3 Diffusion

In solids, atoms move by a process of diffusion. The vacancy mechanism for diffusion in crystals was presented in Section 1.5.3 and illustrated with Fig. 1.7. Mention was made of interstitial diffusion and interstitialcy diffusion. Mass transport in glasses and liquids can also occur by atomic-level diffusion, but for gases or fluids of low viscosity there are larger-scale convective currents with dynamics quite different from diffusion.[1]

The diffusion equation has the same mathematical form as the equation for heat conduction, if solute concentration is replaced by heat or by temperature. The heat equation has been known for centuries, and methods for its solution have a long history in classical mathematical physics. Some of these methods are standard for diffusion in materials, such as the basic solutions of Gaussian functions and error functions for one-dimensional problems. This Chapter 3 also presents the method of separation of variables for three-dimensional problems with Cartesian and cylindrical coordinates. The Laplacian is separable in nine other coordinate systems, each with their own special functions and orthogonality relationships, but these are beyond the scope of this book. For the problems in ellipsoidal coordinates, for example, the reader may consult classic texts in mathematical physics (e.g., (19)). Today finite element methods are practical for many problems, and often prove more efficient than analytical methods.

Because diffusion depends on atomic-scale processes, changes in the local atomic structure during diffusion can depreciate the diffusion equation because the "diffusion constant," D, is not constant. This can be a serious problem when using the diffusion equation to describe the kinetics of a phase transformation. By deriving the diffusion equation from the kinetic master equation, however, we can later replace the assumption of random atomic jumps with an assumption of chemically-biased jumps to predict the kinetics of chemical ordering or mixing. This is the subject of Chapter 22. This Chapter 3 concludes by showing how the kinetic master equation can lead to thermodynamic equilibrium.

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[1] Convective currents can be driven by differences in density, such as the rising of a hot liquid in a gravitational field.

3.1 The Diffusion Equation

Writing the kinetic master equation in the form of Eq. 1.25 motivates a matrix description of the kinetic processes

$$\underset{\approx}{W}(\Delta t)\,\underset{\sim}{N}(t) = \underset{\sim}{N}(t+\Delta t) \tag{3.1}$$

where $\underset{\sim}{N}(t)$ is a column vector that we lay out along the bins of Fig. 1.9a, and $\underset{\approx}{W}(\Delta t)$ is a two-dimensional matrix that gives the new contents after time Δt. Two such matrix elements are shown in Fig. 1.9b. This approach has an advantage for numerical computations. If Δt is small, after m intervals of Δt the new contents of the bins will be

$$\left[\underset{\approx}{W}(\Delta t)\right]^{m}\,\underset{\sim}{N}(t) = \underset{\sim}{N}(t+m\Delta t)\ . \tag{3.2}$$

The following assumptions are fundamental to the diffusion equation, and to our construction of a kinetic master equation for diffusion. They are important to remember whenever using the diffusion equation for a problem in materials science.

- all atoms have the same jump probability (unaffected by the presence of other atoms)
- if an atom has probability δ of jumping out of a bin in Fig. 1.9, it has an equal probability $\delta/2$ of going left or right (in three dimensions the probability is shared as $\delta/6$ between left, right, up, down, in, out)
- an atom can jump only into an adjacent bin (but this is not an essential assumption for obtaining the diffusion equation as shown by Problem 2 in Chapter 9)

For our matrix equation we first arrange the two column vectors in correspondence with the bins in Fig. 1.9a, $\{n\}$, and their contents $\{N\}$

$$\underset{\sim}{N}(t) = \left[N_1(t), N_2(t)\ldots N_{n-1}(t), N_n(t), N_{n+1}(t)\ldots\right]\ . \tag{3.3}$$

For the structure of $\underset{\approx}{W}(\Delta t)$, first assume zero atom jumps in the time Δt. In this case $\underset{\approx}{W}(\Delta t)$ must be the identity matrix, $\underset{\approx}{I}$, with all 1's on its diagonal, and 0's elsewhere. The operation of this identity matrix on the vector $\underset{\sim}{N}(t)$ preserves the contents of all bins at time $t+\Delta t$, so in this case $\underset{\approx}{I}\,\underset{\sim}{N}(t) = \underset{\sim}{N}(t+\Delta t)$.

Next, assume each atom has only a small probability δ of leaving its bin in the time interval Δt. The probability of it remaining in the bin is therefore $1-\delta$, and its probability of entering an adjacent bin is $\delta/2$. Likewise, the probability of an atom entering a bin from an adjacent bin is also $\delta/2$. The W-matrix is close to diagonal,