diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Phenomenological Coefficients in Solid-State Diffusion: an Introduction

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Abstract
In this review, which is intended as an introduction to the subject, we introduce the phenomenological transport coefficients in solid-state diffusion and discuss their structure and physical meaning. Next, we discuss the Darken, the Manning, the Moleko, Allnatt and Allnatt and the Heumann expressions which relate the phenomenological coefficients to the (measurable) tracer diffusion coefficients. Finally, we discuss the relationships (sum-rules) among the phenomenological coefficients themselves in randomly mixed systems and note their applicability for simplifying collective diffusion problems.

Keywords: Phenomenological coefficient, diffusion, atomic transport, alloys, tracer diffusion coefficient

1. Introduction

In 1855, Fick introduced his famous First Law describing a linear relationship between a flux J_i of a diffusing species i and its concentration gradient dC_i/dx [1]:

$$J_i = -D_i \frac{dC_i}{dx} \qquad (1)$$

where D_i is the diffusion coefficient. Fick's First Law is frequently insufficient as a condition for attaining equilibrium of species i because it does not recognize all driving forces, direct and indirect, acting on i. The Onsager flux equations of irreversible processes achieve this through the postulate of linear relations between the fluxes and the driving forces, see for example [2,3]:

$$J_i = \sum_j L_{ij} X_j \tag{2}$$

where the L_{ij} are the phenomenological coefficients and X_i are the driving forces. The matrix of phenomenological coefficients is frequently simply called the ***L*** matrix. The great importance of the phenomenological coefficients stems from their independence of driving force. The Onsager flux equations have been used very extensively in theoretical treatments of collective diffusion problems such as chemical diffusion and ionic conductivity especially in multicomponent systems. Although the physical meaning of a diffusion coefficient is very well appreciated, in our experience the physical meaning of a phenomenological coefficient is rather less so. The purpose of this paper is to provide a little insight into the phenomenological coefficients, their structure, the relations between the phenomenological coefficient and the diffusion coefficients, and relations among the phenomenological coefficients themselves. The approach that we will take is one for non-specialists in the area.

2. The phenomenological coefficients

Some insight into the phenomenological coefficients can be gained by analysing diffusion in a binary alloy AB where the vacancy mechanism is operating. The Onsager flux equations can be written from Equation 2 as:

$$J_A = L_{AA} X_A + L_{AB} X_B \tag{3a}$$

$$J_B = L_{BB} X_B + L_{BA} X_A \tag{3b}$$

Since atoms, either A or B, exchange with vacancies in order to diffuse, the flux of vacancies J_V is equal and opposite to the total flux of atoms and is given by:

$$J_V = -(J_A + J_B) \tag{4}$$

We need not introduce the vacancies as a formal component here with the attendant driving forces because we have also made the assumption that the vacancies are always maintained at their equilibrium concentrations. This condition is achieved by requiring that sources and sinks of vacancies such as dislocations are sufficiently numerous and active during the diffusion process. In these equations we have introduced the diagonal phenomenological coefficients L_{AA} and L_{BB} and the off-diagonal coefficients L_{AB} and L_{BA}. According to the Onsager reciprocity theorem, $L_{AB} = L_{BA}$ and the ***L*** matrix is therefore symmetric. We simply have three independent coefficients.

Let us now consider a 'thought experiment' in which the A atoms in a homogeneous binary AB 'alloy' can respond to some external force such as an electric field but the B

atoms cannot. This is expressed by writing the driving force on *A* as $X_A=q_AE$ (where *E* is the electric field and q_A is the positive charge (say) on *A*) and writing the driving force on *B* simply as $X_B=0$. Now we might first expect that the *A* atoms would simply then drift in the field and the *B* atoms would not. The Onsager flux equations show indeed that the flux of *A* is given by:

$$J_A=L_{AA}\,q_A\,E \qquad (5)$$

In other words, there is a response of *A* in the direction of the electric field (we will see later that the diagonal phenomenological coefficients are required to be positive).
But the Onsager flux equations also show that the flux of *B* is not in fact zero but is given by:

$$J_B=L_{AB}\;q_A\,E \qquad (6)$$

This last equation says that *B* should also drift in the field even though the *B* atoms do not actually feel the field directly. It could very loosely be said that the drifting *A* atoms appear to 'drag' the *B* atoms along with them thereby giving rise to a flux of *B* atoms. In principle, the off-diagonal phenomenological coefficient L_{AB} can in fact be either positive or negative depending on the details of the particular atomistic model chosen. If L_{AB} were to be negative, it would mean that the *B* atoms would actually drift *up-field* whilst the *A* atoms drift down-field.

Now let us consider another 'thought experiment' where *both A* and *B* atoms in the alloy can respond equally to some external force such as an electric field. This is expressed by writing the driving forces on *A* and *B* simply as $X_A=qE$ and $X_B=qE$ (where *E* is the electric field and *q* is the positive charge (say) on both species). The Onsager flux equations (Equation 3a) show that the flux of *A* atoms is now given by:

$$J_A=L_{AA}\,q\,E+L_{AB}\,q\,E \qquad (7)$$

In other words, there is a response of *A* to the electric field, but, depending on the sign of L_{AB}, this flux could be larger (from a positive value of L_{AB}) or less (from a negative value of L_{AB}) than what it was before. The flux equations (Equation 3b) also show that the flux of *B* is now given by:

$$J_B=L_{BB}\,q\,E+L_{AB}\,q\,E \qquad (8)$$

The situation for the *B* atoms is similar to that for the *A* atoms. Even though both the *A* and *B* atoms have the same charge and could be expected to drift in the same direction, this is not necessarily the case if L_{AB} is very large and negative compared with one of the diagonal phenomenological coefficients. It is then possible to have, for example, a situation where the *A* atoms drift down-field but for the *B* atoms to actually drift up-field even though the *direct* force on the *B* atoms would be to send them down-field.

These examples suffice for the reader to appreciate that *in principle* the off-diagonal coefficient can be responsible not only for an atomic flux in the first place but also it can change the magnitude and even the direction of an atom flux.

In 1905, Einstein introduced his famous equation relating the diffusion coefficient D to the mean square of the displacement $\boldsymbol{R}$ of a particle in a long time t [4]:

$$D^* = \langle \boldsymbol{R}^2 \rangle / 6t \tag{9}$$

where the Dirac brackets <> indicate an average over a large number of particles. In Equation 9 the diffusion coefficient is understood to be a tracer diffusion coefficient and the implication is that we can follow each particle explicitly. This is indicated by the superscript * placed on D. The tracer diffusion coefficient is usually expanded for isotropic solid-state diffusion according to the 'hopping model' wherein an atom hops or jumps from one site to another with a long residence time at lattice sites between the jumps:

$$D^* = a^2 n f / 6t \tag{10}$$

where a is the jump length, n is the number of jumps in time t and f is the tracer correlation factor. The latter factor was introduced first by Bardeen and Herring in 1952 [5] to take into account the correlation in the directions of the walk taken by a particular atom or tracer atom because of the proximity of a vacancy. For a complete random walk with no correlations between the directions of tracer atom jumps then $f = 1$. This would be the case for a lone interstitial diffusing in an interstitial solid solution. On the other hand, if every tracer atom jump taken is immediately cancelled out by a reverse jump then $f \rightarrow 0$. This would be the case if the tracer atom (in this case an impurity) happened to have an extremely high exchange frequency with a vacancy compared with the surrounding host atoms. From Equation 10 the tracer diffusion coefficient is seen to be the product of two parts, *a correlated part*, as embodied in the tracer correlation factor, and *an uncorrelated part* that contains the jump distance squared and the jump frequency (n / t).

The tracer correlation factor itself can be expanded as:

$$f = 1 + 2\sum_{j=1}^{\infty} < \cos\theta^{(j)} > \tag{11}$$

where $< \cos\theta^{(j)} >$ is the average of the cosine of the angle between a first jump and the j'th succeeding jump of a tracer atom. Any given jump can be the first one since correlation is independent of the time origin. We would expect $< \cos\theta^{(j)} >$ to approach zero as $j \rightarrow \infty$ as the correlations die out, i.e. jumps that are separated by very many intervening jumps will be uncorrelated. In solid-state diffusion $< \cos\theta^{(1)} >$ is invariably negative because the first jump is more likely than random to be reversed, either as the direct result of the vacancy still being present as the nearest neighbour to the tracer atom, or perhaps as a result of a re-ordering jump immediately following a disordering one, or, of course, a combination of both. The $<\cos\theta^{(j)}>$ also alternate in sign. The phenomenon of tracer correlation is the subject of an extensive literature over roughly a fifty year period. It has been reviewed a number of times, see especially the classic review by Le Claire [6] and the texts [2,3].

In a very important paper published in 1982, Allnatt [7] showed that the phenomenological coefficients can also be expressed in a form very similar to the Einstein Equation (Equation 9):

$$L_{ii} = < \mathcal{R}_i \cdot \mathcal{R}_i > /6VkTt \tag{12a}$$

$$L_{ij} = < \mathcal{R}_i \cdot \mathcal{R}_j > /6VkTt \tag{12b}$$

where V is the volume of the system, k is the Boltzmann constant, T is the absolute temperature and $\mathcal{R}_i$ and $\mathcal{R}_j$ are the collective displacements of species i and species j in the time t. The collective displacement of a species in each case can also be thought of as the displacement of the centre of mass of that species. In a 'thought experiment', one imagines a volume V containing N sites on which two species A and B are homogeneously distributed. This might be a binary alloy. If one allows diffusion to occur for some time t and then calculates the displacements of the centres of mass of the A atoms ($\mathcal{R}_A$) and of the B atoms ($\mathcal{R}_B$) in that time t, then repeats the experiment a large number of times in order to produce the ensemble average <>, one would be able to use Equation 12 to calculate the diagonal phenomenological coefficients L_{AA}, L_{BB} and the off-diagonal coefficient L_{AB}. In fact, this is precisely what is routinely done in Monte Carlo computer simulations of diffusion to calculate these phenomenological coefficients; see, for example, [8,9]. Finally, it is worth noting that the form of Equation 12a means that the diagonal phenomenological coefficients must inevitably be positive. As we have already noted, the off-diagonal phenomenological coefficients can be positive or negative. It is sometimes rather loosely said that the origin of L_{AB} is in the 'interference' of the motion of A and B. This interference comes about because both A and B compete for the same defects. This comment covers cases such as A and B diffusing via different ends of a vacancy pair on cation and anion sublattices (say in an ionic compound). If A and B are able to diffuse completely independently in a material then L_{AB} would equal zero.

We have already seen that the tracer diffusion coefficient can be decomposed into a correlated part (the tracer correlation factor) and a non-correlated part (principally the product of the jump distance squared and the jump frequency). It turns out that the phenomenological coefficients can also be decomposed into analogous correlated and uncorrelated parts.

$$L_{ii} = f_{ii} a^2 C_i n_i / 6kTt \tag{13a}$$

$$L_{ij} = f_{ij}^{(i)} a^2 C_i n_i / 6kTt \tag{13b}$$

or, alternatively:

$$L_{ij} = f_{ij}^{(j)} a^2 C_j n_j / 6kTt \tag{13c}$$

where $C_i = c_i N/V$ (c_i is the site fraction of the i species and N is the total number of lattice sites in the system of total volume V). The correlated parts of the phenomenological coefficients, the f_{ij} , are termed correlation functions or, more commonly, collective correlation factors. In very much the same way that the tracer correlation factor itself can be expressed in terms of the average cosines of the angles between a given jump of a tracer atom and its succeeding jumps, see Equation 11, the diagonal and off-diagonal collective correlation factors can also be expressed in terms of the average of the cosines of the angle between a given jump of a species and the subsequent jump of the same (diagonal) species or another (off-diagonal) species [10]. The diagonal correlation factors are given by (c.f. Equation 11):

$$f_{ii} = 1 + 2\sum_{m=1}^{\infty} < \cos\theta_{ii}^{(m)} > \tag{14}$$

where $< \cos\theta_{ii}^{(m)} >$ is the average of the cosine of the angle between some jump of an atom of species i and the m'th succeeding jump of the same *or any other atom* of species i. Similar to the tracer case discussed above for $< \cos\theta^{(1)} >$, the quantity $< \cos\theta_{ii}^{(1)} >$ is invariably negative. This is discussed in a little detail below. The expressions for the off-diagonal correlation factors are a deal more complicated in notation but they are structurally related to Equation 14. For simplicity, they are given here only for a binary system:

$$f_{AB}^{(A)} = \sum_{m=1}^{\infty} < \cos\theta_{AB}^{(m)} > + \frac{C_B n_B}{C_A n_A} \sum_{m=1}^{\infty} < \cos\theta_{BA}^{(m)} > \tag{15a}$$

$$f_{AB}^{(B)} = \frac{C_A n_A}{C_B n_B} \sum_{m=1}^{\infty} < \cos\theta_{AB}^{(m)} > + \sum_{m=1}^{\infty} < \cos\theta_{BA}^{(m)} > \tag{15b}$$

where $< \cos\theta_{AB}^{(m)} >$ is the average cosine of the angle between any given jump of the A species and the m'th succeeding jump of the B species and analogously for $< \cos\theta_{BA}^{(m)} >$.

It is instructive to compare the nature of the well-known tracer correlation effect with the collective correlation effect. Consider the hexagonal lattice in Figure 1a. Here, *all* of the atoms are chemically A atoms. We assume that the atom shown as a hatched circle is a tracer of the A species and that it and the vacancy have just exchanged places. The conventional basic argument to describe the tracer correlation effect notes that *because the vacancy is still neighbouring to the tracer after a given jump of a tracer*, the tracer will then have a greater than a random probability (i.e. greater than 1/6 here) of reversing its next jump. This leads of course to $<\cos\theta^{(1)}>$ being negative as noted earlier. Collective correlation is rather different. Let us again assume that the tracer atom (which is of the A species) and the vacancy have just exchanged places. The next jump of the A species clearly can be any one of the atoms in Figure 1a since they are all A atoms including the marked one. Accordingly, in this example there can be no correlation in the jumps of the A species and $<\cos\theta_{AA}^{(1)}>$=0. It is also worth noting too that the jumps of the A species mirror those of the vacancy.

Now let us consider Figure 1b. The situation is very similar to the one just discussed except that now several B atoms are present. For simplicity, we will assume that the B atoms have exactly the same exchange frequency with the vacancy as the A atoms. Again we will assume for convenience that one of the A atoms (shown as hatched circle) is a tracer of A and has just exchanged with the vacancy. The mere presence of the B atoms means that the possibilities for the next jump of the A species are now reduced. In fact, the more B atoms that are present the fewer the possibilities there are for an A species jump. But the tracer A atom must still be there however. Because of this, the probability for that particular A species atom to jump as the next A species jump is enhanced. This has the effect of making $<\cos\theta_{AA}^{(1)}>$ negative. The more B atoms that are present, the more negative $<\cos\theta_{AA}^{(m)}>$ becomes. In the limit, where all of the A atoms have been replaced by B atoms except for the tracer one, the next A species jump can only be that tracer A atom. At this point, the collective correlation factor of the A species f_{AA} now simply becomes synonymous with the tracer correlation factor for the A atoms, f_A.

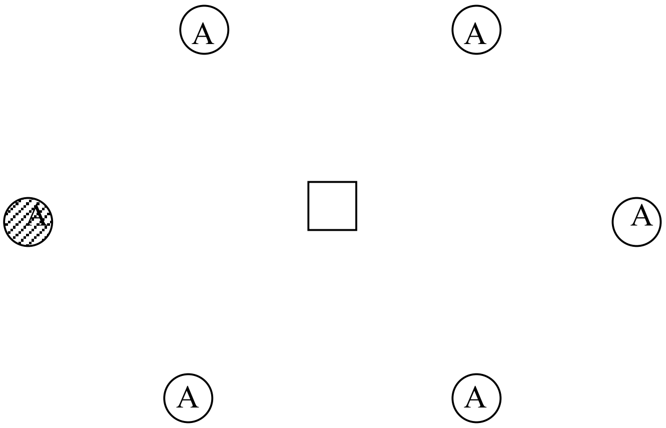

Figure 1a. Illustration of tracer and collective correlation effects (see text).

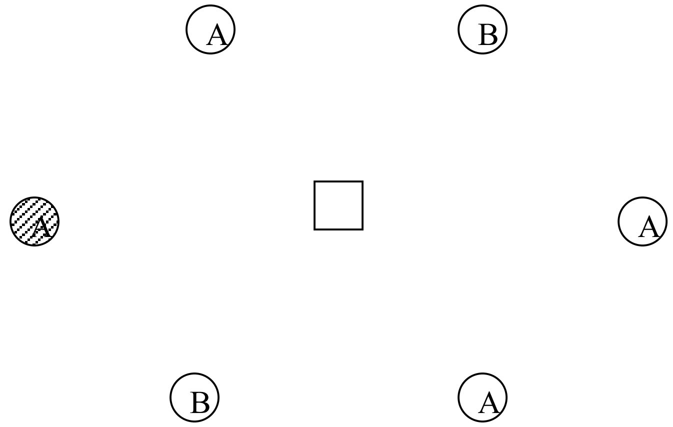

Figure 1b. Illustration of tracer and collective correlation effects (see text)

Let us briefly consider Figure 1b in order to examine off-diagonal collective correlation effects. Again we assume for convenience that one of the A atoms (the hatched one) is a tracer of *A* and has just exchanged places with the vacancy. In other words the first jump is an *A* atom jump. We are now interested in the next jump of the *B* species. Clearly, the tracer atom must still be there: its presence changes the possible types of jumps so that the first cosine $<\cos \theta_{AB}{}^{(1)}>$ will increase as the number of *B* atoms increases.

3. Relations between the phenomenological coefficients and tracer diffusion coefficients

The direct measurement of the phenomenological coefficients in the solid state is very difficult. Accordingly, there has been sustained interest in developing relations between the phenomenological coefficients and the (measurable) tracer diffusion coefficients. The first of these are the Darken Relations [11]. In essence, the Darken assumption is the neglect of the off-diagonal phenomenological coefficients entirely. The diagonal phenomenological coefficients can then be related to the corresponding tracer diffusion coefficients; for example, in a binary *AB* alloy, L_{AA} is then simply related to the tracer diffusion coefficient of *A*, D_A^*:

$$L_{AA} = C_A D_A^* / kT\,, \qquad L_{AB} = 0 \tag{16}$$

We have already seen that the neglect of the off-diagonal phenomenological coefficient can be dangerous in principle. However, in most cases, it is reasonable as a first rough approximation.

The second set of relations between the phenomenological coefficients and tracer diffusion coefficient are the Manning Relations [12,13] which were developed originally for the random alloy in which the various atomic species and the isolated vacancy are randomly mixed. In the Manning Relations, the phenomenological coefficients are directly related to the tracer diffusion coefficients by:

$$L_{ii} = \frac{C_i D_i^*}{kT}\left(1 + \frac{2C_i D_i^*}{M_0 \sum\limits_k C_k D_k^*}\right), \qquad L_{ij} = \frac{2C_i D_i^* C_j D_j^*}{kT(M_0 \sum\limits_k C_k D_k^*)}, \quad \text{for } i \neq j. \qquad (17)$$

where $M_0 = 2f_0/(1-f_0)$ and f_0 is the geometric tracer correlation factor for the lattice, e.g. f_0=0.78146… for the f.c.c. lattice [6]. It is worth noting that the Manning Relations can also be obtained on the basis of two somewhat intuitive assumptions without recourse to the random alloy model [14], thereby suggesting that they have more general validity. Indeed, various computer simulations have shown that the Manning Relations are quite good approximations, even for ordered alloys, at least at low levels of order before concatenated mechanisms such as the six-jump cycle start to become important [15-17]. The Manning Relations have also been re-derived specifically for the ordered alloy [18].

The self-consistent theory of Moleko, Allnatt and Allnatt [19] also provides relations between the phenomenological coefficients and the tracer diffusion coefficients for the random alloy, but these relations are not expressible in a convenient closed form. Nonetheless, it is still possible to use straightforward numerical methods to find all of the L_{ij} from a given set of tracer diffusion coefficients for all of the atomic species [20]. Computer simulations [9] have shown these relations to be more accurate than those provided by Manning and described above.

The third relation is the Heumann relation [21] that was determined after consideration of the five-frequency model, see also [3,22]. This model, which was first proposed by Lidiard [23], is very useful for describing solute and host diffusion kinetics in f.c.c. metals and f.c.c. sublattices in ionic crystals when the vacancy-solute interaction is localized. The five frequencies in the model refer to the following: a vacancy-host atom (A) exchange frequency w_0, a vacancy-host (A) exchange frequency w_1 referring to a 'rotational jump' around a solute atom i.e. from one nearest neighbour site to another of the solute, a vacancy-solute (B) exchange frequency w_2, a vacancy-host (A) atom exchange frequency w_3 that brings the vacancy to a site neighbouring to the solute atom (this is usually called the 'associative jump'), and finally a vacancy-host atom (A) exchange frequency w_4 that is the reverse of the w_3 jump (this is usually called the 'dissociative jump'). It can be shown that for a dilute alloy in the limit where the solute concentration $C_B \rightarrow 0$, the ratio of $L_{AB}(0) / L_{BB}(0)$ is given by [21]:

$$\frac{L_{AB}(0)}{L_{BB}(0)} = \frac{D_A^*(0)}{D_B^*(0)}\left(f_0^{-1} - \frac{D_A^I(0)}{D_A^*(0)} \right) \tag{18}$$

where $D_A^*(0)$, $D_B^*(0)$ are the tracer diffusion coefficients of A and B and $D_A^I(0)$ is the intrinsic diffusion coefficient of A in the dilute alloy at the limit $C_B \rightarrow 0$.

4. Relations among the phenomenological coefficients

Recently, various relations, usually called ‘sum-rules’, have been identified between the phenomenological coefficients in randomly mixed systems, in effect reducing the number of independent phenomenological coefficients. These relations are of quite some interest. First of all, the assumption of random mixing in diffusion problems is a very common one indeed. Experience gained from many Monte Carlo computer simulations has shown that a non-random distribution of components does not change the basic diffusion kinetics behaviour very much unless long range order or clustering is present. In other words, the effect on the jump frequency and the correlation factors, tracer or collective, of a non-random distribution is relatively small. Indeed, the main effect of a change in the distribution of the components is in fact in the thermodynamic factor appearing in expressions for the chemical diffusion coefficient. In general, the thermodynamic factor can be treated quite separately from the jump frequency and correlation parts. In collective diffusion problems it has been found that a considerable degree of simplification is frequently possible through the use of sum-rule relations: solution of problems such as demixing in oxides [24], chemical diffusion in mixed cation ionic crystals [25] and chemical diffusion in multicomponent alloys [26] have all benefited considerably through the application of these sum-rules.

Here, as an example, we will deal with the relation or sum-rule between the phenomenological coefficients in the random alloy model with the vacancy mechanism operating. The random alloy model is an important model because it is a convenient vehicle for describing the diffusion kinetics in concentrated multicomponent alloys. In the random alloy model, the atom-vacancy exchange frequencies, w_i, can be considered in two rather different ways. In the first way, the frequencies can be classified simply as explicit frequencies that depend only on the species of the atom and not the surroundings. For example, in the binary random alloy, w_A then simply represents the A atom vacancy exchange frequency of a given A atom at all compositions and environments. In the second and more general way, one considers that the w_i represent an *average* frequency of species i at a given composition. For example, in the binary random alloy, w_A would then represent the *average* frequency of a given A atom as it migrates through the lattice sampling the various environments. Since the average environment of an atom will obviously change with composition, then the w_i can also be expected to change with composition, see for example [27].

In 1989, Moleko and Allnatt identified the following sum-rule for the M-component random alloy with the vacancy mechanism operating and at arbitrary vacancy concentration [28]:

$$\sum_{i=1}^{M} L_{ij} w_j / w_i = A c_V w_j C_j , \qquad j = 1,\ldots, M \tag{19}$$

where A is given by $A = z\, a^2/6kT$ (z is the coordination number and a is the jump distance for a vacancy jump). In effect, the sum-rule relates the phenomenological coefficients to the vacancy-atom exchange frequencies and, in so doing, reduces the number of independent phenomenological coefficients. For example, in the binary random alloy, there is only one independent phenomenological coefficient and not three. In the ternary random alloy, the number of phenomenological coefficients is reduced from six to three. This sum-rule was implied in earlier diffusion kinetics work on the random alloy model at a very low vacancy concentration, see, for example, the Manning formalism [13], but was simply not identified as such at the time. The sum-rule can also be restated in terms of the collective correlation factors as:

$$\sum_{i=1}^{M} f_{ij}^{(j)} w_j / w_i = 1 , \qquad j = 1,\ldots,M \tag{20}$$

The derivation of the sum-rule is beyond the depth of the present introductory review but the general principle can be described readily in words. We consider a random alloy with the vacancy mechanism operating. We assume that an atom of species i has just made a jump. We accept this jump as the initial point in time and take a 'snapshot' of the system. Then, for each quantity like L_{ij}, we need to consider how the system changes from the initial configuration (after the jump of the i atom) during the jumping of the vacancies: i.e. after the first jump, the second jump and so on. At each moment in time we choose a vacancy randomly from the current configuration (there is a specific probability for the system to get to this configuration starting with the initial one), then we choose a *random direction* and find an atom of some type (or another vacancy). Accordingly, for each direction there is a defined probability that the vacancy makes an exchange with the atom there. If this is an atom of species j then a contribution to the cosine between the first jump of the i atom and the final jump of the j atom (the basic quantity in L_{ij} see Equations 14, 15) is equal to the probability for a system to get to the current configuration multiplied by the vacancy concentration and multiplied by the vacancy-atom j exchange frequency (and divided by the co-ordination number). Therefore each contribution of this type for a different atomic species j differs from one another only by the corresponding exchange frequency. After all the summations are done we end up with the sum-rule relation as shown in Equation 19.

For the binary alloy AB the sum-rule relation is:

$$L_{AA} + \frac{w_A}{w_B} L_{AB} = L_{AA}^{(0)} = c_V C_A w_A A , \tag{21a}$$

$$L_{BB} + \frac{w_B}{w_A} L_{AB} = L_{BB}^{(0)} = c_V C_B w_B A \,, \tag{21b}$$

where c_V is the vacancy fraction.

Since the identification of the first sum-rule by Moleko and Allnatt for the vacancy mechanism in the random alloy [28], various sum-rule relations have been identified for a number of other mechanisms and situations including the dumb-bell interstitial mechanism in the binary random alloy [29], the divacancy mechanism in the f.c.c. random alloy [30], the vacancy-pair mechanism in strongly ionic materials with randomly mixed cations [31], the vacancy mechanism for a model of an intermetallic compound (with randomly mixed sublattices) [32] and certain parts of a reduced five-frequency model for solute and solvent diffusion in the f.c.c. lattice with the vacancy mechanism operating [33]. No doubt further sum-rules relating the phenomenological coefficients will emerge in the future.

5. Conclusions

In this review, which was intended to provide an introduction to the subject, we introduced the phenomenological transport coefficients in solid state diffusion and discussed their structure and physical meaning. Next, we discussed the Darken, the Manning, the Moleko, Allnatt and Allnatt and the Heumann expressions relating the phenomenological coefficients to the (measurable) tracer diffusion coefficients. Finally, we discussed the relationships (sum-rules) among the phenomenological coefficients themselves in randomly mixed systems and noted their applicability for simplifying collective diffusion problems.

Acknowledgments

We wish to thank the Australian Research Council for its support of this research under the Discovery Project Grants Scheme. One of us (I.V.B.) wishes to thank the Australian Research Council for the award of a Professorial Fellowship.

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