Lecture 7 – Random Walks and Diffusion

- Sections 5.2 and 5.3 in the textbook
- Random walks
- Diffusion equation
- Fick’s Law
Random walks

- Particles in a fluid collide at a rate of $\gamma$, which depends on:
  - the number density of molecules, $\rho$
  - the cross section of the molecule, $\sigma$
  - the average relative speed of molecules, $\langle |v| \rangle$, which in turn depends on the energy/temperature of the fluid

- the distance a particle travels between collisions (the mean free path) is defined as

$$\lambda = \frac{1}{\sqrt{2} \rho \sigma}$$
Calculating net displacement, $k$

- In a one-dimensional random walk, a particle moves in steps. The length of a step is the mean free path, $\lambda$.

- For each step, the particle can either move left or right – the directions have equal probabilities of $\frac{1}{2}$ and do not depend on the direction of the previous step.

- Let $i =$ number of steps to the right and $j =$ number of steps to the left.

- The net displacement, $k = i - j$. 
Calculating the probability of $k$

- After 4 steps, a particle is 2 steps to the right of where it started:

\[
N = 4 \\
k = 2 \\
i = 3 \\
j = 1 \\
H_1, H_2, H_3, T_1 \\
\vdots \\
H_1, H_2, H_3, T_1 = H_2, H_1, H_3, T_1 \\
\text{H's are indistinguishable} \\
\text{T's are indistinguishable} \\
\text{total of arrangements} = \frac{4!}{3!1!} \\
\text{for } k = 2
\]
Probability of being a net distance, k

\[
P(k) = \frac{\text{# of arrangements of } i \text{ and } j \text{ steps}}{\text{Total # of possible arrangements}} = \frac{n!}{(i^i)(j^j)(k^k)}
\]

\[
P(k) = \frac{n!}{2^i \cdot i^i \cdot i^i \cdot j^j \cdot j^j \cdot k^k}
\]

\[
\text{Stirling's Approximation is used when } n \text{ is large:}
\]

\[
\ln(n!) = n \ln(n) - n - \frac{1}{2} \ln(2\pi) + \ldots
\]

\[
\ln(P(k)) = \ln(n!) - \ln(i!) - \ln(j!) - \ln(k!)
\]

\[
= n \ln(n) - n - \frac{1}{2} \ln(2\pi) - \left[\ln(i! \cdot j! \cdot k! \cdot \frac{k}{2})\right] - \left[\ln(i! \cdot j! \cdot k! \cdot \frac{k}{2})\right]
\]

\[
= n \ln(n) - n - \frac{1}{2} \ln(2\pi) - \left[\ln(i!) \cdot \ln(j!) \cdot \ln(k!) \cdot \ln\left(\frac{k}{2}\right)^2\right]
\]

\[
= n \ln(n) - n - \frac{1}{2} \ln(2\pi) - \frac{1}{2} \left[\ln(i!) \cdot \ln(j!) \cdot \ln(k!) \cdot \ln\left(\frac{k}{2}\right)^2\right]
\]

\[
= n \ln(n) - n - \frac{1}{2} \ln(2\pi) - \frac{1}{2} \left[\ln(i!) \cdot \ln(j!) \cdot \ln(k!) \cdot \ln\left(\frac{k}{2}\right)^2\right]
\]

\[
= \frac{1}{2} \ln(n^2) \cdot \ln\left(\frac{k}{2}\right)^2 - \frac{1}{2} \ln(k^2) \cdot \ln\left(\frac{k}{2}\right)^2
\]

\[
P(k) = e^{-\frac{k^2}{2Nk^2}}
\]

k = net # of steps away from the starting location

k (distance) \rightarrow x (continuous)

\[
\lambda = \text{mean free path}
\]

\[
P(x) = \frac{\text{initialisation factor}}{x^2}{\int_0^\infty e^{-x^2} dx = \pi^2N^2x^2}^{\frac{1}{2}}
\]

\[
A = \frac{1}{2\pi x^2}
\]

\[
P(x) = \frac{1}{(2\pi x^2)^{1/2}} e^{-\frac{x^2}{2x^2}}
\]

\[
N\lambda^2 = L
\]

L = "characteristic distance"
Probability for 3 dimensional system

\[
P(x) = \frac{1}{(2\pi N \lambda^2)^{\frac{1}{2}}} e^{-\frac{x^2}{2N\lambda^2}} \quad \text{1D system}
\]

3 Dimensions - Cartesian coordinates

\[
P(x, y, z) = P(x) \cdot P(y) \cdot P(z) = \frac{1}{(2\pi N \lambda^2)^{\frac{3}{2}}} e^{-\frac{(x^2 + y^2 + z^2)}{2N\lambda^2}}
\]

(direcctions are independent)

Polar coordinates:

\[
r = (x^2 + y^2 + z^2)^{\frac{1}{2}}
\]

\[
P(r) = \frac{4\pi}{(2\pi N \lambda^2)^{\frac{3}{2}}} e^{-\frac{r^2}{2N\lambda^2}} r^2
\]
\[ P(r) = \frac{4 \pi}{(2\pi N \lambda^2)^{3/2}} e^{-\frac{r^2}{2N\lambda^2}} \]

Recall that \( N \) is the number of collisions = \( \delta t \), \( \delta t \) = rate of collisions

\[ P(r) = \frac{4 \pi}{(2\pi \delta t \lambda^2)^{3/2}} e^{-\frac{r^2}{2\delta t \lambda^2}} \]

Let \( \delta \lambda^2 = D \) ← diffusion constant

\[ P(r) = \frac{4 \pi}{(4\pi D \delta t)^{3/2}} e^{-\frac{r^2}{4D\delta t}} \]

What is the significance of \( D \)?

We know that \( \langle r^2 \rangle = 0 \)

What about \( \langle r^2 \rangle^{1/2} \rightarrow \) root mean square

\[ \langle r^2 \rangle = \int_0^\infty r^2 P(r) \, dr = \frac{\pi}{2(\pi D \delta t)^{3/2}} \int_0^\infty r^4 e^{-\frac{r^2}{4D\delta t}} \, dr \]

\[ = \frac{\pi}{2(\pi D \delta t)^{3/2}} \cdot \frac{3}{8} \pi^{1/2} (2D \delta t)^{5/2} = 6D \delta t = \langle r^2 \rangle \]

\[ \langle r^2 \rangle^{1/2} = \sqrt{6D\delta t} \] Einstein Diffusion equation
**Diffusion constant, D**

- The diffusion constant, $D$ – a measure of how "mobile" a substance is in another substance.

$$D = \frac{\lambda^2 \Delta t}{2} = \frac{1}{2} \frac{\left< v_{AA} \right>^2}{\sigma}$$

(in the case of A diffusing in A)

$D \propto$ relative speed of particles (affected by $T$, mass, molecular interactions)

$D \propto \frac{1}{\rho}$, \(\rho = \# \text{ density}\), $D \propto \frac{1}{\sigma}$
Molecular dynamic simulations to estimate D

- Professor Tuckerman’s group uses molecular dynamics simulations using forces computed directly from the solution of the electronic Schroedinger equation via DFT

**Diffusion of a hydronium ion in water:**

- $D_{DVR} = 0.80 \text{ Å}^2/\text{ps}$
- $D_{PW} = 0.31 \text{ Å}^2/\text{ps}$
- $D_{exp} = 0.67 \text{ Å}^2/\text{ps}$

**Diffusion of OH- ions in water:**


Fick’s Laws of Diffusion

- Fick’s laws of diffusion describe how density gradients affect diffusion rates

\[ \frac{dp}{dx} \Rightarrow \text{driving force for diffusion} \]

Flux, \( J \), is defined as:

\[ J = \frac{\text{\# of molecules}}{\text{area} \cdot \text{time}} \]

\[ J = -D \frac{dp}{dx} \] (steady state \( \Rightarrow \) doesn’t change over time)