MODELLING: DIFFUSION

Introduction to Diffusion

=> Diffusion is a flow of particles down a concentration gradient

↳ Smoke in a room
Ink in water
Redistribution of atoms during a phase transition

Obtaining the equations governing diffusion

Obtaining the equations is outlined in 3 steps:

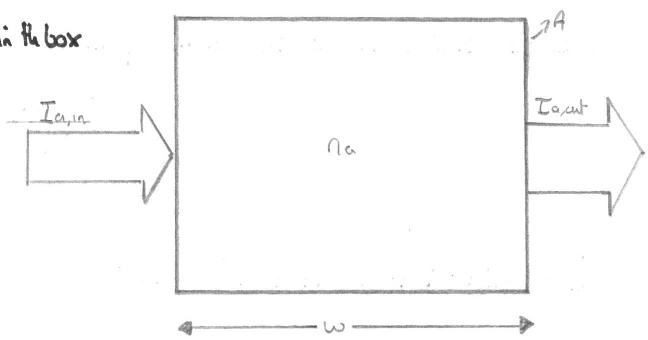
1. Continuity Equation (describes conservation of particles)
2. Write down the rules for the current interms of conc gradient (Ficks first law)
3. We combine Ficks first law with the continuity equation to eliminate the current of particles and produce an equation just in terms of concentration (Fick's second law)

Continuity Equation

- The continuity equation describes a conservation law (for diffusion the no. of particles conserved)
- The equation relates some kind of current to some kind of density
  ↳ For diffusion: Particle current
  Particle density

Continuity Equation in 1D for particles

particle type: a



- The difference in rates in and out leads to a change in the total number of a particles in the box
- Letting the particle currents flow for a time Δt

↳ The change in the number of particles of a in the box is:

$$\Delta n_a wA = \Delta t\,(I_{a,in} - I_{a,out}) \qquad [1]$$

- It is more convenient to work with particle current densities: $J_{a,in} = I_{a,in}/A$
  $J_{a,out} = I_{a,out}/A$

$$\therefore \quad \frac{\Delta n_a}{\Delta t} = \frac{1}{w}(J_{a,in} - J_{a,out}) \qquad [2]$$

w => width
A => cross sectional area
$I_{a,in}$ => flow rate in
$I_{a,out}$ => flow rate out
n_a => number density of a particles
ρ => Total number density of particles in the box

In the limit $w \to 0$ and $\Delta t \to 0$ we assume the current density is a continuous function of position x, giving:

$$\frac{\partial n_a}{\partial t} = -\frac{\partial J_a}{\partial x} \qquad [3]$$ //Continuity equation

When working with diffusion it is convient to work with concentrations rather than number densities.
Let the total number ~~of~~ density of particles in the box be ρ.
We define the concentration of a by $c_a = n_a/\rho$

$\therefore$ We can rewrite [3]:

$$\frac{\partial(\rho c_a)}{\partial t} = \frac{\partial J_a}{\partial x} \qquad [4]$$

MODELLING : Solving Diffusion Equations

The partial differential equation can be tackled in a range of methods and we shall consider one analytical and two numerical ones.

ANALYTIC SOLUTION

We consider the 1D case : $\frac{\partial c_a}{\partial t} = D \frac{\partial^2 c_a}{\partial x^2}$ [1]

An easy way to solve this is to reduce the differential equation into an ~~algebraic~~ ODE equation by way of the Fourier transform.

$$\frac{\partial c_a}{\partial x} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{c}_a(g,t)\, ig e^{igx}\, dg$$

$$\frac{\partial^2 c_a}{\partial x^2} = -\frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{c}_a(g,t)\, g^2 e^{igx}\, dg$$

Substituting back into [1] :

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \left[\frac{\partial \tilde{c}_a(g,t)}{\partial t} + Dg^2 \tilde{c}_a(g,t) \right] e^{igx}\, dg = 0$$

The term inside the brackets must equal zero :

$$\therefore \quad \frac{\partial \tilde{c}_a(g,t)}{\partial t} = -Dg^2 \tilde{c}_a(g,t) \qquad [3]$$

Solving gives a general solution : $\tilde{c}_a(g,t) = e^{-Dg^2 t}\, \tilde{c}_a(g,0)$ [4]

Replacing $\tilde{c}_a(g,0)$ with the Fourier transform of $c_a(x,0)$ // $\tilde{c}_a(g,0) = \int_{-\infty}^{\infty} c_a(x,0) e^{-igx} dx$
Taking the inverse F.T. of [4] gives the standard analytical solution :

$$c_a(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{c}_a(g,t)\, e^{igx}\, dg$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-Dg^2 t} e^{igx}\, \tilde{c}_a(g,0)\, dg$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-Dg^2 t} e^{igx} \int_{-\infty}^{\infty} c_a(x',0) e^{-igx'}\, dx'\, dg$$

$$= \int_{-\infty}^{\infty} \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-Dg^2 t} e^{-ig(x'-x)}\, dg\; c_a(x',0)\, dx'$$

$$= \frac{1}{\sqrt{4\pi D t}} \int_{-\infty}^{\infty} e^{-(x-x')^2/4Dt}\, c_a(x',0)\, dx' \qquad [5]$$

// $\int_{-\infty}^{\infty} e^{-ag^2 - igx}\, dg = \sqrt{\frac{\pi}{a}}\, e^{-x^2/4a}$

NUMERICAL METHOD

Explicit Method

We begin with equation [3] since working with the Fourier transformed concentration allows us to remove derivatives of conc.

We assume we know : $\tilde{c}_a(q,0)$

→ We look to find $\tilde{c}_a(q,t)$ at later times by stepping forward in time steps of Δt

The forward difference approximation is :

$$\frac{\partial \tilde{c}_a(q,t)}{\partial t} \approx \frac{\tilde{c}_a(q,t+\Delta t) - \tilde{c}_a(q,t)}{\Delta t} \quad [9]$$

Substituting [9] into [3] and rearranging gives :

$$\tilde{c}_a(q,t+\Delta t) \approx [1 - Dq^2\Delta t]^n \tilde{c}(q,0) \quad [10]$$

Moving forward one time step Δt is achieved by multiplying the composition $\tilde{c}_a(q,t)$ by the constant $[1-Dq^2\Delta t]$
After n time ~~st~~ steps :

$$\tilde{c}(q, n\Delta t) \approx [1-Dq^2\Delta t]^n \tilde{c}(q,0) \quad [11]$$

For such a solution to remain stable we must ensure that it does not diverge.
This is guarenteed, provided that $|1-Dq^2\Delta t|<1$

if step size too big solution does not work

∴ This puts an upper limit on the allowed value of the time step : $\Delta t < \frac{2}{Dq^2}$

The issue arises that if we wish to retain large values of q, then we must use very small time steps.

Implicit Method

We can overcome the limitations of the explicit method.
Rewriting [3] as :

$$\frac{\partial \tilde{c}(q,t)}{\partial t} = -Dq^2\tilde{c}(q,t+\Delta t)$$

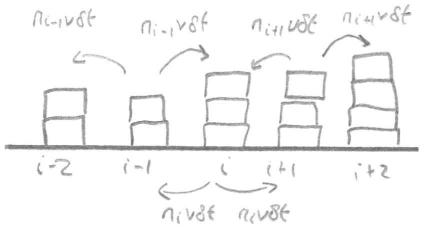
Using the finite difference once more :

$$\tilde{c}(q,\Delta t) \approx \frac{\tilde{c}(q,0)}{1 + Dq^2\Delta t}$$

the larger q the smaller δt must be

Since $1/(1+Dq^2\Delta t) < 1$ $\forall$ +ve Δt The method is stable.
(Not necessary accurate)

MODELLING: Kinetic monte carlo to model diffusion



Consider a long line of bins, within each are a number of disks.
Disks can hop into neighbouring bins with the probability per disc per unit time being ν

If the no. of disks in bin i is n_i, then in a time period δt the average number of discs transferred from bin i to bin $i+1$ is $n_i \nu \delta t$.
The same is true for the average number of disks that will be transferred ~~to~~ from bin i to bin $i-1$

Considering all additions and subtractions:

$$n_i(t+\delta t) = n_i(t) + n_{i-1}\nu\delta t + n_{i+1}\nu\delta t - 2n_i\nu\delta t \quad [1]$$

Rearranging gives:

$$\frac{n_i(t+\delta t) - n_i(t)}{\delta t} = \nu(n_{i+1} - 2n_i + n_{i-1}) \quad [2]$$

In the limit $\delta t \to 0$

$$\frac{\partial n_i}{\partial t} = \nu(n_{i+1} - 2n_i + n_{i-1}) \quad [3]$$

Letting the position of bin i be $x_i = ia$, where a is the distance between bins, we introduce a function of position $n(x)$, satisfying $n(x_i) = n_i$.
Substituting $n(x)$ gives:

$$\frac{\partial n(x_i)}{\partial t} = \nu a^2 \frac{(n(x_i+a) - 2n(x_i) + n(x_i-a))}{a^2} \quad [4]$$

If n varies sufficiently slowly with x we can approximate it by a second order Taylor Expansion

[4] becomes:

$$\frac{\partial n(x_i)}{\partial t} \approx \nu a^2 \frac{\partial^2 n(x_i)}{\partial x^2}$$

// This is the diffusion equation $\nu a^2 = D$

∴ We conclude kinetic processes like diffusion can be represented by a process of random hops with known hopping rates.
The material parameter (diffusion coeff) being related to the hopping rate.