Biophysics I (BPHS 3090)

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“A few years ago, Graham published an extensive investigation on the diffusion of salts in water, in which he more especially compared the diffusibility of different salts. It appears to me a matter of regret, however, that in such an exceedingly valuable and extensive investigation, the development of a fundamental law, for the operation of diffusion in a single element of space, was neglected, and I have therefore endeavoured to supply this omission.”

- A. Fick (1855)
Diffusion (1-D)

From Graham’s observations (~1830):

\[ c(x, t) \]

**Concentration** - of solute in solution \([mol/m^3]\)

\[ \phi(x, t) \]

**Flux** - net # of moles crossing per unit time \(t\) through a unit area perpendicular to the \(x\)-axis \([mol/m^2 \cdot s]\)

\(x, t\)

**Position** \([m]\), **Time** \([s]\)

Note: flux is a vector!
Short Excursion: Microscopic Basis for Diffusion

Brownian motion ⇒ ‘Random Walker’ (1-D)

Ensemble of Random Walkers
Fick’s First Law (1-D)

\[ \phi(x, t) \propto -\frac{\partial c(x, t)}{\partial x} \]
Diffusion Constant $D$

$$\phi(x, t) \propto -\frac{\partial c(x, t)}{\partial x}$$

constant of proportionality?

$$\phi(x, t) = -D \frac{\partial c(x, t)}{\partial x}$$

- diffusion constant is always positive (i.e., $D > 0$)
- determines time it takes solute to diffuse a given distance in a medium
- depends upon both solute and medium (solution)
- *Stokes-Einstein relation* predicts that $D$ is inversely proportional to solute molecular radius
Diffusion Constant $D$

$t = 1$

smaller $D$

larger $D$

$t = 50$
Generalizations

Higher Dimensions:

\[ \phi(x, t) = -D \frac{\partial c(x, t)}{\partial x} \quad \leftrightarrow \quad \vec{\phi} = -D \nabla c \]

where \( \nabla c = \hat{x} \frac{\partial c}{\partial x} + \hat{y} \frac{\partial c}{\partial y} + \hat{z} \frac{\partial c}{\partial z} = \text{grad}(c) \)

Analogous Flux Laws:

Heat Flow (Fourier):

\[ \phi_h = -\sigma_h \frac{\partial T}{\partial x} \]

heat flow, thermal conductivity, and temperature

Electric Conduction (Ohm):

\[ J = -\sigma_e \frac{\partial \psi}{\partial x} \]

current density, electrical conductivity, and electric potential

Convection (Darcy):

\[ \Phi_v = -\kappa \frac{\partial p}{\partial x} \]

fluid flow, hydraulic permeability, and pressure

Diffusion (Fick):

\[ \phi = -D \frac{\partial c}{\partial x} \]
Continuity Equation

⇒ imagine a cube (with face area $A$ and length $\Delta x$) and a time interval $\Delta t$

solute entering from *left* - solute exiting from *right*  
(during time interval $[t, t + \Delta t]$ )

=  
change in amount of solute *inside* cube  
(during time interval $[t, t + \Delta t]$ )

\[
A \Delta t \phi(x, t) = A \Delta x c(x, t)
\]
solute entering from left - solute exiting from right  
(during time interval \([t, t+\Delta t]\) ) = change in amount of solute inside cube  
(during time interval \([t, t+\Delta t]\) )

\[
A \Delta t \phi(x, t + \Delta t/2) - A \Delta t \phi(x + \Delta x, t + \Delta t/2) = A \Delta x c(x + \Delta x/2, t + \Delta t) - A \Delta x c(x + \Delta x/2, t)
\]

\[
\frac{\phi(x + \Delta x, t + \Delta t/2) - \phi(x, t + \Delta t/2)}{\Delta x} = \frac{c(x + \Delta x/2, t + \Delta t) - c(x + \Delta x/2, t)}{\Delta t}
\]
\[
- \frac{\phi(x + \Delta x, t + \Delta t/2) - \phi(x, t + \Delta t/2)}{\Delta x} = \frac{c(x + \Delta x/2, t + \Delta t) - c(x + \Delta x/2, t)}{\Delta t}
\]

\[
\lim_{\Delta t, \Delta x \to 0} \quad \implies \quad \frac{\partial \phi}{\partial x} = -\frac{\partial c}{\partial t}
\]

⇒ conservation of mass within the context of our imaginary cube yielded the continuity equation.
Diffusion Equation

1. Fick’s First Law: \[ \phi = -D \frac{\partial c}{\partial x} \]

2. Continuity Equation: \[ \frac{\partial \phi}{\partial x} = -\frac{\partial c}{\partial t} \]

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \] (Fick’s Second Law)
Diffusion Processes

1. **Equilibrium**: Zero flux and concentration is independent of time

\[ D \neq 0 \Rightarrow \text{concentration is independent of space and time} \]

\[ D = 0 \Rightarrow \text{non-diffusible solute is automatically at equilibrium} \]

2. **Steady-state**: Flux can be non-zero, but flux and concentration are independent of time

\[
\frac{\partial \phi}{\partial x} = 0 \quad \Rightarrow \quad \int \phi_o \, dx = \int -D \, dc \quad \Rightarrow \quad c(x) = c(x_o) - \frac{\phi_o}{D} (x - x_o)
\]

\[ \text{[integrate Fick's 1st Law]} \]

\[ \text{[}x_o\text{ is a reference location where the concentration is known]} \]
3. Impulse Response: Point-source of particles \((n_o \text{ mol/cm}^2)\) at \(t = 0\) and \(x = 0\)

[Dirac delta function \(\delta(x)\)]

Given the initial/boundary conditions:

\[ c(x, t) = n_o \delta(x) \quad \text{at} \quad t = 0 \quad \text{where} \quad \int_{-\infty}^{\infty} \delta(x) \, dx = 1 \]

Need to solve:

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]

[Aside: solution can be found by a # of different methods, one being by separation of variables and using a Fourier transform]

**Solution**

(for \(t > 0\))

\[ c(x, t) = \frac{n_o}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \]
solution to diffusion equation!

\[ f(x, y) = \frac{1}{\sqrt{y}} e^{-x^2 / y} \]