Chapter 2
Microscopic (or Atomic) Diffusion

Abstract Random motion of atoms is described in this chapter. The movement of a substance within a mixture by 'random walk' is governed by the kinetic energy within the system that may be affected by changes in concentration, pressure or temperature. It is impossible to observe the motion of individual atoms in solids, but diffusion occurs and may be observed. The concept of diffusion is shown by a schematic illustration of two planes, λ distance apart, showing the number of atoms n_1 and n_2 in each plane, respectively, and the corresponding fluxes, J_1 and J_2. The atoms diffuse by jumps and the frequency of jumps is related to the flux of atoms. By using the random walk for the diffusion it is possible to calculate the average distance that an atom covers from an initial reference point in all directions when the process is considered over a long period of time. It is shown that the average distance squared is related to the diffusion coefficient.

The movement of a substance within a mixture by 'random walk' is governed by the kinetic energy within the system that may be affected by changes in concentration, pressure or temperature. It is impossible to observe the motion of individual atoms in solids, but diffusion occurs and may be observed. Imagine that the relative motions of atoms occur and assume that this happens by random jumps of atoms from one atomic site to another. This is a 'random walk problem' that should be related to the diffusion coefficients by the consideration of atomic jump frequencies and their jump distances.

2.1 Random Motion of Atoms

Consider, for the sake of simplicity, a simple cubic structure with no specific mechanism. Also assume two neighboring planes of this structure, as presented schematically in Fig. 2.1, with a concentration gradient between them. Let the distance between these planes be λ and the flux in one-directional diffusion be restricted between these two planes. Let the flux of atoms per unit area, n_1 and n_2 between them, be J_1 and J_2, and the jump frequencies (the number of jumps per

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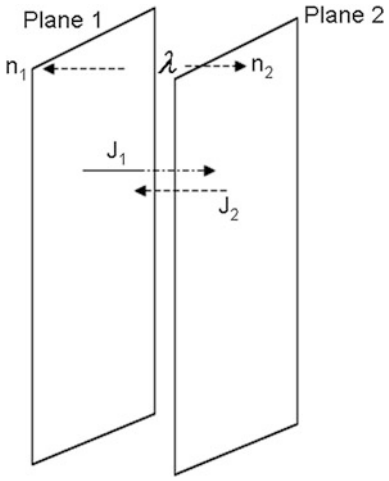

Fig. 2.1 Schematic illustration of two planes, λ distance apart, showing the number of atoms n_1 and n_2 in each plane, respectively, and the corresponding fluxes, J_1 and J_2

second) be Γ_1 and Γ_2. The number of atoms jumping out of plane 1 at time δt is: the number of atomic jumps:

$$1/2 n_1 \Gamma_1 \delta t \tag{2.1a}$$

the number of jumps out of plane 2:

$$1/2 n_2 \Gamma_2 \delta t. \tag{2.1b}$$

Note that the jumps in each direction between the planes are only half of the total jumps, since half the jumps from plane 1 go to the left; similarly, the other half jumps to the right of the plane. So, the net flux per unit time from plane 1 to plane 2 is the difference between expressions (2.1a) and (2.1b) given in unit time.

$$J = (J_1 - J_2) = \frac{1}{2}(\Gamma_1 n_1 - \Gamma_2 n_2) = \frac{1}{2}(n_1 - n_2)\Gamma. \tag{2.1}$$

Now recall that concentration, c, is expressed as the number of atoms per unit volume and n_1 and n_2 are the number of atoms per unit area. Therefore, the number of atoms per unit volume jumping from plane 1 may be written as $c_i = n/\lambda$ and, thus, Eq. (2.1) may be expressed in terms of concentration as:

$$J = \frac{1}{2}(c_1 - c_2)\lambda\Gamma. \tag{2.2}$$

Since, in diffusion, the concentration along distance λ varies slowly, one may express this change in the direction of x as:

$$c_1 - c_2 = -\lambda \frac{\partial c}{\partial x}. \tag{2.2a}$$

Substituting this value into Eq. (2.2), the relation for J in Eq. (2.2) may be given as:

$$J = -\frac{1}{2}\lambda^2 \Gamma \frac{\partial c}{\partial x}. \tag{2.3}$$

This equation is equivalent to Fick's First Law if:

$$D = \frac{1}{2}\lambda^2 \Gamma. \tag{2.4}$$

In the above derivation, it was assumed that the jump frequency is $\Gamma_1 = \Gamma_2 = \Gamma$. This assumption means that the flux of atoms down the concentration gradient is not biased by the direction of the jumps, but rather is a consequence of the different concentrations of atoms on the respective planes. Driving force biases the diffusion; the driving force was not considered in any of these diffusion equations. The various driving forces acting on the diffusion processes and biasing them may be: temperature gradients, gradients of chemical potentials, gradients of electrical potentials, stress gradients, etc. (Philibert 1991).

Note that near the melting point of materials (at least in metals), D is $\sim 10^{-8}$ cm^2 s^{-1}, assuming a jump distance $\lambda \simeq 10^{-8}$ cm, yields $\Gamma \simeq 10^8$ jumps/s. Considering the fact that the Debye frequency is 10^{12}–10^{13} s^{-1} and comparing it with the jump frequency indicates that only 10^4–10^5 successful position changes occur, even around the melting point, while most of the time the atom oscillates near its equilibrium position.

2.2 Random Walk

How may random walks be related to diffusion, a random process? Of the numerous descriptions of the random walk, the most convenient examples are those of Shewmon (1963) or Philibert (1991). Over a long period of time, one may calculate the average distance that an atom covers from the large number of jumps made from an initial reference point in all directions. No correlation effects are considered. Starting from an initial position (the origin), one may plot the path of an atom performing jumps along the vector, r_n, to its final position, by means of its connection, vector R_n, to its initial position, presented by:

$$\mathbf{R_n} = \mathbf{r_1} + \mathbf{r_2} + \mathbf{r_3} + \cdots = \sum_{i=1}^{n} r_i. \tag{2.5}$$

As previously mentioned, $\mathbf{r_i}$ are the vectors of the various jumps. To obtain the magnitude of R_n, both sides of Eq. (2.5) are squared:

$$\begin{aligned} \mathbf{R_n} \cdot \mathbf{R_n} = R_n^2 = {} & r_1 \cdot r_1 + r_1 \cdot r_2 + r_1 \cdot r_3 + \cdots + r_1 \cdot r_n \\ & + r_2 \cdot r_1 + r_2 \cdot r_2 + r_2 \cdot r_3 + \cdots + r_2 \cdot r_n \\ & \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ & + r_n \cdot r_1 + r_n \cdot r_2 + r_n \cdot r_3 + \cdots + r_n \cdot r_n. \end{aligned} \tag{2.6}$$

The arrays of Eq. (2.6) may be rewritten as the series of sums. Consider the sum of the diagonal and semi-diagonal terms. Rewrite Eq. (2.6) as the sum of these terms:

$$R_n^2 = \sum_{i=1}^{n} r_i \cdot r_i + 2\sum_{i=1}^{n-1} r_i \cdot r_{i+1} + 2\sum_{i=1}^{n-2} r_i \cdot r_{i+2} + \cdots \tag{2.7}$$

$$= \sum_{i=1}^{n} r_1^2 + 2\sum_{j=1}^{n-1}\sum_{i=1}^{n-j} r_i \cdot r_{i+j}. \tag{2.7a}$$

Note that the first term on the right-hand side represents the sum of the diagonal terms. The second term represents the sum of those along the semi-diagonal and there are (n − 1) such terms. These terms are: $r_i \cdot r_{i+1}$ and $r_{i+1} \cdot r_i$; being dot products, one may add them to obtain 2 before the sum of the product. This is also the case for the third term in Eq. (2.7). The second and third terms may be combined into a double sum, as shown in Eq. (2.7b). Taking the average over a large number of particles, we may write the average of Eq. (2.7a) as:

$$\langle R_n^2 \rangle = \sum_{1=1}^{n} \langle r_i^2 \rangle + 2\sum_{j=1}^{n-1}\sum_{i=1}^{n-j} \langle r_i \cdot r_{i+j} \rangle. \tag{2.7b}$$

The double sum contains n(n − 1) terms, which is equal to n(n − 1) times the average value of the product, i.e., times $\langle r_i \cdot r_{i+j} \rangle$. For a random walk, this must be equal to zero, because the probability is that each jump in one direction has another particle with a negative jump in the opposite direction. Thus, the second term in Eq. (2.7b) cancels out and we obtain the average value of $\langle R_n^2 \rangle$. In crystalline solids with cubic symmetries, all the jump vectors are equal in magnitude, so it is possible to write R_n^2 (as given in Eq. (2.7c)) for one atom performing n jumps, since the jump distances are equal in magnitude:

$$R_n^2 = \sum_{i=1}^{n} r_1^2 = r_1^2 + r_2^2 + r_3^2 + \cdots + r_n^2 = nr^2. \tag{2.7c}$$

Thus:

$$R_n^2 = nr^2. \tag{2.8}$$

However, for the average distance squared $\langle R_n^2 \rangle$, namely of many atoms performing n jumps, one has to write:

$$\langle R_n^2 \rangle = \sum_{i=1}^{n} \langle r_i^2 \rangle = \ n\langle r^2 \rangle. \tag{2.9}$$

The root-mean square displacement from Eq. (2.9), after n steps of constant length, r, is:

$$R_n = \sqrt{\langle R_n^2 \rangle} = \langle r \rangle \sqrt{n}. \tag{2.10}$$

Now, relate $\langle R_n^2 \rangle$ to D.
Starting with Eq. (2.4), this may be expressed as:

$$\Gamma = \frac{2D}{\lambda^2} \tag{2.11}$$

Γ, in terms of the number of jumps per unit time, is n/t, or:

$$\mathrm{n} = \Gamma \mathrm{t}. \tag{2.11a}$$

Substitute for n in Eq. (2.9) from Eq. (2.11a) and assume that the jump distances in Eqs. (2.9) and (2.11) are equal, to obtain:

$$\langle R^2 \rangle = t \Gamma r^2 \tag{2.11b}$$

or:

$$\Gamma = \frac{\langle R^2 \rangle}{t r^2}. \tag{2.11c}$$

Equating Eqs. (2.11) and (2.11c) yields:

$$\frac{2D}{\lambda^2} = E_{1v}^m \frac{\langle R^2 \rangle}{t r^2}. \tag{2.11d}$$

With the above assumption, that the jump distances are equal (i.e., $r^2 = \lambda^2$), it is possible to describe diffusion in one dimension for a one-dimensional random walk:

$$\langle \mathrm{R}^2 \rangle = 2\mathrm{Dt}. \tag{2.12}$$

Clearly, in three dimensions:

$$\langle \mathrm{R}^2 \rangle = 6\mathrm{Dt} \tag{2.12a}$$

since in a three-dimensional walk $r^2 = x^2 + y^2 + z^2$. In other words, the factor of 3 between Eqs. (2.12) and (2.12a) is a consequence of the fact that, during the derivation of the random walk, the atomic jumps were restricted to one direction only. As such, only one third of the jumps in three dimensions occured along the one-dimensional axis considered in this section.

The concept of the random walk may be summarized by the statement that it is impossible to precisely predict this motion of an atom, since it is random (unlike the case where some factor, for example an electric field, biases the motion of an atom and then there is a drift). There is an analogous concept often cited in connection

with the concept of the random walk—the example a 'drunken sailor', who starts his random walk from a lamppost at position x = 0 and then every second, τ, randomly moves one step, δ, to the left or the right. No one knows where that sailor will end up after n steps, because it is a random walk process. One may, however, examine the probabilities of his ending up in various places. One may study many random walkers and take the average of all of their trajectories to obtain certain 'average' properties. On average (the average taken over many walks), our sailor will get nowhere, $\langle x = 0 \rangle$, being equally likely to take leftward as rightward steps. But the sailor does move and is certainly more likely to cover more and more ground as time goes on. This case is characterized as a random walk, which determines the mean distance squared from the lamppost (the point of origin from which the sailor started his journey) after n steps.

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