Last Time

Solution Strategies

Brute Force: Numerical Methods

Diffusion with Moving Interfaces

Interface Motion due to Heat Absorption at the Interface

Mass Diffusion in an Alloy

3.21 Spring 2001: Lecture 13

Diffusion as a Molecular Process

The derivation of the diffusion equation followed from consideration of a continuum distribution of conserved particles. A treatment of individual molecular or atomic motions as part of a statistical ensemble of diffusing particles will prove to be not only consistent with the continuum approach, but will provide new physical concepts that enhance understanding of diffusive processes.

Below, the fundamental diffusive process—an atomic or molecular displacement—is treated as a random jump occurring with an average frequency Γ. It is instructive to consider how this simple model of random atomic jumps corresponds to the various diffusion systems, or diffusivities discussed above.

First of all, if a jump is truly random, then the probability of a given jump giving a net displacement $\Delta\vec{x}_\circ$ must be exactly the same as jump with displacement $-\Delta\vec{x}_\circ$. Therefore, the expected displacement, $\langle\Delta\vec{x}\rangle$, of a particle after one or more jumps must be identically zero. Furthermore, the expected velocity of the particle, $\langle\vec{v}\rangle = \langle\Gamma\Delta\vec{x}\rangle$, must also be zero. Considering the Einstein drift equation $\langle\vec{v}\rangle = M\nabla\mu$, it must be concluded that the random

walk treatment corresponds to the physical experiment that $\nabla\mu = 0$, which is precisely the case that is intended for the measurement of the self-diffusivity D_i^*; i.e. a diffusion couple of two alloys of the same composition, but differing in isotopic concentration.

Secondly, if the jumps are assumed to take place on a crystalline lattice, then each random displacement $\vec{x_i}$ will be selected from a small subset of all the possible displacements that would be available in the more general case of diffusion in a gas. Treating the general case first, as is done below, leaves the diffusion on the lattice as particular case.

Third, for a process to be completely random, there can be no restriction on the availability of a nearby empty site—the probability of an empty site cannot appear in the simple model of random walk. In the simple random walk process, two atoms may occupy the same space. Therefore, the simple random walk treatment should not correspond to substitutional diffusion on a crystal lattice. However, substitutional crystalline diffusion *can* be treated as a sequence of random hops on a lattice if the "particle" that hops is one of a infinitely dilute concentration of vacancies–a vacancy will always have an occupied neighboring site to hop into in the dilute limit.

In the treatment of the random walk, the average rate at which a walker (i.e. an atom or molecule) takes steps is an empirical frequency

$$\Gamma \equiv \frac{\langle \text{number of successful 'hops'} \rangle}{\text{unit time}} \tag{13-1}$$

A model for Γ will be considered after the treatment of random walks and it will be shown to depend on both a fundamental atomic rate at which an atom attempts a hop, multiplied by the probability of success.

Diffusion as a Random Walk Process

Let Γ be the average rate that a random walker (an atom or molecule) 'take steps.' Γ is an average frequency. $\vec{R}(\Delta\tau)$ be the position of a *particular* random walker:

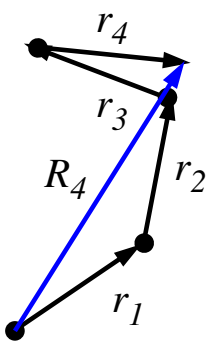

Figure 13-1: Schematic illustration of a random walk as a sequence of uncorrelated hops.

The position of a particular particle (relative to the starting position) after a time $\Delta\tau$ (or $N_\tau = \Gamma\Delta\tau$ hops) will be:

$$\vec{R}(\Delta\tau) = \sum_{i=1}^{N_\tau} \vec{r}_i = \sum_{i=1}^{\Gamma\Delta\tau} \vec{r}_i \tag{13-2}$$

What is meant by a "random jump" is not specified, but could be represented by a number of different processes:

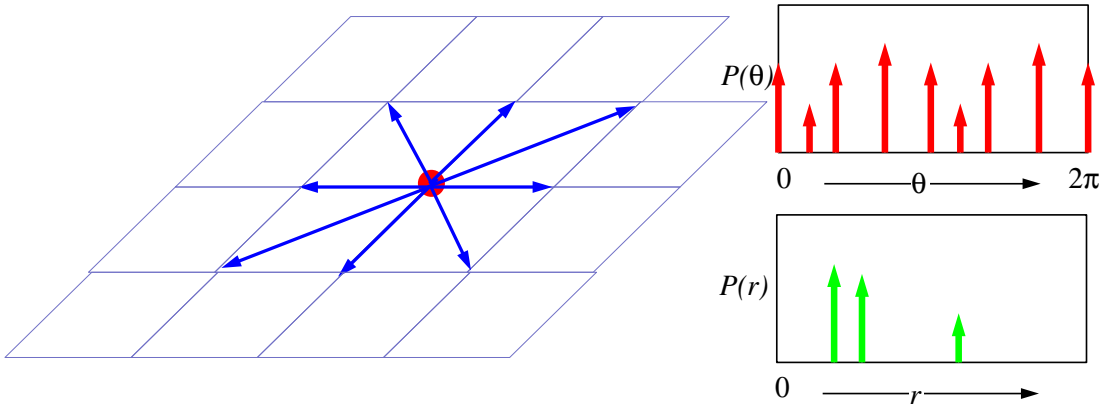

Figure 13-2: Illustration of a random walk on a lattice.

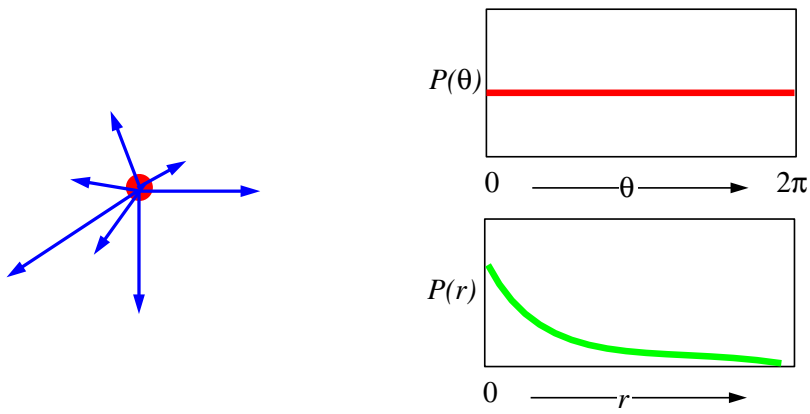

Figure 13-3: Illustration of a random walk.

In either case, the expected value $\langle\vec{R}(\Delta\tau)\rangle = 0$; this is an indication that no particular direction is favored and that the driving force $\nabla\mu = 0$ for a random walk.

However, it should be intuitively clear that the distance between two particles should increase with time. This distance is measured by the spread, or second moment, of the distribution $\langle \vec{R}^2(\Delta\tau)\rangle$:

$$\begin{aligned} R^2(\Delta\tau) = \vec{R}(\Delta\tau)\cdot\vec{R}(\Delta\tau) = \quad & \vec{r}_1\cdot\vec{r}_1 + \vec{r}_1\cdot\vec{r}_2 + \vec{r}_1\cdot\vec{r}_3 + \ldots + \vec{r}_1\cdot\vec{r}_n + \\ & \vec{r}_2\cdot\vec{r}_1 + \vec{r}_2\cdot\vec{r}_2 + \vec{r}_2\cdot\vec{r}_3 + \ldots + \vec{r}_2\cdot\vec{r}_n + \\ & \vdots \\ & \ldots\ldots + \\ & \vdots \\ & \vec{r}_n\cdot\vec{r}_1 + \vec{r}_n\cdot\vec{r}_2 + \vec{r}_n\cdot\vec{r}_3 + \ldots + \vec{r}_n\cdot\vec{r}_n \end{aligned} \tag{13-3}$$

This can be rewritten as a sum along the diagonal and off-diagonal terms:

$$R^2(\Delta\tau) = \sum_{i=1}^{N_\tau} \vec{r}_i\cdot\vec{r}_i + 2\sum_{i=1}^{N_\tau-1}\sum_{j=i+1}^{N_\tau} \vec{r}_i\cdot\vec{r}_j \tag{13-4}$$

Using the relationship $\vec{r}_i\cdot\vec{r}_j = |r_i||r_j|\cos\Delta\theta_{i,j}$, where $\Delta\theta_{i,j}$ is the angle between the ith and jth jump-vectors. Therefore,

$$\langle \vec{R}^2(\Delta\tau)\rangle = N_\tau\langle r^2\rangle + 2\langle\sum_{i=1}^{N_\tau}\sum_{j=i+1}^{N_\tau-1} |\vec{r}_i||\vec{r}_j|\cos\Delta\theta_{ij}\rangle \tag{13-5}$$

Because $\Delta\theta_{ij} = -\Delta\theta_{ji}$,

$$\langle \vec{R}^2(\Delta\tau)\rangle = \Gamma\Delta\tau\langle r^2\rangle + \langle\sum_{i=1}^{N_\tau}\sum_{j=1}^{N_\tau} |\vec{r}_i||\vec{r}_j|\cos\Delta\theta_{ij}\rangle \tag{13-6}$$

No assumption about jump correlations, jump lengths, distribution of values $\Delta\theta_{ij}$, or the number of dimensions has been made.

If the lengths of the jumps do not correlate to the jump-angles:

$$\langle \vec{R}^2(\Delta\tau)\rangle = \Gamma\Delta\tau\langle r^2\rangle\left(1 + \frac{1}{N_\tau}\langle\sum_{i=1}^{N_\tau}\sum_{j=1}^{N_\tau}\cos\Delta\theta_{ij}\rangle\right) \tag{13-7}$$

where $N_\tau = \Gamma\Delta\tau$ and $\langle r^2 \rangle$ have been factored out of both terms.

Define the *Correlation Factor*, f:

$$f \equiv 1 + \frac{1}{N_\tau} \sum_{i=1}^{N_\tau} \sum_{j=1}^{N_\tau} \langle \cos \Delta\theta_{ij} \rangle \tag{13-8}$$

Therefore,

$$\frac{\langle R^2(\Delta\tau) \rangle}{\Delta\tau} = \Gamma \langle r^2 \rangle f \tag{13-9}$$

This is an important equation, it relates the spread of the expected square displacements (or the second moment of the probability distribution) per unit time with three factors that are dictated by the mechanism of diffusion: the rate of successful hops Γ, the average square hop distance $\langle r^2 \rangle$, and a factor related to the correlation between hops, f. If every hop is uncorrelated and the probability of positive displacement $\vec{r}$ is exactly balanced by an equal probability $-\vec{r}$ then $f = 1$.

If, in addition the jumps take place on a lattice with first neighbors only, and all the jumps are uncorrelated, then it can be shown that

$$f = \frac{1 + \langle \cos \Delta\theta \rangle}{1 - \langle \cos \Delta\theta \rangle} \tag{13-10}$$

Diffusion as a Time-Dependent Probability Distribution

In the last section, the expected position and the expected square displacement of a particle was calculated by considering the statistics of a sequence of random jumps. The concept of statistics can be coupled with that of a probability distribution. The probability of finding a particle after a time $\Delta\tau$ will be determined and will be related to the form of a point source solution of the diffusion equation.

Consider a sequence of N_τ random jumps on a one-dimensional lattice. If the random walker is at position n after N_τ jumps (after starting at $n = 0$), then the number of jumps to the right n_R and to the left n_L must satisfy:

$$\begin{aligned} n &= n_R - n_L \\ N_\tau &= n_R + n_L \end{aligned} \tag{13-11}$$

The number of different ways that a random jumper could land at site n from the origin is given by the binomial coefficient:

$$\Omega(n, N_\tau) = \frac{N_\tau!}{n_R! n_L!} = \frac{N_\tau!}{\frac{N_\tau+n}{2}! \frac{N_\tau-n}{2}!} \tag{13-12}$$

Therefore the probability of getting to site n after N_τ jumps is:

$$p(n, N_\tau) = \frac{N_\tau!}{\frac{N_\tau+n}{2}! \frac{N_\tau-n}{2}!} p_R^{n_R} p_L^{n_L} \tag{13-13}$$

If the probability of jumping right $p_R = p_L$ the probability of jumping left, then

$$p(n, N_\tau) = \frac{N_\tau!}{\frac{N_\tau+n}{2}! \frac{N_\tau-n}{2}!} \left(\frac{1}{2}\right)^{N_\tau} \tag{13-14}$$

Using Stirling's formula,

$$Q! = \sqrt{2\pi} Q^{Q+1} e^{-Q} \tag{13-15}$$

and taking the limit $n/N_\tau \ll 1$,

$$p(n, N_\tau) \propto e^{-\frac{n^2}{2N_\tau}} \tag{13-16}$$

which shows that the distribution of a point source in one dimension spreads as a Gaussian.

Using $R = n\langle r \rangle$ and $N_\tau = \Gamma \Delta\tau$:

$$p(R, \delta\tau) \propto e^{-\frac{R^2}{2\langle r^2 \rangle \Gamma \Delta\tau}} \tag{13-17}$$

Normalizing so that for all $\Delta\tau$

$$\int_{-\infty}^{\infty} p(R, \Delta\tau) dR = 1 \tag{13-18}$$

$$p(R, \delta\tau) = \frac{1}{\sqrt{2\pi\Gamma\Delta\tau\langle r^2\rangle}} e^{-\frac{R^2}{2\langle r^2\rangle\Gamma\Delta\tau}} \tag{13-19}$$

Comparing this with the fundamental point solution in 1D:

$$c(x,t) = \int_{-\infty}^{\infty} \frac{c_{ic}(x-\zeta) e^{-\frac{(x-\zeta)^2}{4Dt}}}{\sqrt{4\pi D t}} d\zeta \tag{13-20}$$

The probability distribution can be used to identify the diffusivity with a random process:

$$D = \frac{\Gamma}{2}\langle r^2\rangle \tag{13-21}$$

for uncorrelated jumps ($f = 1$) on a one-dimensional lattice.

Relation of the Self-Diffusivity to a Random Walk

The notion of the continuum limit for the concentration, $c(\vec{r}, t)$ of particles is consistent with an interpretation of the concentration related to a probability of finding a particle of a given type within a small distance of the point $\vec{r}$ at a time t. Treating the concentration as a probability distribution, the second moment of the distribution is related to the mean-square displacement from the average displacement:

$$\langle R^2\rangle(\Delta\tau) = \frac{\int_0^\infty r^2 c(\vec{r}, \Delta\tau) dr}{\int_0^\infty c(\vec{r}, \Delta\tau) dr} \tag{13-22}$$

Suppose all of the particles are located at the origin at time $t = 0$, then if diffusion takes place in three dimensions:

$$c(r, \Delta\tau) = \frac{c_0 4\pi r^2 dr}{(4\pi D\Delta\tau)^{3/2}} e^{-\frac{r^2}{4D\Delta\tau}} \tag{13-23}$$

Because,[26]

$$\begin{aligned} \int_0^\infty x^0 e^{-ax^2} dx &= \frac{1}{2}\sqrt{\frac{\pi}{a}} \\ \int_0^\infty x^2 e^{-ax^2} dx &= \frac{1}{4a}\sqrt{\frac{\pi}{a}} \\ \int_0^\infty x^4 e^{-ax^2} dx &= \frac{3}{8a^2}\sqrt{\frac{\pi}{a}} \end{aligned} \tag{13-24}$$

[26] If the real part of a is greater than zero, as it is for $t > 0$.

$$\langle R^2 \rangle(\Delta\tau) = \frac{12\sqrt{\pi}(D\Delta\tau)^{5/2}}{2\sqrt{\pi}(D\Delta\tau)^{3/2}} = 6D\Delta\tau \tag{13-25}$$

Comparing this to Equation 13-9,

$$D = \frac{\Gamma\langle r \rangle^2 f}{6} \tag{13-26}$$

This relates the macroscopic self-diffusivity to the jump frequency, average hop distance and correlation factor in three dimensions.

Using the point source in two dimensions, the analogous result for diffusion in one dimension is:

$$D = \frac{\Gamma\langle r \rangle^2 f}{4} \tag{13-27}$$

and in general for a point source in N dimensions:

$$D = \frac{\Gamma\langle r \rangle^2 f}{2N} \tag{13-28}$$