

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

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1 Introduction

In this discussion, 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:

$$J_x = -\alpha \frac{d(\text{property})}{dx}$$
$$J_x = \left(\frac{1}{\text{Surface Area}} \right) \left(\frac{d(\text{property})}{dt} \right)$$

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

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

It can be shown (Engel and Reid, Section 34.2) that the total flux in the x-direction (considering one-dimensional diffusion) across a surface is:

$$J = -D \left(\frac{d \tilde{N}}{d x} \right) \quad \text{Fick's First "Law"}$$

where the **diffusion constant**, **D**, is the proportionality constant (or conductance of mass) given in the earlier general expression. The diffusion constant is related to microscopic properties of matter, namely the particles comprising the fluid, through the relation:

$$D = \frac{1}{3} \langle \nu \rangle \lambda$$

where λ is the mean free path of the particle. The average speed, $\langle \nu \rangle$, is determined from our previous kinetic theory analysis.

Having determined the flux across a plane arising from a gradient of matter (i.e., **concentration gradient**), we now address the evolution of the concentration as a function of time and space (location). It is not difficult to accept that the flux generated by the initial concentration gradient will give rise to a varying concentration gradient. Thus, not only will concentration vary with location, but it will vary also with time. Thus, $\tilde{N} = \tilde{N}(x, t)$ in one dimension. The partial differential equation that governs this process is given by the **diffusion equation**, also known as Fick's Second "Law":

$$\frac{\partial \tilde{N}(x, t)}{\partial t} = D \frac{\partial^2 \tilde{N}(x, t)}{\partial x^2}$$

The diffusion equation can be solved using standard techniques of partial differential equations coupled with **initial conditions**, **boundary conditions** to yield a solution for the particle number density as a function of time and location (along the x-direction for the one-dimensional case). For

this solution, the initial condition is that N_o particles are positioned in a plane at $x = 0$:

$$\tilde{N}(x, t) = \frac{N_o}{A} \frac{1}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}}$$

$$\frac{\tilde{N}(x, t)}{(N_o / A)} = \frac{1}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}}$$

If we consider the ratio on the left-hand side of the last equation to be a probability of observing a particle within a small one-dimensional "volume" element, dx centered at x , we can write the **continuous probability distribution for one-dimensional diffusion** as:

$$P(x, t) dx = \frac{1}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}} dx$$

The root-mean-square displacement, $x_{rms} = \sqrt{\langle x^2 \rangle}$, is determined as:

$$\sqrt{\langle x^2 \rangle} = \sqrt{2 D t}$$

2.1 Isotropic Diffusion in Two- and Three-Dimensions

The **continuous probability distribution for two-dimensional, isotropic diffusion** (motion in the two dimensions is uncorrelated) is:

$$P(r, t) dr = \frac{1}{2 D t} e^{-\frac{r^2}{4Dt}} r dr$$

The **continuous probability distribution for three-dimensional, isotropic diffusion** (motion in the three dimensions is uncorrelated) is:

$$P(r, t) dr = \frac{4 \pi}{(4 \pi D t)^{3/2}} e^{-\frac{r^2}{4Dt}} r^2 dr$$

3 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 memory. 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 possibilities, is 2^Δ .

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

$$P(X) = \frac{W_X}{W_{total}} \quad (1)$$

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

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

$$W_X = \frac{\Delta!}{\left(\frac{\Delta+X}{2}\right)! \left(\frac{\Delta-X}{2}\right)!} \quad (3)$$

The probability is then:

$$P(X) \propto e^{-\frac{X^2}{2\Delta}} \quad (4)$$

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.

$$\frac{x^2}{4Dt} = \frac{X^2}{2\Delta} \quad (5)$$

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 :

$$\Delta = \frac{t}{\tau} \tag{6}$$

$$x = (X)(x_o) \tag{7}$$

These definitions give for the diffusion constant:

$$D = \frac{x_o^2}{2\tau} \qquad \textit{Einstein - Smoluchowski Equation} \tag{8}$$

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-Smoluchowski expression for the diffusion constant?