Transport Properties: Diffusion, Fick's Laws, Random Walks

16th February 2009

1 Introduction

In this discusison, we explore aspects of describing how systems change in time from an initial state to a final state. Effectively, we are interested in that non-equilibrium regime during which system properties change.

System properties change in response to perturbations from equilibrium (external forces)

System properties that can change include: 1). matter(diffusion), 2). energy (temperature), 3). momentum (viscosity)

2 Fluxes

Quantity transferred through a given *area* per unit *time*
Flux occurs because of a *spatial and time-varying gradient* of an associated system property.
Flux occurs in *opposition* to *spatial gradient*
Flux continues until the gradient is nullified and equilibrium is reached.
Flux continues until external force stop

The most general relation for a flux in the x-direction is:

$$J_x = -\alpha \frac{d(property)}{dx} \tag{1}$$

This relates a flux to a gradient of a property (not specifically defined to be anyting at this point)

Flux is a **linear response**; this treatment assumes a **perturbative displacement** from equilibrium.

Figure 35.1 from Engel and Reid

Once the barrier is removed, particles will "flow" from regions of high concentration (probability) to regions of low concentration(probability). The **particle density** is the variable $\tilde{N}$.

A natural question is: **What is the time-dependence of the concentration profile?**

3 Mass Transport: Fick's Laws and Diffusion

Here we derive Fick's First Law of Diffusion (not really a law; just a mass balance).

Consider the following spatial density profile for an ideal gas (we only consider diffusion in one dimension, along the x-direction).

The flux plane is located at $x = 0$; **this is the plane through which we will derive the flux**. Two other planes at $-\lambda$ and $+\lambda$ are also shown. The λ are located at distances from the flux plane that correspond to the **mean free path** of the gas particles.

First, we need to determine the **net flux** at the flux plane (x=0). The **net flux** is:

$$J_{netflux} = J_{-\lambda} - J_{+\lambda} \tag{2}$$

Thus, we need to find the expression for the flux at a plane. For the **x-direction**, this is given by:

$$J_x = \tilde{N} \int\limits_0^\infty v_x f(v_x) dv_x \tag{3}$$

Substituting the Maxwell distribution of **speeds** (discussed in previous lectures):

$$\mathbf{J_x = \tilde{N} \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}} = \frac{\tilde{N}}{4} v_{ave}} \tag{4}$$

Now, we need to find the **local density at the planes,** $J_{-\lambda}$ **and** $J_{+\lambda}$. These densities are $\tilde{N}(\lambda)$ and $\tilde{N}(-\lambda)$ (the two planes on either side of the flux plane drawn above).

Taylor expand the number density about x=0 (the location of the **flux plane**:

$$\tilde{N}(\lambda) = \tilde{N}(x = 0) + \lambda \frac{d\tilde{N}}{dx}|_{x=0} \tag{5}$$

$$\tilde{N}(-\lambda) = \tilde{N}(x = 0) - \lambda \frac{d\tilde{N}}{dx}|_{x=0} \tag{6}$$

We can now determine the net flux as follows:

$$J_{netflux} = J_{-\lambda} - J_{+\lambda} \tag{7}$$

$$\mathbf{J_{netflux}} = -\frac{1}{2}\mathbf{v_{ave}}\lambda\left(\frac{d\tilde{N}}{dx}\right)_{x=0} \tag{8}$$

This is nominally the kinetic theory result for the diffusion constant!. comparing the last equation to the general form for a flux, we see that the diffusion constant from kinetic theory is dependent on the average speed and the mean free path! these are both results obtained from a knowledge of the Maxwell distrubtion of speeds.

An alternate form takes into account that fact that not all particles leaving the plane at $-\lambda$ will arrive at the flux plane; orientatinlly averaging the mean free path, one finds that roughly one-third of the particles do not reach the flux plane, leaving 2/3 of the above result. This leaves:

$$\mathbf{J_{netflux}} = -\frac{1}{3}\mathbf{v_{ave}}\lambda\left(\frac{d\tilde{N}}{dx}\right)_{x=0} \tag{9}$$

The diffusion constant is now:

$$D = \frac{1}{3}v_{ave}\lambda \tag{10}$$

This is the result of Fick's First Law that we are looking for:

$$\mathbf{J_x} = -\mathbf{D}\left(\frac{d\tilde{N}}{dx}\right)_{x=0} \tag{11}$$

4

4   Fick's Second Law

In the last section, we discussed the relation between flux and the spatial gradient of concentration (in one dimension). We know that the flux leads to an equiilibration over time; thus, the density profile is not only varying in the spatial dimension, but also in time. That is, $\tilde{N} = \tilde{N}(x,t)$. We know turn to determining the **time** evolution of the densitiy profile. This gives us a sense of how matter will disperse in space and time.

If we consider the following Figure,

we can write a mass balance for the volume between x and $x + dx$ as follows:

$$\frac{\delta N}{\delta t} = In - Out \tag{12}$$

$$\frac{\delta N}{\delta t} = (A)(J_x) - (A)(J_{x+dx}) \tag{13}$$

$$\frac{\delta N}{\delta t} = A(J_x - J_{x+dx}) \tag{14}$$

$$\tag{15}$$

Now, we can determine the expression for **concentration** changing with time by dividing both sides by **Volume, V** as:

$$\frac{\delta(\frac{N}{V})}{\delta t} = \frac{A}{V}(J_x - J_{x+dx}) \tag{16}$$

$$\frac{\delta \tilde{N}}{\delta t} = \frac{A}{V}(J_x - J_{x+dx}) \tag{17}$$

$$\tag{18}$$

We also see from the figure that $\frac{A}{V} = \frac{1}{\delta x}$. Thus:

$$\frac{\delta \tilde{N}}{\delta t} = \frac{(J_x - J_{x+dx})}{\delta x} \tag{19}$$

$$\frac{\delta \tilde{N}}{\delta t} = -\frac{\delta J}{\delta x} \tag{20}$$

$$\tag{21}$$

In the limit of an infinitesimal width dx, we obtain:

$$\frac{d\tilde{N}}{dt} = -\frac{dJ}{dx} \tag{22}$$

$$\tag{23}$$

Substuting Ficks's first law for the flux, J, yields finally, **Fick's Second Law (Diffusion Equation)**:

$$\frac{d\tilde{N}(x,t)}{dt} = D\frac{d^2\tilde{N}(x,t)}{dx^2} \tag{24}$$

From this we see that the time dependence of the concentration profile depends on the second derivative, and effectively, the **curvature** of the concentration gradient profile. **The more severe the curvature, the faster the rate of change**.

6

This second order differential equation can be solved in a variety of ways using the appropriate **boundary conditions**. In this case, one needs to specify things like the initial concentration profile in order to determine a specific solution. For the present, we present a solution for the case where one starts **with N_o particles confined to a plane of surface A at time t=0**:

$$\tilde{N}(x,t) = \frac{N_o}{2A\sqrt{\pi Dt}}e^{\frac{-x^2}{4Dt}} \tag{25}$$

Figure 35.5 in Engel and Reid shows representative profiles of the particle density for various times. For small times, the curvature is large; thus, more rapid relaxation of the concentration profile towards it flat profile at equilibration (infinitely long times).

Probabilistic Interpretation of the Solution to the Diffusion Equation

We can also consider the solution of the diffusion equation as a represenation of the probability of finding a particle at a position x at a particular time, t; the initial position is $x = 0$ by construction.

As such, we can use this **probability distribution** to determine **an average value**; in this case, we are interested in the **root mean square (rms)** displacement of the particle. This metric of average dynamics intuitively should depend on the diffusion constant and time. To derive this, we apply the usual approach for averages:

$$x_{rms} = \langle x^2 \rangle^{\frac{1}{2}} = \left[\frac{A}{N_o} \int_{-\infty}^{\infty} x^2 \tilde{N}(x,t)dx \right]^{\frac{1}{2}} \tag{26}$$

$$x_{rms} = \sqrt{2Dt} \tag{27}$$

Thus, the roo-mean-square displacment does indeed depend on the diffusion constant and time (both to the power one-half).

For diffusion in 3-D, the equivalent expression for the scalar distance of displacement r_{rms} is simply:

$$r_{rms} = \sqrt{6Dt} \qquad (28)$$

5 Diffusion as a Random Walk

We end by a discussion of the diffusion as a **random process, or random walk**. This suggests one can approach the problem from a **statistical perspective**, invoking the formalism of probability distributions, large numbers, and statistical averages. (Aside: the process we'll consider is actually **stochastic** and such processes are of immense importance in the workings and understanding of the securities markets that are so important to our daily lives).

A random walk process is generally defined as one for which there is no correlation between sequential steps; i.e., there is no memeory. Based on the discussion of diffusion, and the motion of a particle in between collisions, after which there is no memory of the collision, fits this random walk process.

Let's consider a one-dimensional random walk along the x-dimension. Here are the rules:
1. take one step in either positive or negative x-direction 2. there is no bias to which direction one goes from the current position
The question we pose:

What is the probability of reaching position X (equivalently having travelled a distance X) from the origin after having taken Δ total steps?

Some definitions: Δ is the **total** number of steps
Δ_- is the number of steps in the **negative** x direction
Δ_+ is the number of steps in the **positive** x direction
$X = \Delta_+ - \Delta_-$
$\Delta = \Delta_+ + \Delta_-$

The weight of position X is essentially the **number of ways of reaching X given Δ total steps with Δ equal to the sum of the positive and negative steps, and X being the difference**.

Without the constraint of having to arrive at X given the total number of steps, the total number of ways of executing Δ steps, each with only 2 pos-

sibilities, is 2^Δ.

The probability of reaching position X then, is simply the ratio:

$$P(X) = \frac{W_X}{W_{total}} \tag{29}$$

$$P(X) = \frac{W_X}{2^\Delta} \tag{30}$$

What is W_X? (Recall: The number of ways of arriving at X given a total of Δ steps)

$$W_X = \frac{\Delta!}{\left(\frac{\Delta+X}{2}\right)! \left(\frac{\Delta-X}{2}\right)!} \tag{31}$$

The probabiilty is then:

$$P(X) \propto e^{\frac{-X^2}{2\Delta}} \tag{32}$$

Looking back to the diffusion equation solution, we see similarities; the particle density, $\tilde{N}$ is also proportional to a Gaussian distribution function. Equating the two results, we can draw some analogies.

$$\frac{x^2}{4Dt} = \frac{X^2}{2\Delta} \tag{33}$$

Note how the question for the random walk example was posed; what is the probability of arriving at X after a total number of steps. The total number of steps can be plausibly reasoned to be some total time, based upon some characteristic time per step!

Ascribe realistic interpretation for Δ and X:

$$\Delta = \frac{t}{\tau} \tag{34}$$

$$x = (X)(x_o) \tag{35}$$

These definitions give for the diffusion constant:

$$D = \frac{x_o^2}{2\tau} \qquad\qquad Einstein - Smoluchowski\ Equation \tag{36}$$

What is the difference between the random walk timestep, τ for benzene and argon?

What is obtained for the diffusion constant if the mean free path and average time between collisions (derive from kinetic theory) are applied in the Einstein-Smoluchoswki expression for the diffusion constant?