Lecture 10c: Diffusion – Fick’s Laws

**Learning objectives:** After this lecture, you will be able to:

1. Explain how random microscopic motion leads to a macroscopic flux (Fick’s law).
2. Explain how a concentrated region of solute in a fluid spreads out over time (diffusion equation).
3. Understand where and how small living cells rely on diffusion for transport.
4. Explain that the macroscopic diffusion equations tell us the amount of stuff that diffuses in a given time, for given concentration conditions.
5. Explain how Fick’s first law relates flux to a concentration gradient: \( J(x) = -D \frac{dc(x)}{dx} \).
6. Explain how Fick’s second law (diffusion equation) relates changes in concentration in both position and time: \( \frac{dc(x,t)}{dt} = D \frac{d^2c(x,t)}{dx^2} \).
7. Explain why and how concentration gradients relax over time.

**Pre-reading:** We have two main ideas for this lecture, Fick’s 1st and 2nd law.

**Fick’s first law** relates the diffusive molecular flux to the concentration. It says that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that’s proportional to the concentration gradient (spatial derivative, \( \frac{dc}{dx} \), or in simplistic terms the concept that a solute will move from a region of high concentration to a region of low concentration across a concentration gradient. In one (spatial) dimension, Fick’s first law is: \( J_x = -D \frac{dc}{dx} \), where:

- \( J_x \) is the "diffusion flux" [\# molecules per unit area per unit time], for example \( \text{mol/m}^2 \text{s} \). The flux \( J_x \) measures the amount of substance that will flow through a small area during a small time interval.
- \( D \) is the diffusion coefficient with dimensions of [\( \text{m}^2/\text{s} \)].
- \( C \) is the concentration with dimensions of \( \text{amount of substance/m}^3 \), for example \( \text{mol/m}^3 \).

As we saw in the previous lecture, \( D \) is proportional to the squared velocity of the diffusing particles, which depends on the temperature, viscosity of the fluid and the size of the particles according to the Stokes-Einstein relation. In dilute water solutions the diffusion coefficients of most ions are similar and have values at room temperature in the range of \( 0.6 \times 10^{-9} \) to \( 2 \times 10^{-9} \) \( \text{m}^2/\text{s} \). For larger biological molecules the diffusion coefficients is smaller and normally ranges from \( 10^{-11} \) to \( 10^{-10} \) \( \text{m}^2/\text{s} \).

**Fick’s second law** predicts how diffusion causes the concentration to change with time:

\[
\frac{dc(x,t)}{dt} = D \frac{d^2c(x,t)}{dx^2}
\]

If there is a concavity in the concentration of molecules as a function of \( x \) (i.e. \( \frac{d^2c(x,t)}{dx^2} \neq 0 \)), the concentration at position \( x \) will change with time.
Summary: Diffusion and Random Walks

1. We developed a fundamental relation between the diffusion coefficient, distance, and time by considering a random walk.

\[ 1 - \text{dimension: } \langle x^2 \rangle = 2Dt \quad 2 - \text{dimensions: } \langle x^2 \rangle = 4Dt \quad 3 - \text{dimensions: } \langle x^2 \rangle = 6Dt \]

2. For a random walk \[ D = \frac{\delta^2}{2\tau} \] where \( \delta \) is step size and \( \tau \) is time between steps. When dealing particles in a fluid \( D \) can be measured or approximated (see below equations).

3. The Einstein-Smoluchowski equation \( Df = k_B T \) is the most general relation between diffusion and friction.

4. The Stokes-Einstein equation is specifically for spheres, but works very well to approximate the diffusion coefficient of even non-spherical molecules: \[ D = \frac{k_B T}{6\pi \eta} \]

Today:

- Understand how random microscopic motion leads to a macroscopic flux (Fick's law)

- Understand how a concentrated region of solute in a fluid spreads out over time (diffusion equation)

- Fick’s first law tells us how the flux relates to the concentration: This allows us to calculate, for example, the amount of solute passing through a membrane, like skin or a contact lens

- The diffusion equation tells us how the concentration \( c(x,t) \) changes with position and time.

Fick's law, diffusion equation motivation

Very useful in calculating practical things:
- How much oxygen gets into the blood stream from the lungs
- How the kidneys work in filtering the blood
- How capillaries take gases in/out from the interstitial fluid.

- How things pass across membranes
- How big prokaryotic cells can be* (No motor proteins?)
- How to get the caffeine out of coffee beans
- Interpreting MRI of the brain
Physical Sciences 2: Lecture 10c

Activity 1: Flux Intuition

Imagine that 100 of your peers in PS2 are deep in thought, and are therefore pacing from left to right and right to left between the rows of seats in the lecture hall. Due to the thoughts of physics, the pacing takes the form of a random walk with $\tau = 1$ sec. and $\delta = 1$ ft. to the left/right, with the direction randomly chosen at each second.

1. Initially, the people pacing are spread evenly throughout the room, so 50 people are left of the centerline of the room and 50 people are right of the centerline of the room (see image). After 10 seconds of pacing, how many people do you expect to be right of the centerline?
   
   a) 40  b) 60  c) 55  d) 45  e) 50

2. Here, we define “flux” to be the rate that people cross the center of the room from left to right, minus the rate that people cross the center of the room from right to left (i.e. flux measures how quickly the number of people on the right is increasing). What is the flux of people across the centerline? (hint: the answer should be the same regardless of units)
   
   a) 10  b) -10  c) 5  d) -5  e) 0

3. A few minutes after class has started, 20 more people come into class confused by the pacing, but in their enthusiasm for physics, they all join the random pacing starting on the left side of the room. How will their joining change the flux of people across the centerline? (remember: left to right across the centerline is positive flux)
   
   a) flux increases  b) flux decreases  c) flux stays the same

4. Imagine that, instead of joining a few minutes into class, those 20 people came in and join the pacing (again starting on the left) an hour after class started. Now tired, but still pacing, everyone (including those additional 20 people) is taking a 6-inch step once every 2 seconds. How does the flux of people across the centerline now compare to the flux from question 3, above?
   
   a) the new flux is higher  b) the new flux is lower  c) the new flux is the same
**Activity 2: Quantifying how much ‘stuff’ diffuses**

*Defining concentration and flux:*

**Concentration** $c(x, t)$ = number of molecules per unit volume at a position $x$ and time $t$.

**Flux:** $J_x$ = number $N$ of molecules passing an area $A$ in time $t$ (and moving in the $x$-direction).

Now consider what happens if we have a gradient in concentration of solute, $\frac{dc}{dx}$.

Model: each molecule does a random walk and is equally likely to move left or right (like on previous page).

1. How should the sign of flux $J_x$ depend on the sign of $\frac{dc}{dx}$, the gradient in the concentration — if $\frac{dc}{dx}$ is negative, then flux should be:

   ![Diagram showing flux with negative and positive directions]

   *It may be helpful to consider a tube in which the concentration increases linearly from left to right, as shown below, and sketch the concentration as a function of position.*

2. How should the flux depend on the diffusion coefficient $D$ (proportional or inversely proportional) — if $D$ decreases, then flux should (consider problem 4 from the previous page):

   ![Diagram showing decrease in concentration and diffusion]

   **Fick’s first law**

   On average, molecules move toward regions of lower concentration. $J_x = -\frac{dc}{dx}D$ or $J_x = -\frac{\Delta c}{\Delta x}D$. 


Am I getting it: Fick’s first law

Oxygen molecules are diffusing in a small water-filled cylindrical tube with \( D_{O_2} = 1 \times 10^3 \, \mu m^2/s \). Below are plots showing two different concentrations of \( O_2 \) molecules in water \( C(x, t = 0) \) as a function of \( x \), along the small tube.

1. What can you say about the flux of diffusing \( O_2 \) molecules at 2\( \mu m \) versus the flux at 1\( \mu m \) for the concentration shown on the graph to the right?

(a) \( J_x(2 \mu m) > J_x(1 \mu m) \), both to the right
(b) \( J_x(2 \mu m) < J_x(1 \mu m) \), both to the right
(c) \( J_x(2 \mu m) = J_x(1 \mu m) \), both to the right
(d) \( J_x(2 \mu m) > J_x(1 \mu m) \), both to the left
(e) \( J_x(2 \mu m) < J_x(1 \mu m) \), both to the left
(f) \( J_x(2 \mu m) = J_x(1 \mu m) \), both to the left
(g) \( J_x(2 \mu m) = J_x(1 \mu m) = 0 \)

\[
J_x = -\frac{dC}{dx} D
\]

2. What can you say about the flux of diffusing \( O_2 \) molecules at 2\( \mu m \) versus the flux at 1\( \mu m \) for the concentration shown on the graph to the right?

(a) \( J_x(2 \mu m) > J_x(1 \mu m) \), both to the right
(b) \( J_x(2 \mu m) < J_x(1 \mu m) \), both to the right
(c) \( J_x(2 \mu m) = J_x(1 \mu m) \), both to the right
(d) \( J_x(2 \mu m) > J_x(1 \mu m) \), both to the left
(e) \( J_x(2 \mu m) < J_x(1 \mu m) \), both to the left
(f) \( J_x(2 \mu m) = J_x(1 \mu m) \), both to the left
(g) \( J_x(2 \mu m) = J_x(1 \mu m) = 0 \)

3. What is the magnitude of the flux \( |J_x(2 \mu m)| \)?

(a) \( 1 \, O_2 \) molecule/(\( \mu m^2 \cdot s \))
(b) \( 10 \, O_2 \) molecules/(\( \mu m^2 \cdot s \))
(c) \( 10^2 \, O_2 \) molecules/(\( \mu m^2 \cdot s \))
(d) \( 10^3 \, O_2 \) molecules/(\( \mu m^2 \cdot s \))
(e) \( 10^4 \, O_2 \) molecules/(\( \mu m^2 \cdot s \))

\[
|J_x|=\left|\frac{dC}{dx}\right| D
= \left(\frac{2 \text{ mole}/\mu m^3 - 1 \text{ mole}/\mu m^3}{2 \mu m - 1 \mu m}\right) \cdot 10^3 \mu m^2/s
\]
Activity 3: Fick's second law (diffusion equation)

Fick's first law \( J_x = -D \frac{dc}{dx} \) gives us a relation for the flux. We can calculate the flux when we know the concentration gradient.

But what if the concentration \( c \) and the gradient \( dc/dx \) change over time (non-steady state diffusion)? Describing these time-dependent diffusion problems with Fick's 1st law can be quite tedious!

We want to find a relationship that determines \( c(x, t) \) for all time given an initial concentration \( c(x, 0) \).

1. To the right are two graphs of particle concentration versus x-position at \( t = 0 \), \( c(x, 0) \).
   - One moment later will the concentration at \( x_A \), where the curvature \( \frac{d^2c(x,t)}{dx^2} \) is positive, increase or decrease?
   - At \( x_B \), where the curvature \( \frac{d^2c(x,t)}{dx^2} \) is negative, the concentration will:

2. If the particle size is smaller, therefore making the diffusion coefficient \( D \) larger, will the concentration increase/decrease happen faster or slower?
   - Faster
   - Slower

Fick's second law

\[
\frac{dc(x,t)}{dt} = \frac{d^2c}{dx^2} D
\]

3. The concentration of a protein in a long cylindrical axon at time \( t = 0 \) is represented by the solid curve on the graphs below. If the protein is allowed to diffuse, on which of the following graphs does the dashed line represent a possible distribution of the protein at some later time \( t > 0 \)?

A  
![Concentration vs Position](image)

B  
![Concentration vs Position](image)

C  
![Concentration vs Position](image)

D  
![Concentration vs Position](image)
Fick’s Laws – practice problems (if time permits)

Diffusion through a thin membrane: steady-state

1. Consider potassium ions crossing a biological membrane 10 nm thick. $D$ for potassium in the membrane is $1.0 \times 10^{-16} \text{ m}^2/\text{s}$.

(a) **What number of potassium ions per second** will move across an area 100 nm x 100 nm if the concentration difference across the membrane is maintained at 0.50 mol/liter $(3 \times 10^{26} \text{ ions/m}^3)$? (b) Discuss how the flux changes if we increase or decrease the membrane thickness.

Note: 1 litre $= 10^{-3} \text{ m}^3$

\[
J_x = \frac{\Delta N}{A \Delta t} \quad \Rightarrow \quad \Delta N = J_x A \Delta t
\]

\[
= (-D \frac{\Delta c}{\Delta x}) A \Delta t
\]

\[
= \frac{3 \times 10^{-6} \text{ ions}}{\text{s}} \times \frac{10^{-8} \text{ m}^2}{5} \times (10^{-7} \text{ m})^2
\]

\[= 3 \times 10^4 \text{ ions}\]

2. You don’t always consume oxygen at the same rate. If you exercise, your oxygen consumption rate goes up (i.e. $J_x$ increases). Which part of Fick’s 1st law can account for this increase in O$_2$ flux?