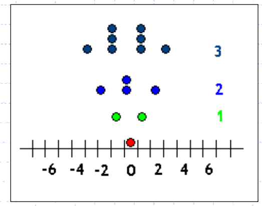
Physical Chemistry

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 ½ 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

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

Calculation of averages in a one-dimensional random walk

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

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

- Examples:

$$< q > = 0$$

$$< q^2 > = m$$

- 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 K
  - P = 1 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

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

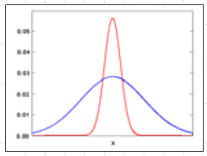
- Technically only correct for either even or odd q, but we “smooth” the probability over many steps
- Gaussian function
- Normalized probability distribution function

Gaussian functions

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

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

- 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	4.35×10^{-5} m^2 s^{-1}	4.52×10^{-5} m^2 s^{-1}
Argon	1.54×10^{-5} m^2 s^{-1}	1.57×10^{-5} m^2 s^{-1}
Krypton	0.93×10^{-5} m^2 s^{-1}	0.93×10^{-5} m^2 s^{-1}
Xenon	0.57×10^{-5} m^2 s^{-1}	0.58×10^{-5} m^2 s^{-1}

Diffusion in three dimensions

- Assume the diffusion in the three dimensions is uncorrelated

$$P(x,y,z;t)dxdydz = P(x,t)P(y,t)P(z,t)dxdydz$$

$$= \frac{1}{(4\pi Dt)^{3/2}}\exp\left(-\frac{x^2+y^2+z^2}{4Dt}\right)dxdydz$$

- 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

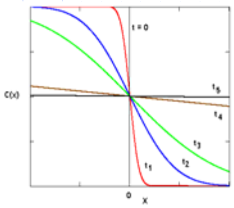
$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) = D\left(\frac{\partial^2 c}{\partial x^2}\right)$$

- 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/($10^{-4}m^2s^{-1}$)	Liquid (25°C)	D/($10^{-9}m^2s^{-1}$)
H_2	1.5	H_2O	2.4
O_2	0.19	CH_3OH	2.3
N_2	0.15	C_6H_6	2.2
CO_2	0.10	Hg	1.7
C_2H_4	0.09	C_2H_5OH	1.0
Xe	0.05	C_3H_7OH	0.6

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