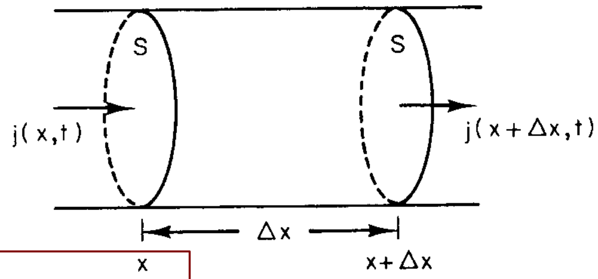
Chapter 4: Transport in an Infinite Medium

Part II

Continuity Equation: 1D



- Hence,

$$\frac{\partial}{\partial t}N(x,t) = -(S\Delta x)\frac{\partial}{\partial x}j(x,t)$$

- Then, the continuity equation in 1D is,

$$\frac{\partial C}{\partial t} = -\frac{\partial j}{\partial x}$$

Brownian Motion

- Application of thermal equilibrium at temperature T
- Kinetic energy in 1D = $k_B T/2$
- Kinetic energy in 3D = $3k_B T/2$
- Random motion → mean velocity $\bar{v} = 0$
  - can only deal with mean-square velocity $\overline{v^2}$

$$\frac{1}{2} m\overline{v^2} = \frac{3k_B T}{2} \Rightarrow v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}$$

Motion in a Gas

- Brownian motion of particles: collisions
- Mean Free Path
  - Average distance between successive collisions
- Collision Time
  - Average time between successive collisions

Motion in a Gas

- Consider *N*(*x*) to be number of particles without collision after a distance *x*
- For short distances *dx*, probability of collision is proprtional to *dx*

$$dN = N(x)\left(\frac{1}{\lambda}\right)dx \quad \rightarrow \quad N(x) = N_0 e^{-x/\lambda}$$

Motion in a Gas

- Average distance = mean free path

$$\bar{x} = \frac{1}{N_o}\int_0^\infty x\frac{N(x)}{\lambda}dx = -\lambda\left[e^{-x/\lambda}\left(\frac{x}{\lambda}+1\right)\right]_0^\infty = \lambda$$

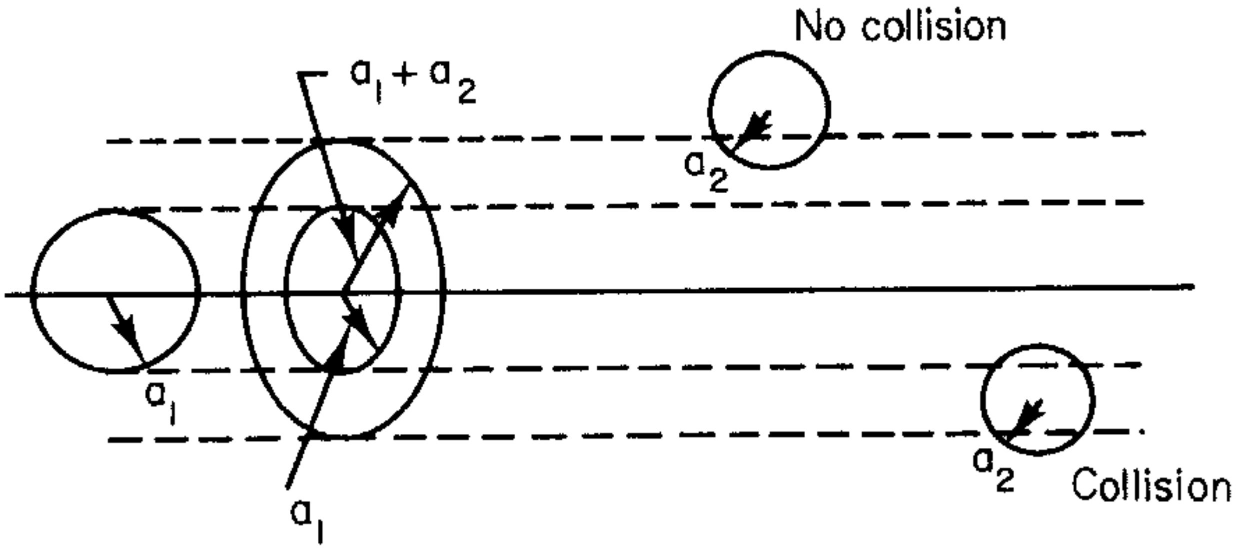
- Similar argument can be made for time

$$N(x) = N_0 e^{-x/t_c}$$

  - Collision time = t_c

Motion in a Gas

- Need to evaluate λ and t_c
- Consider one particle moving with a radius a_1
- Consider stationary particles with radius a_2



- Calculate collision possibilities

Motion in a Gas

- After moving a distance x, volume covered is given by,

$$V(x) = \pi(a_1 + a_2)^2 x$$

- On average, when a particle travels mean free path, there is one collision
  - Average number of particles in $V(\lambda)=1$
  - Concentration = $1/V(\lambda)$

$$C = 1/V(\lambda) = 1/\pi(a_1 + a_2)^2 \lambda \Rightarrow \lambda = \frac{1}{\pi(a_1 + a_2)^2 C}$$

Motion in a Gas

- Collision *Cross Section* is $\pi(a_1 + a_2)^2$
  - Important for radiation interaction
- Example: gas at STP, volume of 1 mol = 22.4 L ($C = 2.7\times10^{25} m^{-3}$), $a_1 = a_2 = 0.15$ nm
  - $\lambda = 0.13\ \mu m$
  - 1000 times the molecular diameter
  - Assumption of infrequent collisions justified

Motion in a Gas

- Given mean free path λ,

$$t_c = \frac{\lambda}{\overline{v}}$$

- Taking the average speed as v_{rms},

$$t_c \approx \lambda \left(\frac{m}{3k_B T} \right)^{1/2}$$

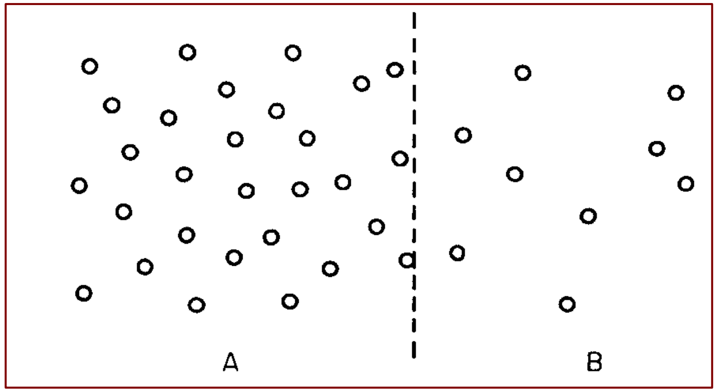
  - Dependence on $m^{1/2}$ and λ
  - For air and room temperature, $t_c = 2 \times 10^{-10}$ s

Motion in a Liquid

- Direct substitution in Gas equations?
- For water,
  - $\lambda = a = 0.1$ nm $\rightarrow$ assumption broken
  - $t_c \sim 10^{-13}$ s $\rightarrow$ much more frequent
  - Wrong calculations
  - However, concept appears to be valid!

Diffusion: Fick's First Law

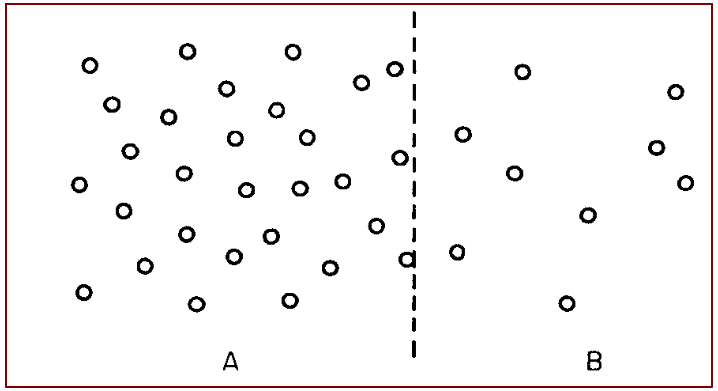
- Diffusion: random movement of particles from a region of higher concentration to a region of lower concentration
- Diffusing particles move independently
- Solvent at rest
  - Solute transport



Diffusion: Fick's First Law

- If solute concentration is uniform, no net flow
- If solute concentration is different, net flow occurs

$$j_x = -D\frac{\partial C}{\partial x}$$



D: Diffusion constant (m^2s^{-1})

Diffusion: Fick's First Law

TABLE 4.3. Various forms of the transport equation.

Substance flowing	Equation	Units of j	Units of the constant
Particles	$j_s = -D \frac{\partial C}{\partial x}$	$\mathrm{m^{-2}\ s^{-1}}$	$\mathrm{m^2\ s^{-1}}$
Mass	$j_m = -D \frac{\partial C}{\partial x}$	$\mathrm{kg\ m^{-2}\ s^{-1}}$	$\mathrm{m^2\ s^{-1}}$
Heat	$j_H = -\kappa \frac{\partial T}{\partial x}$	$\mathrm{J\ m^{-2}\ s^{-1}}$ or $\mathrm{kg\ s^{-3}}$	$\mathrm{J\ K^{-1}\ m^{-1}\ s^{-1}}$
Electric charge	$j_e = -\sigma \frac{\partial V}{\partial x}$	$\mathrm{C\ m^{-2}\ s^{-1}}$	$\mathrm{C\ m^{-1}\ s^{-1}\ V^{-1}}$ or $\Omega^{-1}\ \mathrm{m^{-1}}$
Viscosity (y component of momentum transported in the x direction)	$\frac{F}{S} = -\eta \frac{\partial v_y}{\partial x}$	$\mathrm{N\ m^{-2}}$ or $\mathrm{kg\ m^{-1}\ s^{-2}}$	$\mathrm{kg\ m^{-1}\ s^{-1}}$ or Pa s

Diffusion: Fick's Second Law

- Consider 1D case
- Fick's first law

$$j_x = -D\frac{\partial C}{\partial x}$$

- Continuity equation

$$\frac{\partial C}{\partial t} = -\frac{\partial j}{\partial x}$$

Diffusion: Fick's Second Law

- Combining Fick's first law and continuity equation,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

→Fick's second law

- 3D Case,

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right)$$

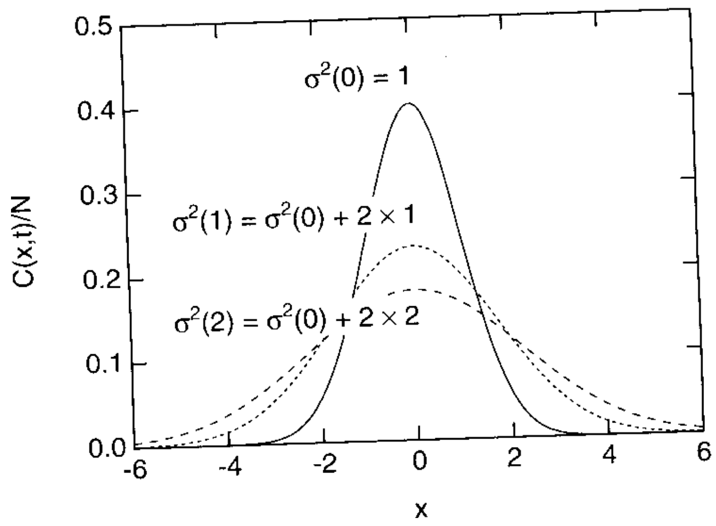
Diffusion: Fick's Second Law

- Solving Fick's second law for C(x,t)
  - Substitution

$$C(x,t) = \frac{N}{\sqrt{2\pi}\sigma(t)} e^{-x^2/2\sigma^2(t)}$$

where,

$$\sigma^2(t) = 2Dt + \sigma^2(0)$$



Problem Assignments

- Information posted on web site
- Problems 1,4,5,6,8,18,19