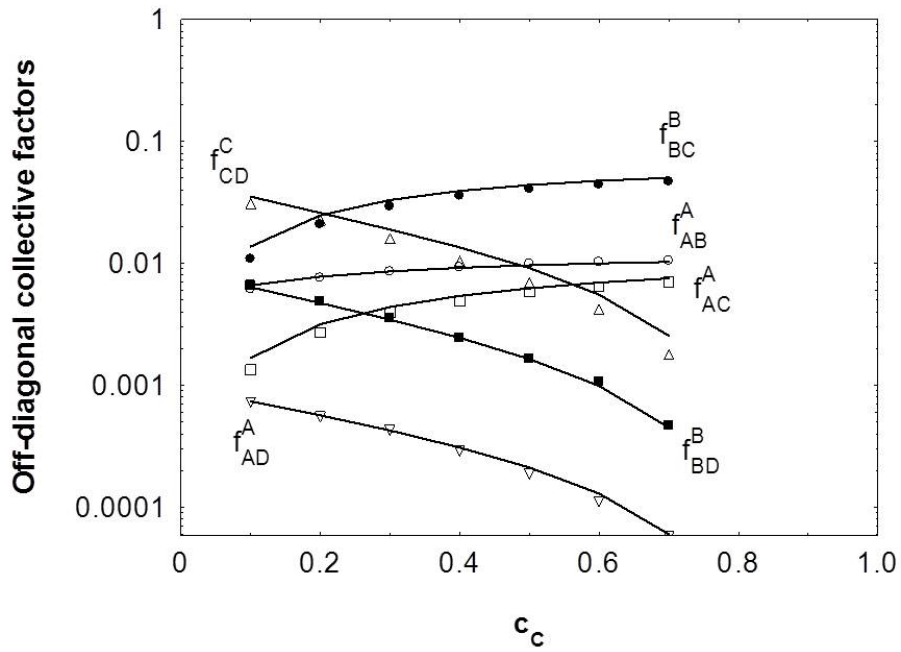


Figure 3b.

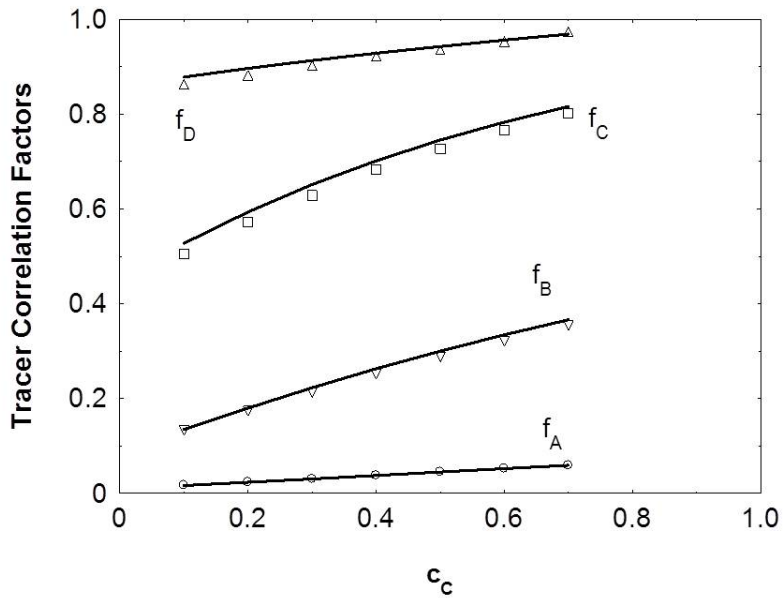


Figure 3c. Diagonal collective correlation factors a), and off-diagonal collective correlation factors b), and all tracer correlation factors c), as function of c_C for 4-component system (ABCD) alloy with $w_B = 0.1w_A$, $w_C = 0.01w_A$, $w_D = 0.001w_A$ and for the compositions c_A

$= 0.1, c_B = 0.1, c_D = 1 - c_A - c_B - c_C$. Symbols represent results of MC simulation and the lines represent results of application of MAA-light.

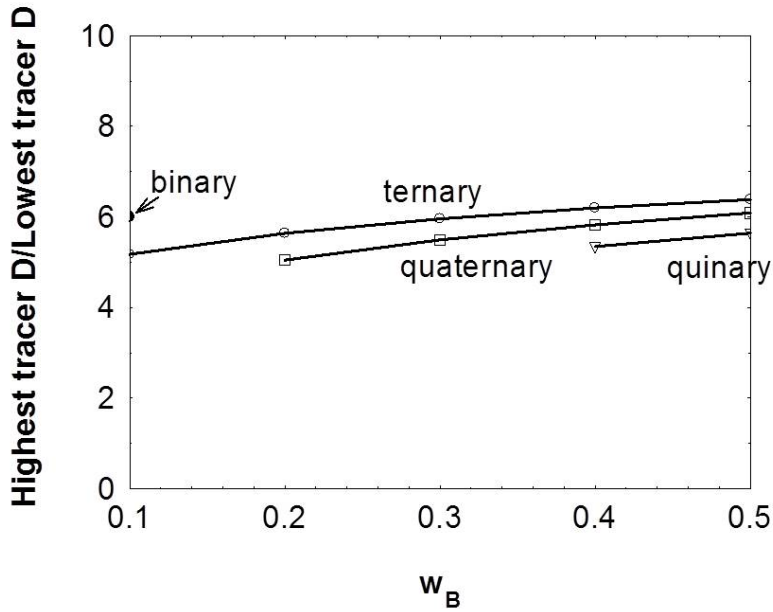


Figure 4a.

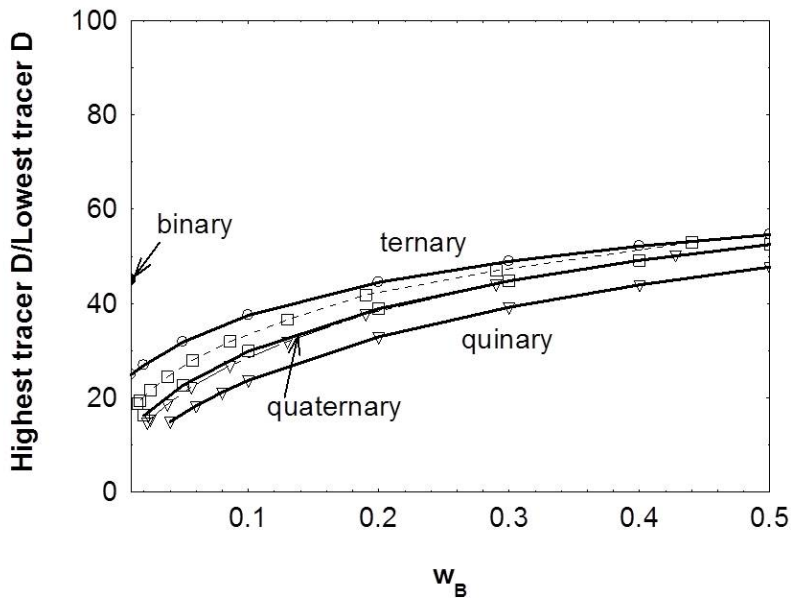


Figure 4b. Ratio of the fastest component (A) to the slowest component (N) tracer diffusion coefficients \mathbf{R} for equi-atomic alloys with different numbers of atomic components (3 – circles, 4 – squares, and 5 – triangles) as a function of the scaled atomic component (B) exchange frequency. In a) ratio of the fastest to the slowest atom mobilities is 10; in b) this

ratio is 100. For further explanation, see text. Solid lines – calculations using MAA-light; dashed lines (in b) only) – calculations made by using HE formalism [11].

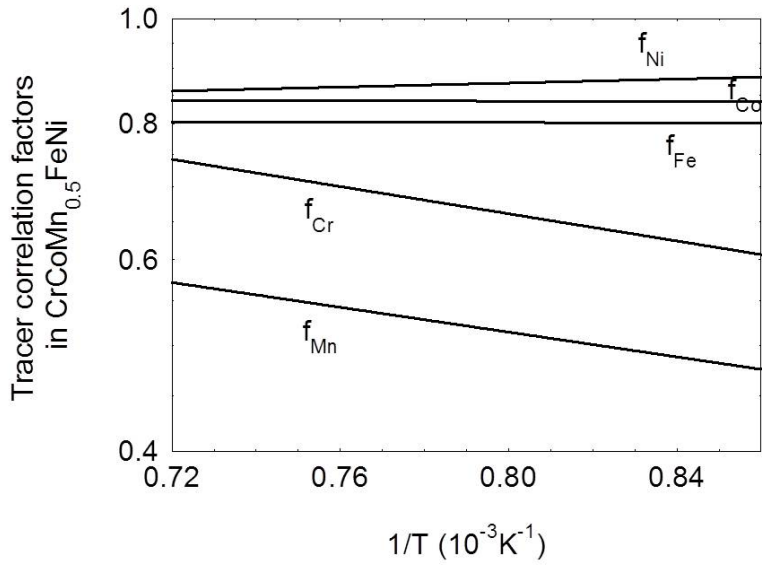


Figure 5. Arrhenius plot of tracer correlation factors in CrCoMn_{0.5}FeNi alloy calculated using diffusion coefficients data from [27] and MAA light.

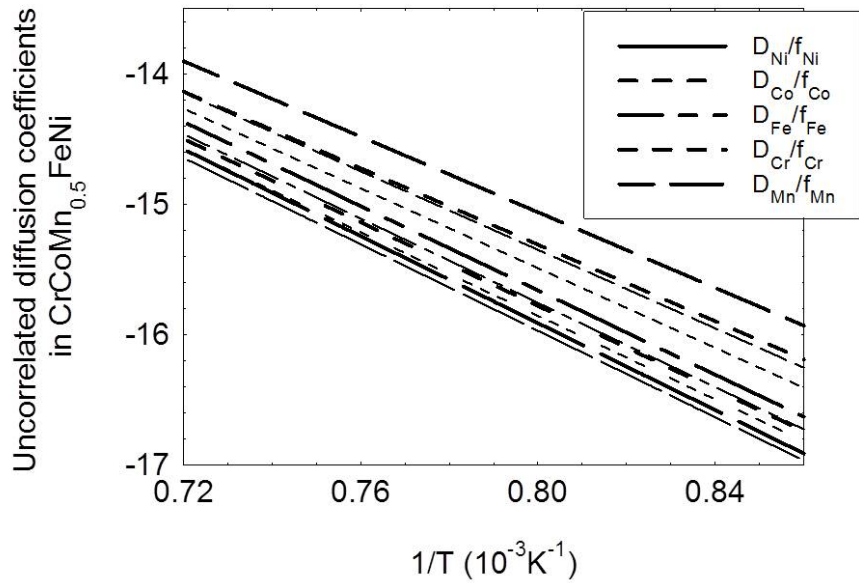


Figure 6. Uncorrelated parts of diffusion coefficients (thick dashed lines) in CrCoMn_{0.5}FeNi alloy calculated using diffusion coefficients data from [27] and MAA-light. Corresponding total diffusion coefficients are shown by thin dashed lines.

