University of Washington
Department of Chemistry
Chemistry 553
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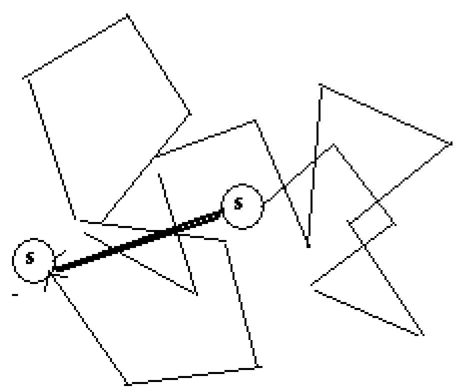
Lecture 1: The Diffusion Equation
Text Reading: Chandrasekhar, Ch. 1.1

A. The Diffusion Equation:

- One of the most fundamental statistical problems is the mathematical treatment of Brownian motion. Applications of Brownian motion occur throughout the physical and biological sciences, as well as in the fields of sociology, urban planning, economics, etc.
- Brownian motion is an example of a stochastic process. A stochastic process describes a process with an indeterminate outcome. Ultimately the properties arising from a stochastic process need to be described with a probability or distribution function f(x,t).
- Brownian motion is exemplified by the irregular pathway flowed by colloidal particles suspended in a fluid. If the trajectory (pathway) of an individual solvent molecule is traced out is appears to be a random walk…The displacement of the solute molecule after a time t is indicated by the dark, bold line. Designate this displacement r. Now, other molecules will be displaced in other directions. For every solute molecule displaced r as shown, there will be another solute molecule with a displacement in the opposite direction -r. These displacements will average to zero. When the displacements of all solute molecules are averaged…the result is zero. That is, $\langle x \rangle = 0$.



- Einstein's approach to modeling Brownian motion proceeds as follows. Without loss of generality we can assume one dimensional motion. Assume the number of particles at time t located between x and x+dx is defined as f(x,t)
- Assume that particles change location by sudden "jumps" that last for a time τ. If the particle starts at a location x', the length of the jump is $\Delta = x' - x$.

- The probability that in a instant of time τ a jump of length Δ occurs is given by the transition probability $\varphi(\Delta,\tau)$. After an instant of time τ, the number of particles at x is given by:

$$f(x,t+\tau)=\int_{-\infty}^{+\infty} f(x+\Delta,t)\varphi(\Delta,\tau)\,d\Delta \tag{1.1}$$

where $f(x+\Delta,t)$ is the number of particles located a distance Δ from x at a time t.

- Equation (1.1) is an integral equation. To obtain f(x,t) we must convert (1.1) to a differential equation. This is done by expanding $f(x,t+\tau)$ around τ=0:

$$f(x,t+\tau)=f(x,t)+\tau\frac{\partial f}{\partial t}+\dots \tag{1.2}$$

- $f(x+\Delta,t)$ is similarly expanding around Δ=0:

$$f(x+\Delta_x,t+\tau)=f(x,t)+\Delta_x\frac{\partial f}{\partial x}+\frac{\Delta_x^2}{2}\frac{\partial^2 f}{\partial x^2}+\dots \tag{1.3}$$

- Put (1.2) and (1.3) into (1.1) to obtain:

$$\begin{aligned} f(x,t)+\tau\frac{\partial f}{\partial t} &\approx \int_{-\infty}^{+\infty}\left[f(x,t)+\Delta_x\frac{\partial f}{\partial x}+\frac{\Delta_x^2}{2}\frac{\partial^2 f}{\partial x^2}\right]\varphi(\Delta_x,\tau)\,d\Delta_x \\ &= \int_{-\infty}^{+\infty} f(x,t)\varphi(\Delta_x,\tau)\,d\Delta_x+\int_{-\infty}^{+\infty}\Delta_x\frac{\partial f}{\partial x}\varphi(\Delta_x,\tau)\,d\Delta_x+\int_{-\infty}^{+\infty}\frac{\Delta_x^2}{2}\frac{\partial^2 f}{\partial x^2}\varphi(\Delta_x,\tau)\,d\Delta_x \end{aligned} \tag{1.4}$$

- Now the first integral on the right is;

$$\int_{-\infty}^{+\infty} f(x,t)\varphi(\Delta_x,\tau)\,d\Delta_x=f(x,t)\int_{-\infty}^{+\infty}\varphi(\Delta_x,\tau)\,d\Delta_x=f(x,t) \tag{1.5}$$

- The second integral on the right is:

$$\int_{-\infty}^{+\infty}\Delta_x\frac{\partial f}{\partial x}\varphi(\Delta_x,\tau)\,d\Delta_x=\frac{\partial f}{\partial x}\int_{-\infty}^{+\infty}\Delta_x\varphi(\Delta_x,\tau)\,d\Delta_x=0 \tag{1.6}$$

where the integral $\int_{-\infty}^{+\infty}\Delta_x\varphi(\Delta_x,\tau)\,d\Delta_x=0$ because the function $\varphi(\Delta,\tau)$ is even, i.e. $\varphi(\Delta_x,\tau)=\varphi(-\Delta_x,\tau)$.

- The third integral is treated as follows:

$$\int_{-\infty}^{+\infty}\frac{\Delta_x^2}{2}\frac{\partial^2 f}{\partial x^2}\varphi(\Delta_x,\tau)\,d\Delta_x=\frac{1}{2}\frac{\partial^2 f}{\partial x^2}\int_{-\infty}^{+\infty}\Delta_x^2\varphi(\Delta_x,\tau)\,d\Delta_x=\frac{\langle\Delta_x^2\rangle}{2}\frac{\partial^2 f}{\partial x^2} \tag{1.7}$$

Where $\langle\Delta_x^2\rangle$ is the mean squared displacement of the Brownian particle.

- Using the results for these three integrals (1.4) reduces to:

$$\frac{\partial f}{\partial t}=D\frac{\partial^2 f}{\partial x^2} \tag{1.8}$$

where the coefficient of diffusion $D=\frac{\langle\Delta_x^2\rangle}{2\tau}$.

- This result is for a single dimension. In three dimensions the mean squared displacement is $\left\langle \Delta^2 \right\rangle = \left\langle \Delta_x^2 \right\rangle + \left\langle \Delta_y^2 \right\rangle + \left\langle \Delta_z^2 \right\rangle$. If motion in all three dimensions is equivalent we have: $\left\langle \Delta_x^2 \right\rangle = \left\langle \Delta_y^2 \right\rangle = \left\langle \Delta_z^2 \right\rangle = \frac{\left\langle \Delta^2 \right\rangle}{3}$ and the diffusion coefficient is

$$D = \frac{\left\langle \Delta^2 \right\rangle}{6\tau} \tag{1.9}$$

- In three dimensions (1.8) is:

$$\frac{\partial f}{\partial t} = D\left(\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \right) = D\nabla^2 f \tag{1.10}$$

- For (1.8) given a delta function initial condition $f\left(x,0\right) = \delta\left(x\right)$
- Solve (1.8) by defining the Fourier transform of f(x,t):

$$\psi\left(s,t\right) = FT\left(f\left(x,t\right); x \to s\right) = \int_{-\infty}^{+\infty} f\left(x,t\right) e^{isx} dx$$

$$\therefore FT\left(\partial_x f\left(x,t\right); x \to s\right) = \int_{-\infty}^{+\infty} \partial_x f\left(x,t\right) e^{isx} dx = -is\psi\left(s,t\right) \tag{1.11}$$

$$FT\left(\partial_x^2 f\left(x,t\right); x \to s\right) = \int_{-\infty}^{+\infty} \partial_x^2 f\left(x,t\right) e^{isx} dx = -s^2\psi\left(s,t\right)$$

- And FT equation (1.8)

$$\begin{aligned} \frac{\partial\psi\left(s,t\right)}{\partial t} &= \partial_s\psi\left(s,t\right) = -s^2 D\psi\left(s,t\right) \\ \therefore \psi\left(s,t\right) &= \psi\left(s,0\right) e^{-s^2 Dt} \end{aligned} \tag{1.12}$$

where $\psi\left(s,0\right) = \int_{-\infty}^{+\infty} \delta\left(x\right) e^{isx} dx = 1$. Now inverse transform:

$$\begin{aligned} f\left(x,t\right) &= FT^{-1}\left(\psi\left(s,t\right)\right) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \psi\left(s,t\right) e^{-isx} ds \\ &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-s^2 Dt} e^{-isx} ds = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \end{aligned} \tag{1.13}$$

- Note using (1.13) the following averages may be calculated:

$$\begin{aligned} \left\langle x \right\rangle &= \int_{-\infty}^{+\infty} xf\left(x,t\right) dx = \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{+\infty} xe^{-x^2/4Dt} dx = 0 \\ \left\langle x^2 \right\rangle &= \int_{-\infty}^{+\infty} xf\left(x,t\right) dx = \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{+\infty} x^2 e^{-x^2/4Dt} dx = 2Dt \end{aligned} \tag{1.14}$$