

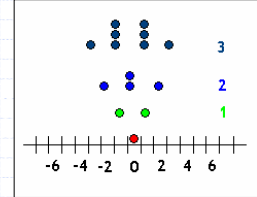
Physical Chemistry

Lecture 2

Diffusion and random walks

Random walk in one dimension

- ◆ Particle hops from site to site
 - Only one step per hop
- ◆ Probability of hopping in either direction is $\frac{1}{2}$ for each step
- ◆ Calculate probability that, after m steps, the particle is at position q



Mathematics of random walks

- ◆ Probability has two factors

$$P(q; m) = \left(\frac{1}{2}\right)^m C(n, p)$$

- ◆ Number of ways to end up at q is a **combinatorial factor** based on the number of positive steps, p , and the number of negative steps, n

$$C(n, p) = \frac{m!}{n! p!} = \frac{m!}{\binom{m+q}{2} \binom{m-q}{2}}$$

Calculation of averages in a one-dimensional random walk

- ◆ Use the probability, P , to get averages of functions of the distance in m steps

$$\overline{f(q)} = \sum_{q=-m}^{+m} P(q, m) f(q) = \left(\frac{1}{2}\right)^m \sum_{q=-m}^{+m} \frac{m!}{\binom{m+q}{2} \binom{m-q}{2}} f(q)$$

- ◆ Examples:

$$\overline{q} = 0$$

$$\overline{q^2} = m$$

- ◆ The average position does not appear to change with number of steps, but the square of the distance traveled does.

Example random walk

- ◆ Movement of He in a given time

- $T = 298.15 \text{ K}$
- $P = 1 \text{ bar}$

- ◆ Distance moved

$$\Delta x = \sqrt{x^2 - x^2} = \sqrt{m\lambda} = \sqrt{z t \lambda}$$

TIME	Δx
1 second	1.6 cm
1 minute	12.1 cm
1 hour	93.9 cm
1 day	460 cm
1 week	1220 cm

- ◆ Typical flask is of the order of 10 cm in diameter.

- In one minute, a molecule samples a reasonable fraction of the environment in that flask.

Small-step-size, large-step-number random walk

- ◆ Treat the distribution function, P , as a continuous function

$$P(q, m) = \frac{2}{\sqrt{2\pi m}} \exp\left(-\frac{q^2}{2m}\right)$$

- ◆ Technically only correct for either even or odd q , but we "smooth" the probability over many steps

- ◆ Gaussian function

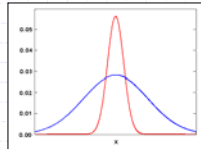
- ◆ Normalized probability distribution function

Gaussian functions

- Occur in many different situations where random processes affect the experiment

$$P(x, \sigma) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{x^2}{2\sigma^2}\right)$$

- Shape is determined by the standard deviation, σ
 - Large σ , wide function
 - Small σ , narrow function
- Random noise is gaussian



Diffusion from a point source

- Random movement of molecules is **diffusion**
- Described by a parameter, D , the diffusion coefficient
- Diffusion in one dimension described by the probability distribution

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

Gas-phase diffusion

- Diffusion coefficient related to gas-kinetic parameters $D = k v \lambda$
 - where $k = 0.5$ from simple kinetic theory
 - $k = 0.599$ from more accurate theory
- Measured and calculated gas diffusion coefficients at 273.15 K and 1.01325 bar

Noble Gas	Diffusion Coefficient	
	Calculated	Experimental
Neon	$4.35 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$	$4.52 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$
Argon	$1.54 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$	$1.57 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$
Krypton	$0.93 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$	$0.93 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$
Xenon	$0.57 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$	$0.58 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$

Diffusion in three dimensions

- Assume the diffusion in the three dimensions is uncorrelated

$$P(x, y, z; t) dx dy dz = P(x, t) P(y, t) P(z, t) dx dy dz$$

$$= \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{x^2 + y^2 + z^2}{4Dt}\right) dx dy dz$$
- In spherical co-ordinates it simplifies and depends only on r

$$P(r, \theta, \phi; t) d\Omega = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right) r^2 \sin \theta dr d\theta d\phi$$

Macroscopic diffusion

- Diffusion eliminates concentration gradients
- Diffusion can be expressed in terms of the changes in concentrations
- Mass flux across an area, J
- Fick's first law** in one dimension: diffusion is "caused" by a concentration gradient

$$J = -D \frac{\partial c}{\partial x}$$

Macroscopic diffusion

- Fick's second law**: The rate of change of concentration in a volume is determined by the gradient of the flux across its boundaries

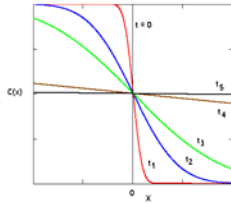
$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) = D \left(\frac{\partial^2 c}{\partial x^2} \right)$$

- In three dimensions

$$\frac{\partial c}{\partial t} = D \nabla^2 c$$

Solutions of Fick's equations

- ◆ Depends on boundary conditions
- ◆ Example: diffusion between two tubular regions, like from sugar water into pure water in a pipe



"Typical" diffusion coefficients

Gas (0°C)	D/(cm ² s ⁻¹)	Liquid (25°C)	D/(cm ² s ⁻¹)
H ₂	1.5	H ₂ O	0.000024
O ₂	0.19	CH ₃ OH	0.000023
N ₂	0.15	C ₆ H ₆	0.000022
CO ₂	0.10	Hg	0.000017
C ₂ H ₄	0.09	C ₂ H ₅ OH	0.000010
Xe	0.05	C ₃ H ₇ OH	0.000006

Summary

- ◆ Random walk is a simple theory of movement
- ◆ Diffusion describes the results of random movement of molecules
 - Random-walk derivation
 - Fick's Laws
- ◆ Diffusion coefficient characterizes the material