12 Irreversible Thermodynamics and Diffusion

12.1 General Remarks

So far, we have discussed the usual descriptions of atomic transport in solids such as diffusion and ionic conduction. Fick's first law was introduced as a postulate describing a linear relationship between the flux of a diffusing species i and its concentration gradient. Ohm's law describes a linear relation between the flux of charged species and the gradient of the electric potential. Fourier's law is a linear relation between the flux of heat and the temperature gradient. However, these simple laws may not be sufficient even within the stated limitation of linear effects. For example, Fick's first law is sometimes insufficient for attaining equilibrium of species i because it does not recognise all driving forces, direct or indirect, acting on i. It may be necessary to allow that a concentration gradient in one species gives rise to a flux of another.

Diffusion, electrical conduction, and heat flow are examples of irreversible processes. Non-equilibrium thermodynamics provides a general phenomenological theory of such processes. In this chapter, we briefly introduce the macroscopic equations of this theory suggested for the first time by Lars Onsager (1903–1976), the Norwegian Nobel laureate of 1968. Wide-ranging treatments, especially of macroscopic formulations of this theory can be found in textbooks of de Groot and Mazur [1] and Haase [2]. A treatment with emphasis on the foundations of irreversible thermodynamics by statistical mechanics has been provided by Kreuzer [3].

Non-equilibrium thermodynamics is based on three major assumptions:

1. The Onsager transport equations of atoms, heat, and electrons are linear relations between the fluxes $\boldsymbol{J}_i$ and the so-called generalised thermodynamic forces $\boldsymbol{X}_i$. The phenomenological response for the complete set of n fluxes assumes a linear form

$$\boldsymbol{J}_i = \sum_{j=1}^{n} L_{ij} \boldsymbol{X}_j \,, \tag{12.1}$$

   where L_{ij} are called the *phenomenological coefficients* or *transport coefficients*. The matrix of coefficients is also called the *Onsager matrix* or simply the **L** matrix. The great importance of the phenomenological coefficients stems from their independence of driving forces. For example, in solid-state diffusion problems the coefficients L_{ij} are functions of temperature and pressure, but they do not depend on the gradient of the chemical potential.

2. The Onsager matrix is composed in part of diagonal terms, L_{ii}, connecting each generalised force with its conjugate flux. For example, a gradient of the chemical potential causes a generalised diffusion 'force', and the associated diffusion response is determined by the material's diffusivity. Similarly, an applied temperature gradient creates a generalised force associated with heat flow. In this case, the amount of heat flow is determined by the thermal conductivity.

   The Onsager matrix also contains off-diagonal coefficients, L_{ij}. Each off-diagonal coefficient determines the influence of a generalised force on a non-conjugate flux. For example, a concentration gradient of one species can give rise to a flux of another species. The electric field, which exerts a force on electrons in metals to produce an electric current has a cross-influence on the flow of heat, known as the *Peltier effect.* Conversely, the thermal force (temperature gradient) that normally causes heat flow, also has a cross-influence on the distribution of electrons – known as the Thomson effect. The Thomson and Peltier effects combine and provide the basis for *thermoelectric devices*: thermopiles can be used to convert heat flow into electric current; in thermocouples a voltage is produced by a temperature difference. Another example is that an electronic current and the associated 'electron wind' causes a flow of matter called *electromigration* (see also Chap. 11). Electromigration can be a major cause for the failure of interconnects in microelectronic devices.

   The Onsager matrix is symmetric, provided that no magnetic field is present. The relationship

$$L_{ij} = L_{ji} \tag{12.2}$$

   is known as the *Onsager reciprocity theorem.*

3. The central idea of non-equilibrium thermodynamics is that each of the thermodynamic forces acting with its flux response dissipates free energy and produces entropy. The characteristic feature of an irreversible process is the generation of entropy. The rate of entropy production, σ, is basic to the theory. It can be written as:

$$T\sigma = \sum_{i}^{n} \boldsymbol{J}_i \boldsymbol{X}_i + \boldsymbol{J}_q \boldsymbol{X}_q \,. \tag{12.3}$$

   $\boldsymbol{J}_i$ denotes the flux of atoms i and $\boldsymbol{J}_q$ the flux of heat.

   The thermodynamic forces require some explanation: $\boldsymbol{X}_i$ and $\boldsymbol{X}_q$ are measures for the imbalance generating the pertinent fluxes. The thermal force $\boldsymbol{X}_q$

$$\boldsymbol{X}_q = -\frac{1}{T}\boldsymbol{\nabla} T \tag{12.4}$$

is determined by the temperature gradient ∇T. When only external forces are acting, the $\boldsymbol{X}_i$ are identical with these forces. If, for example, an ionic system with ions of charge q_i is subject to an electric field $\boldsymbol{E}$, each ion of type i experiences a mechanical force $\boldsymbol{F}_i = q_i\boldsymbol{E}$. In the presence of a composition gradient the appropriate force is related to the gradient of chemical potential $\nabla\mu_i$. Then, the thermodynamic force X_i is the sum of the external force exerted by the electric field and the gradient of the chemical potential of species i:

$$\boldsymbol{X}_i = \boldsymbol{F}_i - T\boldsymbol{\nabla}\left(\frac{\mu_i}{T}\right) = \boldsymbol{F}_i - \boldsymbol{\nabla}\mu_i \,. \tag{12.5}$$

Here the gradient of the chemical potential is that part due to gradients in concentration, but not to temperature.

Thermodynamic equilibrium is achieved when the entropy production vanishes:

$$\sigma = 0\,. \tag{12.6}$$

Then, there are no irreversible processes any longer and the thermodynamic forces and the fluxes vanish.

12.2 Phenomenological Equations of Isothermal Diffusion

In this section, we apply the phenomenological transport equations to solid-state diffusion problems. We give a brief account of some major aspects relevant for transport of matter, which are treated in more detail in [4–6]. The phenomenological equations are on the one hand very powerful. On the other hand, they lead quickly to cumbersome expressions. Therefore, only a few examples will be given. Detailed expressions for the phenomenological coefficients in terms of the elementary jump characteristics must be provided by atomistic models.

Here, we consider the consequences of phenomenological equations for isothermal diffusion. In a binary system we have 3 transport coefficients – two diagonal ones and one off-diagonal coefficient. For a ternary system six transport coefficients must be taken into account. One of the crucial questions is, whether the off-diagonal terms are sufficiently different from zero to be important for data analysis. If they are negligible, the analysis can be largely simplified. This assumption in made in some models for diffusion, e.g., in the derivation of the Darken equations for a binary system (see Chap. 10). We shall see below, however, that neglecting off-diagonal terms is not always justified.

12.2.1 Tracer Self-Diffusion in Element Crystals

Fundamental mobilities of atoms in solids can be obtained by monitoring radioactive isotopes (‘tracers’) (see Chap. 13). Let us consider the diffusion of an isotope A^* in a solid A, where A^* and A are chemically identical. Let us further suppose that diffusion occurs via vacancies (index V). Taking into account the reciprocity relations, the Onsager flux equations can be written as[1]:

$$\begin{aligned}
J_{A^*} &= L_{A^*A^*}X_{A^*} + L_{A^*A}X_A + L_{A^*V}X_V,\\
J_A &= L_{A^*A}X_{A^*} + L_{AA}X_A + L_{AV}X_V,\\
J_V &= L_{A^*V}X_{A^*} + L_{AV}X_A + L_{VV}X_V\,.
\end{aligned} \tag{12.7}$$

Let us now suppose that in an isothermal experiment vacancies are always maintained at thermal equilibrium. This is possible if sources and sinks of vacancies such as dislocations are sufficiently numerous and active during the diffusion process. Under such conditions, the chemical potential of vacancies is constant everywhere and hence $X_V = 0$. Then, the flux equations for the components apply directly in the laboratory reference frame:

$$\begin{aligned}
J_{A^*} &= L_{A^*A^*}X_{A^*} + L_{A^*A}X_A\\
J_A &= L_{A^*A}X_{A^*} + L_{AA}X_A\,.
\end{aligned} \tag{12.8}$$

Tracer atoms A^* and matrix atoms A form an ideal (isotopic) solution. Let C_{A^*} and C_A denote their concentrations and μ_{A^*} and μ_A their chemical potentials, respectively. These are:

$$\begin{aligned}
\mu_{A^*} &= \mu^0_{A^*}(p,T) + k_{\mathrm{B}}T\ln C_{A^*},\\
\mu_A &= \mu^0_A(p,T) + k_{\mathrm{B}}T\ln C_A\,.
\end{aligned} \tag{12.9}$$

The reference potentials $\mu^0_{A^*}(p,T)$ and $\mu^0_A(p,T)$ depend on pressure and temperature but not on concentration. The corresponding forces are

$$\begin{aligned}
X_{A^*} &= -k_{\mathrm{B}}T\frac{1}{C_{A^*}}\frac{\partial C_{A^*}}{\partial x},\\
X_A &= -k_{\mathrm{B}}T\frac{1}{C_A}\frac{\partial C_A}{\partial x}\,.
\end{aligned} \tag{12.10}$$

For tracer self-diffusion in an element crystal we have

$$J_{A^*} + J_A = 0\,, \tag{12.11}$$

i.e. the fluxes are equal in magnitude and opposite in sign. Furthermore, since $C_{A^*} + C_A$ is constant, the concentration gradients are equal in magnitude and opposite in sign, i.e. $\partial C_{A^*}/\partial x = -\partial C_A/\partial x$. We then have

$$J_{A^*} = -\underbrace{\left(\frac{L_{A^*A^*}}{C_{A^*}} - \frac{L_{A^*A}}{C_A}\right)k_{\mathrm{B}}T}_{D_A^{A^*}}\frac{\partial C_{A^*}}{\partial x}, \tag{12.12}$$

$$J_A = -\left(\frac{L_{AA}}{C_A} - \frac{L_{A^*A}}{C_{A^*}}\right)k_{\mathrm{B}}T\frac{\partial C_A}{\partial x}\,. \tag{12.13}$$

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[1] For simplicity reasons we consider unidirectional flow (in x direction) and omit the vector notation.

Since $J_{A^*} = -J_A$ we get:

$$\frac{L_{A^*A^*}}{C_{A^*}} - \frac{L_{A^*A}}{C_A} = \frac{L_{AA}}{C_A} - \frac{L_{A^*A}}{C_A^*} . \tag{12.14}$$

Recalling that the diffusivity of a tracer is defined through Fick's law

$$J_{A^*} = -D_A^{A^*} \frac{\partial C_{A^*}}{\partial x} , \tag{12.15}$$

we obtain by comparison with Eqs. (12.12):

$$D_A^{A^*} = \left(\frac{L_{A^*A^*}}{C_{A^*}} - \frac{L_{A^*A}}{C_A} \right) k_{\mathrm{B}} T = \left(\frac{L_{AA}}{C_A} - \frac{L_{A^*A}}{C_{A^*}} \right) k_{\mathrm{B}} T \tag{12.16}$$

Since for tracer diffusion always $C_{A^*} \ll C_A$, we also have

$$D_A^{A^*} = \frac{L_{A^*A^*}}{C_{A^*}} k_{\mathrm{B}} T = \left(\frac{L_{AA}}{C_A} - \frac{L_{A^*A}}{C_{A^*}} \right) k_{\mathrm{B}} T . \tag{12.17}$$

The first term on the right-hand side of Eq. (12.17) is sometimes denoted as the 'true' self-diffusion coefficient, $D_A^A \equiv k_{\mathrm{B}} T L_{AA}/C_A$. The quantity D_A^A denotes self-diffusion in the absence of a tracer – a quantity that is difficult to measure directly[2]. We then get

$$D_A^{A^*} = \underbrace{\left[1 - \frac{L_{A^*A}}{L_{AA}} \frac{C_A}{C_{A^*}} \right]}_{f} D_A^A , \tag{12.18}$$

where f is the correlation factor of tracer self-diffusion (see Chap. 7). This equation shows that the coupling between the fluxes is the origin of correlation effects. For $L_{A^*A} = 0$ the correlation factor would be unity. We also note that in addition to the defect two atomic species (here A^* and A) must be present to obtain correlation. This is a rule that we have already stated in Chap. 4.

12.2.2 Diffusion in Binary Alloys

In this section, we discuss the Onsager equations for solid-state diffusion via vacancies in a substitutional binary alloy and the structure and physical meaning of the pertinent phenomenological coefficients. We suppose that the system is isothermal and that external forces are absent, i.e. $X_q = 0$ and $F_i = 0$. We then have a system of two atomic components A and B and vacancies (index V) on a single lattice. Taking into account the reciprocity relations the Onsager flux equations can be written as:

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[2] In favourable cases, PFG-NMR (see Chap. 13) can be applied to measure this quantity.

$$\begin{aligned} J_A &= L_{AA}X_A + L_{AB}X_B + L_{AV}X_V, \\ J_B &= L_{AB}X_A + L_{BB}X_B + L_{BV}X_V, \\ J_V &= L_{AV}X_A + L_{BV}X_B + L_{VV}X_V\,. \end{aligned} \tag{12.19}$$

To promote atomic diffusion, either A or B atoms exchange with vacancies on the same lattice. Therefore, the fluxes defined relative to that lattice (in regions outside the diffusion zone) necessarily must obey

$$J_V = -(J_A + J_B)\,. \tag{12.20}$$

In other words, the flux of vacancies is equal and opposite in sign to the total flux of atoms[3]. In view of the constraint imposed by Eq. (12.20), each term on the right-hand side of Eq. (12.19) must vanish column by column. We get:

$$\begin{aligned} (L_{AA} + L_{AB} + L_{AV})X_A &= 0, \\ (L_{AB} + L_{BB} + L_{BV})X_B &= 0, \\ (L_{AV} + L_{BV} + L_{VV})X_V &= 0\,. \end{aligned} \tag{12.21}$$

These equations must hold for arbitrary values of the forces X_i. Hence each bracket term must vanish separately:

$$\begin{aligned} -L_{AV} &= L_{AA} + L_{AB}\,, \\ -L_{BV} &= L_{AB} + L_{BB}\,, \\ -L_{VV} &= L_{AV} + L_{BV}\,. \end{aligned} \tag{12.22}$$

These equations show that the kinetic coefficients of the vacancy flux are related to those of the atomic species. If Eq. (12.22) is combined with the flux equations (12.19), the following expressions for the fluxes of the atomic species are obtained:

$$\begin{aligned} J_A &= L_{AA}(X_A - X_V) + L_{AB}(X_B - X_V), \\ J_B &= L_{AB}(X_A - X_V) + L_{BB}(X_B - X_V)\,. \end{aligned} \tag{12.23}$$

The vacancy flux may be written as

$$J_V = L_{AV}(X_A - X_V) + L_{BV}(X_B - X_V)\,. \tag{12.24}$$

Let us now assume that vacancies are always maintained close to their thermal equilibrium concentration. Then, the chemical potential of vacancies is constant everywhere and $X_V = 0$. Equations (12.23) then reduce to

$$\begin{aligned} J_A &= L_{AA}X_A + L_{AB}X_B\,, \\ J_B &= L_{AB}X_A + L_{BB}X_B\,. \end{aligned} \tag{12.25}$$

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[3] In this context the reader should also see the discussion of the 'vacancy wind' in Chap. 10.

The chemical potential of a real solid solution is given by

$$\mu_i = \mu_i^0(p,T) + k_{\mathrm{B}}T\ln(N_i\gamma_i)\,, \tag{12.26}$$

where γ_i is the activity coefficient and N_i mole fractions of species i. Using $N_A + N_B \approx 1$, i.e. $C_V \ll C_A + C_B$, we obtain:

$$\begin{aligned} J_A &= -\underbrace{\left(\frac{L_{AA}}{N_A} - \frac{L_{AB}}{N_B}\right) k_{\mathrm{B}}T\mathit{\Phi}}_{D_A^I}\frac{\partial N_A}{\partial x}, \\ J_B &= -\underbrace{\left(\frac{L_{BB}}{N_B} - \frac{L_{AB}}{N_A}\right) k_{\mathrm{B}}T\mathit{\Phi}}_{D_B^I}\frac{\partial N_B}{\partial x}\,. \end{aligned} \tag{12.27}$$

Here we have used that the Gibbs-Duhem relation of thermodynamics provides an additional constraint: the factors $(1 + \partial\ln\gamma_A/\partial\ln N_A)$ and $(1+\partial\ln\gamma_B/\partial\ln N_B)$ are equal to each other. This common factor is abbreviated by $\mathit{\Phi}$ and denoted as the *thermodynamic factor* (see Chap. 10). We note that one common thermodynamic factor exists for binary alloys. For ternary or higher order systems several thermodynamic factors are necessary.

Equations (12.27) have the form of Fick's first law with diffusion coefficients, D_A^I and D_B^I, denoted as the *intrinsic diffusion coefficients*:

$$\begin{aligned} D_A^I &= \frac{L_{AA}}{N_A}\left(1 - \frac{L_{AB}N_A}{L_{AA}N_B}\right) k_{\mathrm{B}}T\mathit{\Phi}, \\ D_B^I &= \frac{L_{BB}}{N_B}\left(1 - \frac{L_{AB}N_B}{L_{BB}N_A}\right) k_{\mathrm{B}}T\mathit{\Phi}\,. \end{aligned} \tag{12.28}$$

The intrinsic diffusivities are in general different and can be determined separately. The two quantities that are usually measured to obtain the intrinsic diffusivities are (i) the chemical interdiffusion coefficient $\tilde{D}$, and (ii) the Kirkendall velocity v_K (see Chap. 10):

In interdiffusion plus Kirkendall experiments, diffusion couples (either A-B or $\mathrm{A}_x\mathrm{B}_{1-x}$-$\mathrm{A}_y\mathrm{B}_{1-y}$) are studied and the initial interfaces contain inert markers. The fluxes J_A and J_B relative to the local crystal lattice are generally such that their sum is non-zero, which according to Eq. (12.20) implies that the vacancy flux is also non-zero. Since the fluxes vary with position one also has:

$$\mathrm{div}J_V = \mathrm{div}(-J_A - J_B) \;\neq\; 0\,. \tag{12.29}$$

This condition requires vacancies to disappear or to be created at inner sources or sinks (e.g., dislocations) in the diffusion zone of the sample. When this occurs, regions where diffusion fluxes are large will move relative to regions where fluxes are small. The concentration distribution after an interdiffusion experiment, analysed with respect to the unaffected ends of the couple, links the concentration gradients to the fluxes of atoms relative to the fixed parts of the sample. In the simplest case these fluxes are

$$\begin{aligned} J'_A &= J_A - N_A(J_A + J_B)\,, \\ J'_B &= J_B - N_B(J_A + J_B)\,. \end{aligned} \tag{12.30}$$

Here we have assumed that the velocity v of the local lattice relative to the non-diffusing parts of the sample is $-v(J_A + J_B)$. This implies that there is no change in the cross-section or shape of the sample, i.e. that the vacancies condense on lattice planes perpendicular to the diffusion flow. It also implies that the volume per lattice site remains constant. From Eqs. (12.27), (12.30), and $N_A + N_B = 1$, because the vacancy site fraction is very small, it also follows

$$\begin{aligned} J'_A &= -(N_B D^I_A + N_A D^I_B)\frac{\partial N_A}{\partial x}, \\ J'_B &= -(N_B D^I_A + N_A D^I_B)\frac{\partial N_B}{\partial x}\,. \end{aligned} \tag{12.31}$$

The quantity

$$\tilde{D} = N_B D^I_A + N_A D^I_B\,. \tag{12.32}$$

is the *interdiffusion coefficient* introduced already in Chap. 10. It is the same for both components. The Kirkendall velocity v_K characterises the motion of the diffusion zone relative to the fixed end of the sample and can be observed by inserting inert markers (see Chap. 10). Since $\partial N_A/\partial x = -\partial N_B/\partial x$ it is given by:

$$v_K = (D^I_A - D^I_B)\frac{\partial N_A}{\partial x}\,. \tag{12.33}$$

The Kirkendall effect is a consequence of unequal intrinsic diffusivities and results from the non-zero vacancy flux in the diffusion zone.

We now have convinced ourselves that the equations of Darken and Manning discussed in Chap. 10 have a basis in the phenomenological equations. We note, however, that although measurements of interdiffusion and the Kirkendall shift have been made on a number of alloy systems it is clear that only two quantities, D^I_A and D^I_B, can be obtained. This is insufficient to deduce the three independent phenomenological coefficients L_{AA}, L_{AB}, and L_{BB} for a binary alloy system.

Such a situation, in which the number of experimentally accessible quantities is less than the number of the independent Onsager coefficients, is not uncommon. This is one reason for the theoretical interest in these coefficients. It is also the reason for the interest in relations between the phenomenological coefficients. Such relations are called ‘sum rules’. Sum rules have been identified in several cases [6] and some of them are discussed in Sect. 12.3.2.

12.3 The Phenomenological Coefficients

The physical meaning of diffusion coefficients is well appreciated. However, this is less so for the phenomenological coefficients. The purpose of this section is to provide some insight into the phenomenological coefficients, their structure, relations between phenomenological coefficients and diffusion coefficients, and relations among phenomenological coefficients. An introduction for non-specialists in this area, which we follow in parts below, has been given by Murch and Belova [6].

Consider, for example, diffusion in a binary alloy. We have eliminated the vacancies as a third component because we have made the assumption that vacancies are maintained at their equilibrium concentration. Then, it suffices to introduce the phenomenological coefficients L_{AA}, L_{AB}, and L_{BB} as we have done in the previous section. According to the Onsager reciprocity theorem the $\mathbf{L}$ matrix is symmetric, i.e. $L_{AB} = L_{BA}$. We simply have three independent coefficients, two diagonal ones and one off-diagonal coefficient.

Let us now consider a 'thought experiment': suppose that A atoms in a binary AB alloy can respond to an external electric field E but the B atoms cannot. This is expressed by writing the driving force on A with charge q_A as $X_A = q_A E$, whereas the driving force on B is $X_B = 0$. One might first expect that the A atoms would simply drift in the field and the B atoms would be unaffected. The Onsager flux equations show indeed that the flux of A atoms is given by $J_A = L_{AA} q_A E$. But the Onsager flux equations also show that the flux of B atoms is not zero but given by $J_B = L_{AB} q_A E$. This equation says that the B atoms should also drift in the field, although the B atoms do not feel the field directly. 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 coefficient L_{AB} can be either positive or negative depending on the type of interaction. If L_{AB} were to be negative, it would mean that the B atoms would drift up-field whilst the A atoms drift down-field. This example may suffice to illustrate that the off-diagonal coefficient can be responsible not only for an atomic flux but also that it can change the magnitude and even the direction of an atom flux.

As discussed in Chap. 4, the tracer diffusion coefficient is related to the mean square of the displacement $\boldsymbol{R}$ of a particle during time t as [8]:

$$D^* = \frac{\langle \boldsymbol{R}^2 \rangle}{6t}\,, \tag{12.34}$$

where the brackets $\langle\rangle$ indicate an average over an ensemble of a large number of particles. This relation is called the *Einstein relation* or sometimes also the *Einstein-Smoluchowski relation.* The diffusion coefficient is understood to be a tracer diffusion coefficient indicated by the superscript * placed on D. The implication is that in principle we can follow each particle explicitly.

The Einstein expression for tracer diffusion coefficient is usually expanded for solid-state diffusion according to 'hopping models', in which atoms jump from one site to another in a lattice with a long residence time at lattice sites between the jumps. For the simplest case, diffusion on a cubic Bravais lattice with jump distance d and jump rate Γ, we have (see Chap. 6)

$$D^* = \frac{1}{6} d^2 \Gamma f \tag{12.35}$$

where f is the tracer correlation factor. This equation shows that the tracer diffusion coefficient is the product of two parts: a *correlated part* embodied in the tracer correlation factor and an *uncorrelated part* that contains the jump distance squared and the jump rate. We remember that according to Eq. (7.22) the tracer correlation factor can be expanded as

$$f = 1 + 2 \sum_{j=1}^{\infty} \langle \cos \theta^{(j)} \rangle \, . \tag{12.36}$$

$\langle \cos \theta^{(j)} \rangle$ is the average of the cosine of the angle between the first and the j's succeeding tracer jump. In vacancy-mediated solid-state diffusion $\langle \cos \theta^{(1)} \rangle$ is invariably negative because the first jump is more likely to be reversed, either as the result of the vacancy being still present at the nearest-neighbour site to the tracer, or perhaps as a result of re-ordering jump immediately following a disordering one, or a combination of both. For a vacancy mechanism the values of $\langle \cos \theta^{(j)} \rangle$ also alternate in sign. The phenomenon of tracer correlation has been the subject of an extensive literature over several decades and is discussed in Chap. 7.

In 1982 ALLNATT [7] showed on the basis of a linear response theory that the phenomenological coefficients for isothermal diffusion in solids can be expressed via generalised Einstein formulae, similar in character to the Einstein-Smoluchowski relation. These relations can be written as:

$$\begin{aligned} L_{ii} &= \frac{\langle \boldsymbol{R}_i \cdot \boldsymbol{R}_i \rangle}{6 V k_{\mathrm{B}} T t}, \\ L_{ij} &= \frac{\langle \boldsymbol{R}_i \cdot \boldsymbol{R}_j \rangle}{6 V k_{\mathrm{B}} T t}, \end{aligned} \tag{12.37}$$

where $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$ are the collective displacements of atoms i and j, V is the volume of the system. The collective displacement of a species in each case can be thought of as the displacement of the centre of mass of that species. Imagine in a 'thought experiment' a volume V containing N lattice sites on which two species A and B are randomly distributed. This might represent a binary alloy. Let diffusion occur for some time t. Then, we calculate the displacements of the centres of mass of A atoms, $\boldsymbol{R}_A$, and of B atoms, $\boldsymbol{R}_B$, and repeat the experiment a large number of times in order to produce the ensemble average. In this way, we would be able to calculate the phenomenological coefficients L_{AA}, L_{BB}, and L_{AB} from Eqs. (12.37). This provides indeed a convenient route for the evaluation of the phenomenological coefficients in Monte Carlo computations (see, e.g., [9, 10]).

Similar to the tracer diffusion coefficient the phenomenological coefficients can be decomposed into correlated and into non-correlated parts

$$\begin{aligned} L_{ii} &= \frac{f_{ii} d^2 C_i n_i}{6 k_\mathrm{B} T t}, && (12.38) \\ L_{ij} &= \frac{f_{ij}^{(i)} d^2 C_i n_i}{6 k_\mathrm{B} T t}, \quad \text{or} \quad \text{alternatively} && (12.39) \\ L_{ij} &= \frac{f_{ij}^{(j)} d^2 C_j n_j}{6 k_\mathrm{B} T t}\,. && (12.40) \end{aligned}$$

n_i denotes the number of jumps of species i during the time t. $C_i = N_i N/V$ with N_i denoting the fraction of species i and N the total number of sites in volume V. The correlated parts of the phenomenological coefficients, the f_{ij}, are denoted as the *correlation functions or collective correlation factors*. In very much the same way that the tracer correlation factors can be expressed in terms of the average cosines of the angles between a given jump of the tracer and its succeeding jumps via Eq. (12.36), 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) or another (off-diagonal) species. The diagonal correlation factors are given by

$$f_{ii} = 1 + 2 \sum_{k=1}^{\infty} \langle \cos \theta_{ii}^{(k)} \rangle \,, \qquad (12.41)$$

where $\langle \cos \theta_{ii}^{(k)} \rangle$ is the average of the cosine of the angle between some jump of an atom of species i and the k'th succeeding jump of the same or another atom of species i. The expressions for the off-diagonal collective correlation factors are a bit more complicated in notation, but they are structurally related to Eq. (12.41). For simplicity, the following expression are given only for a binary system:

$$\begin{aligned} f_{AB}^{(A)} &= \sum_{k=1}^{\infty} \langle \cos \theta_{AB}^{(k)} \rangle + \frac{C_B n_B}{C_A n_A} \sum_{k=1}^{\infty} \langle \cos \theta_{BA}^{(k)} \rangle, && (12.42) \\ f_{AB}^{(B)} &= \frac{C_A n_A}{C_B n_B} \sum_{k=1}^{\infty} \langle \cos \theta_{AB}^{(k)} \rangle + \sum_{k=1}^{\infty} \langle \cos \theta_{BA}^{(k)} \rangle \,, && (12.43) \end{aligned}$$

where $\langle \cos \theta_{ij}^{(k)} \rangle$ is the average cosine of the angle between any given jump of the i species and the k'th succeeding jump of the j species.

12.3.1 Phenomenological Coefficients, Tracer Diffusivities, and Jump Models

Tracer diffusion coefficients are directly accessible from experiments (see Chap. 13). On the other hand, direct measurements of phenomenological coefficients are difficult. Accordingly, there is interest in relations between the tracer diffusivities and phenomenological coefficients. There are also expressions for phenomenological coefficients in terms of atomistic hopping models. In what follows, we consider examples of such relations and expressions.

Relations for Self-diffusion: In the previous section, we obtained equations which related kinetic coefficients for an element crystal to the tracer self-diffusion coefficient. After some algebra we get

$$L_{A^*A^*} \approx \frac{C_{A^*} D_A^{A^*}}{k_\mathrm{B} T} \tag{12.44}$$

and

$$L_{AA^*} = L_{A^*A} = \frac{C_{A^*} D_A^{A^*}}{k_\mathrm{B} T} \frac{(1-f)}{f} \,. \tag{12.45}$$

The off-diagonal transport coefficient is related to tracer correlation. For uncorrelated diffusion, i.e. for $f = 1$, it vanishes.

Relations for Dilute Binary Alloys: For a dilute alloy of solute B in solvent A, i.e. for $N_B \to 0$ we have $\Phi \to 1$. It can be shown that $\L_{BB}/N_B$ approaches a finite value, whereas L_{AB}/N_A goes to zero. Then, we get from the second equation (12.28):

$$D_B^I(0) = k_\mathrm{B} T \frac{L_{BB}}{N_B} = D_A^{B^*}(0) \,, \tag{12.46}$$

where $D_A^{B^*}(0)$ is the solute diffusion coefficient at infinite dilution. It is measurable, e.g. by using tracer B^*. From the first equation (12.28) we have

$$D_A^I(0) = \frac{L_{AA}}{C_A} \left(1 - \frac{L_{AB} N_A}{L_{BB} N_B}\right) k_\mathrm{B} T \neq \frac{L_{AA}}{N_A} k_\mathrm{B} T \,. \tag{12.47}$$

In this case the off-diagonal term L_{AB} cannot be neglected.

It may be of some interest to consider in a very dilute alloy the phenomenological coefficients in the framework of the five-frequency model of diffusion suggested by LIDIARD. This model is described in Chap. 7. It is very useful for describing solute and solvent diffusion in a very dilute binary alloy. We remind the reader that in this model five exchange jump-rates between vacancies and A or B atoms are specified, namely: ω_2 for solute-vacancy exchange, ω_1 for rotation of the vacancy-solute complex, ω_3 (ω_4) for dissociation (association) of the vacancy-solute complex, and ω for vacancy jumps in the solvent. According to [4] the phenomenological coefficients are:

$$
\begin{aligned}
L_{AA} &= \frac{d^2\omega C_V}{k_\mathrm{B}T}\left(1 - 12N_B\frac{\omega_4}{\omega_3}\right)\omega \\
&\quad - \frac{d^2 C_V N_B}{k_\mathrm{B}T}\frac{\omega_4}{\omega_3}\left[\frac{40\omega_1\omega_3 + 40\omega_3^2 + 14\omega_2\omega_3 + 4\omega_1\omega_2}{\omega_1 + \omega_2 + 7\omega_3/2} + \frac{7\omega_3\omega}{\omega_4}\right] \\
L_{BB} &= \frac{d^2 C_V N_B}{k_\mathrm{B}T}\frac{\omega_4}{\omega_3}\frac{\omega_2(\omega_1 + 7\omega_3/2)}{\omega_1 + \omega_2 + 7\omega_3/2} \\
L_{AB} &= \frac{d^2 C_V N_B}{k_\mathrm{B}T}\frac{\omega_4}{\omega_3}\frac{\omega_2(-2\omega_1 + 7\omega_3)}{\omega_1 + \omega_2 + 7\omega_3/2}
\end{aligned}
\tag{12.48}
$$

The so-called *Heumann relation* [18] was also derived on the basis of the five-frequency model. It can be shown that in the limit $C_B \to 0$, the ratio of $L_{AB}(0)/L_{BB}(0)$ is given by:

$$
\frac{L_{AB}(0)}{L_{BB}(0)} = \frac{D_A^{A^*}(0)}{D_A^{B^*}(0)}\left[\frac{1}{f} - \frac{D_A^I(0)}{D_A^{A^*}(0)}\right], \tag{12.49}
$$

where $D_A^{A^*}(0), D_A^{B^*}(0)$ are the tracer diffusivities of A and B and $D_A^I(0)$ the intrinsic diffusion coefficient of A in the limit $C_B \to 0$.

Relations for Concentrated Binary Alloys: Let us first briefly consider relations based on the original DARKEN equations [11]. In essence, Darken neglects the off-diagonal coefficients entirely. If this is assumed, the diagonal phenomenological coefficients can be related to the corresponding tracer diffusion coefficient in a binary alloy:

$$
L_{AA} \approx \frac{N_A D_A^{A^*}}{k_\mathrm{B}T}, \quad L_{BB} \approx \frac{N_B D_B^{B^*}}{k_\mathrm{B}T}, \quad L_{AB} = 0\,. \tag{12.50}
$$

The Darken equations neglect all correlation information as embodied in tracer correlation factors, collective correlation factors, and vacancy-wind factors [24]. The neglect of the off-diagonal phenomenological coefficients can be dangerous. However, in most cases, it is reasonable as a first approximation.

The *random alloy model* with the vacancy mechanism introduced by MANNING is probably the most important model for dealing with diffusion in concentrated alloys that are disordered [12, 13]. The atomic species A and B exchange sites with vacancies with the jump rates ω_A or ω_B, respectively. Then, the Darken relation is replaced by the *Darken-Manning relation* which includes the *vacancy wind corrections* (see Chap. 10). In the random alloy model, the phenomenological coefficients are directly related to the tracer diffusion coefficients via the *Manning relations*:

$$
\begin{aligned}
L_{ii} &= \frac{N_i D_i^{i^*}}{k_\mathrm{B}T}\left[1 + \frac{(1-f)}{f}\frac{N_i D_i^{i^*}}{N_A D_A^{A^*} + N_B D_B^{B^*}}\right], \\
L_{AB} &= \frac{(1-f)}{f}\frac{N_A D_A^{A^*} N_B D_B^{B^*}}{k_\mathrm{B}T(N_A D_A^{A^*} + N_B D_B^{B^*})}\,.
\end{aligned}
\tag{12.51}
$$

f is the tracer correlation factor: e.g., $f = 0.781$ for the fcc lattice and $f = 0.732$ for the bcc lattice.

The random alloy model seems to have more general validity. Computer simulations by MURCH AND COWORKERS have shown that the Manning relations are quite good approximations, even for ordered alloys, at least at low levels of order [14–16]. The Manning relations have also been re-derived for ordered alloys [17].

12.3.2 Sum Rules – Relations between Phenomenological Coefficients

Various relations usually called *sum rules* have been identified between the phenomenological coefficients in randomly mixed systems. Sum rules reduce the number of independent phenomenological coefficients.

As an example, we consider the sum rules between the phenomenological coefficients in the random alloy model with a vacancy mechanism. The atom-vacancy exchange rates ω_i can be considered in two rather different ways. In the first way, one can consider them as explicit jump rates that depend only on the species i and not on the surroundings. For example, ω_A in the binary random alloy then simpls represents the average jump rate of a given A atom at all compositions and environments. In the second more general way, one considers that the ω_i represent an average jump rate of species i as it migrates through the lattice sampling the various environments. Since the average environment of an atom will change with composition, the ω_i can also be expected to change with composition.

MOLEKO AND ALLNATT [19] identified the following sum rules for an n-component random alloy for diffusion via a vacancy mechanism:

$$\sum_{i=1}^{n} L_{ij}\frac{\omega_j}{\omega_i} = \frac{Zd^2}{6k_{\mathrm{B}}T} C_V \omega_j N_j, \quad j = 1, \ldots, n\,. \qquad (12.52)$$

Here Z is the coordination number and d the jump distance. Equations (12.52) relate the phenomenological coefficients to the vacancy-atom exchange rates and reduce the number of independent phenomenological coefficients.

In addition, we mention that the sum rules can be restated in terms of collective correlation factors as:

$$\sum_{i=1}^{n} f_{ij}^{(j)}\frac{\omega_j}{\omega_i} = 1, \quad j = 1, \ldots n\,. \qquad (12.53)$$

For a *binary random alloy* the sum rule relations (12.52) reduce to two equations:

$$L_{AA} + L_{AB}\frac{\omega_A}{\omega_B} = \frac{Zd^2}{6k_{\mathrm{B}}T}C_V\omega_A N_A, \tag{12.54}$$

$$L_{BB} + L_{AB}\frac{\omega_B}{\omega_A} = \frac{Zd^2}{6k_{\mathrm{B}}T}C_V\omega_B N_B\,. \tag{12.55}$$

Hence there is only one independent coefficient and not three. In a ternary random alloy, the number of independent coefficients is reduced from six to three. On the other hand, the reader should keep in mind that the random alloy model introduces two vacancy jump rates for a binary alloy and three jump rates for a ternary alloy.

For the derivation of sum rules we refer the reader to the original papers. The sum rules introduced by MOLEKO AND ALLNATT for the random alloy model were the first ones that were discovered. In the meantime, various sum rules have been identified for a number of other mechanisms and situations by MURCH AND COWORKERS. Such situations include the dumb-bell interstitial mechanism in the binary random alloy [20], the divacancy mechanism in the fcc random alloy [21], the vacancy-pair mechanism in ionic materials with randomly mixed cations [22], and for an intermetallic compound with randomly mixed sublattices [23]. Interdiffusion data in multicomponent alloys as a source of quantitative fundamental diffusion information are summarised in [24].

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