COMMONWEALTH OF AUSTRALIA

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Liquids: Diffusion and Randomness

Lecture 26

Soft Matter: Nematics – Properties and Applications

Lecture 27

Liquids: Diffusion and Randomness

Lecture 28

Liquids: Chemical kinetics

Dimensionality and random walks

By the end of this lecture, we will understand the following "joke":

- A drunk man will find his way home.
- A drunk bird may get lost forever.

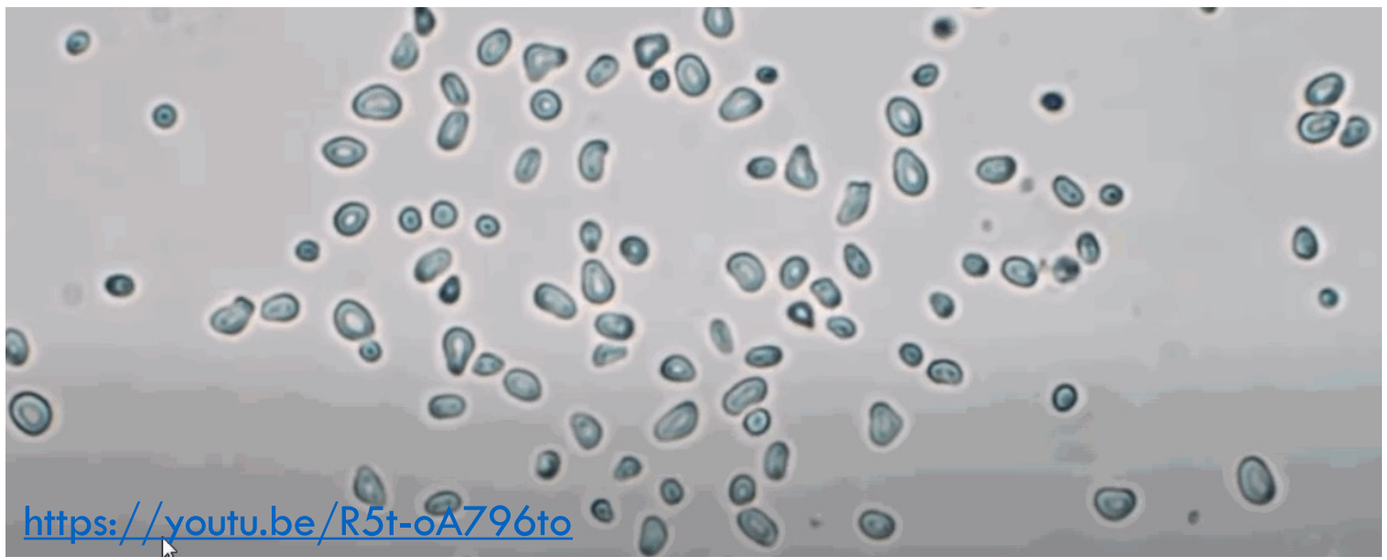
Shizuo Kakutani



Image: Warner Bros.

Brownian Motion

- If one observes small particles suspended in a fluid under the microscope, one can observe random motion, which increases with increasing temperature.
- This observation was first made in1856 by Robert Brown (1773-1858), a Scottish botanist, on pollen. Brown also did significant research on Australian flora.





Robert Brown



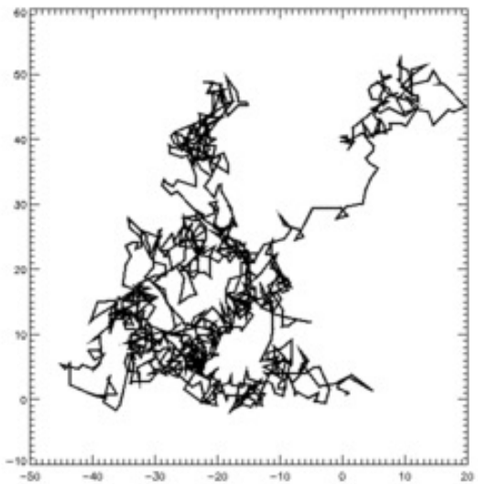
Banksia brownii

Random walks: definition and approximations

Q1

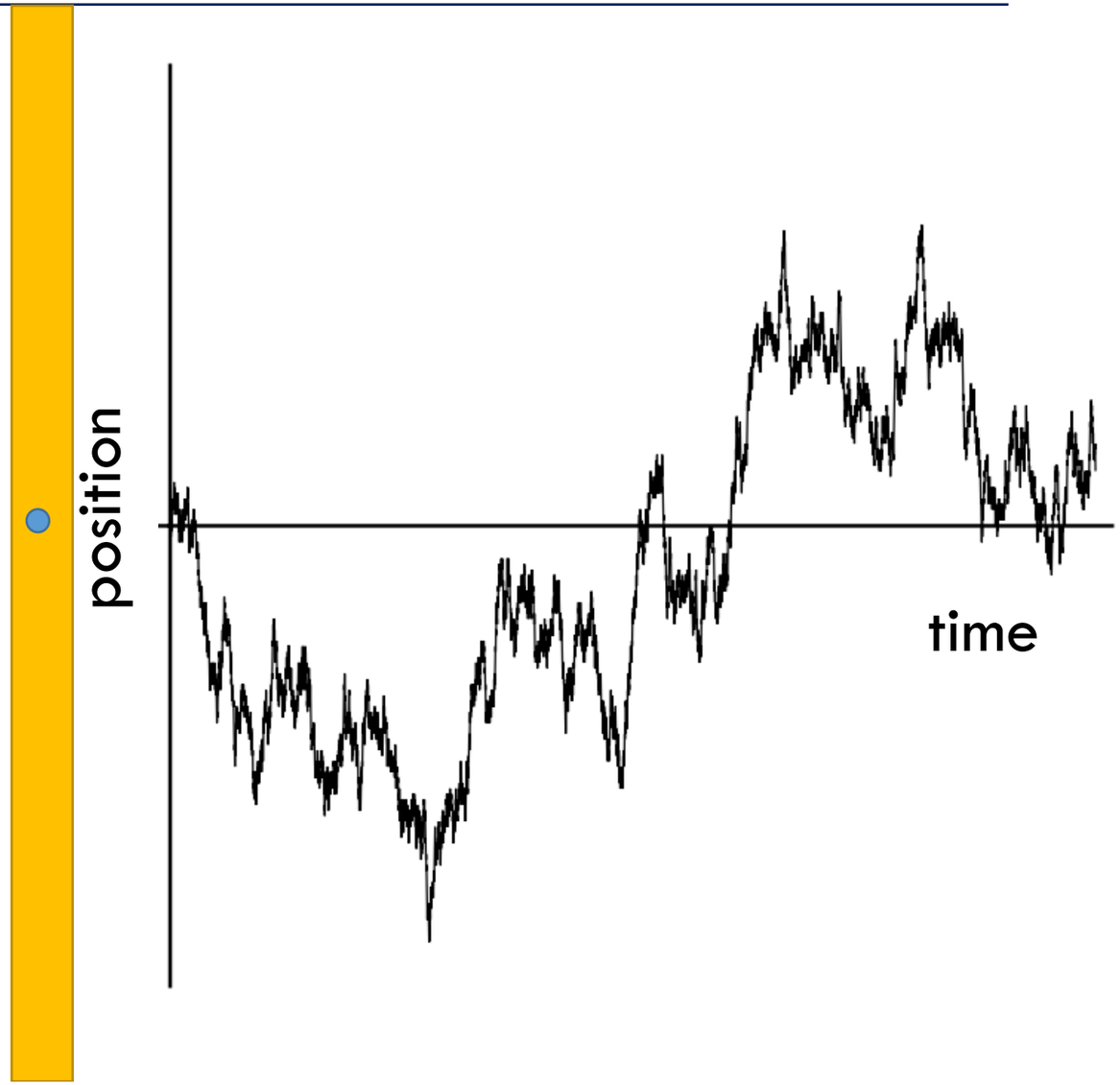
- A series of steps chosen randomly.
- A good model for Brownian motion, but also used in polymer chemistry, exciton motion, mathematical ecology, population genetics, financial economics, …
- The distribution of steps is usually symmetrical, so that the "expected" position of the particle does not drift from its initial location.
- Simple lattice-based walks, where each step is ±1 in a chosen Cartesian direction can be scaled to match the hop frequency and mean free path length of molecular diffusion.

100 simulated steps of Brownian motion in two dimensions



Random walks: recurrence vs transience

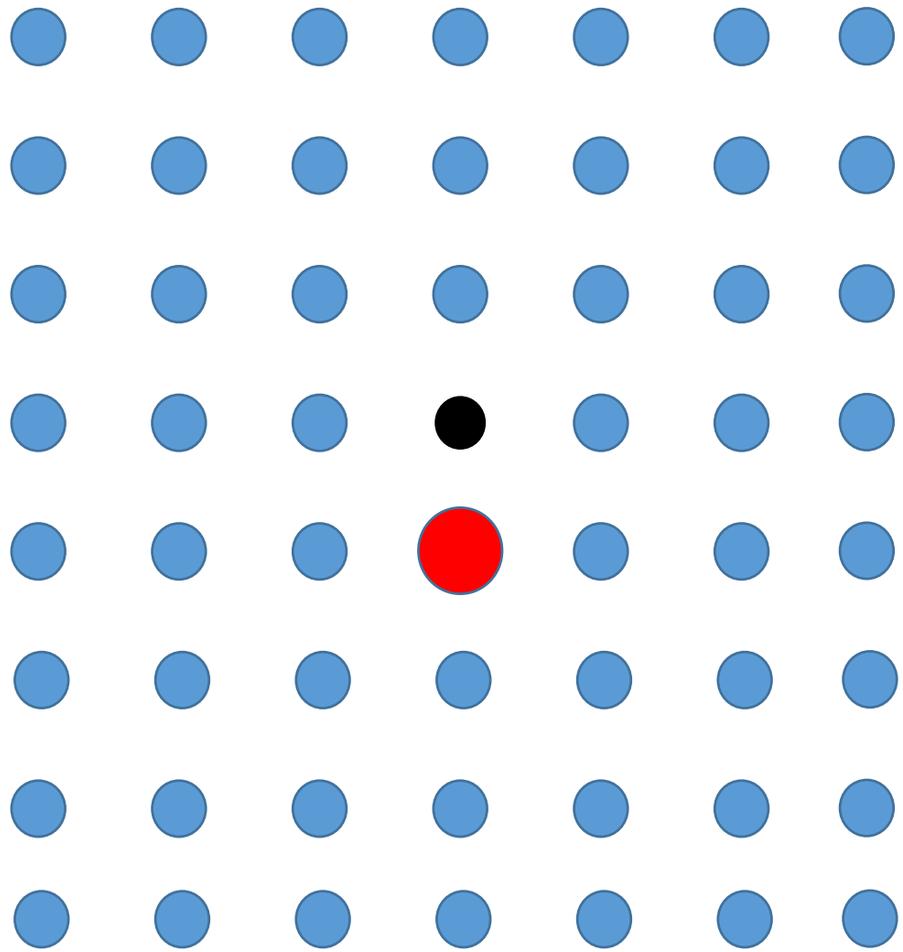
- Random walks in 1 dimension can be plotted against time. Each time the chart passes through the axis, the particle revisited its starting position.
- In "recurrent" random walks the particle is guaranteed to visit its initial position infinitely often.
- The time intervals between these revisits can be short or long.
- In "transient" random walks, the particle may or may not return to its initial position.



Random walks: recurrence vs transience

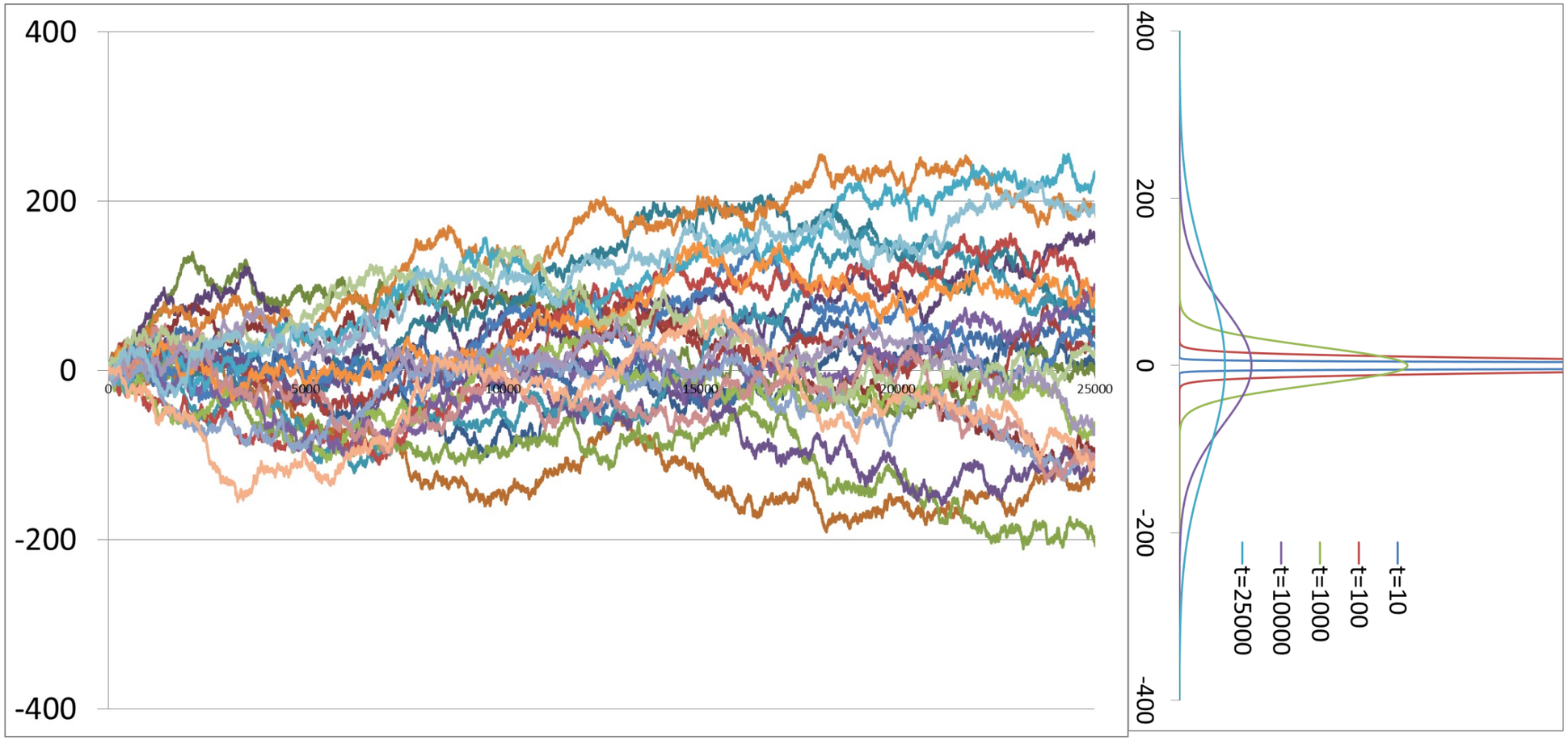
Q2

- Suppose an electron is knocked off its atom by a photon in a solar cell. What is the probability that it will return to the original atom and recombine with the hole if it is diffusing freely in a random walk on an infinite lattice?
- In 1d and 2d, these unbiased random walks are recurrent.
- In 3d (and above) they are transient. The chance of a return on an infinite cubic lattice is only 34%.
- This is good news for solar cells! Why…?



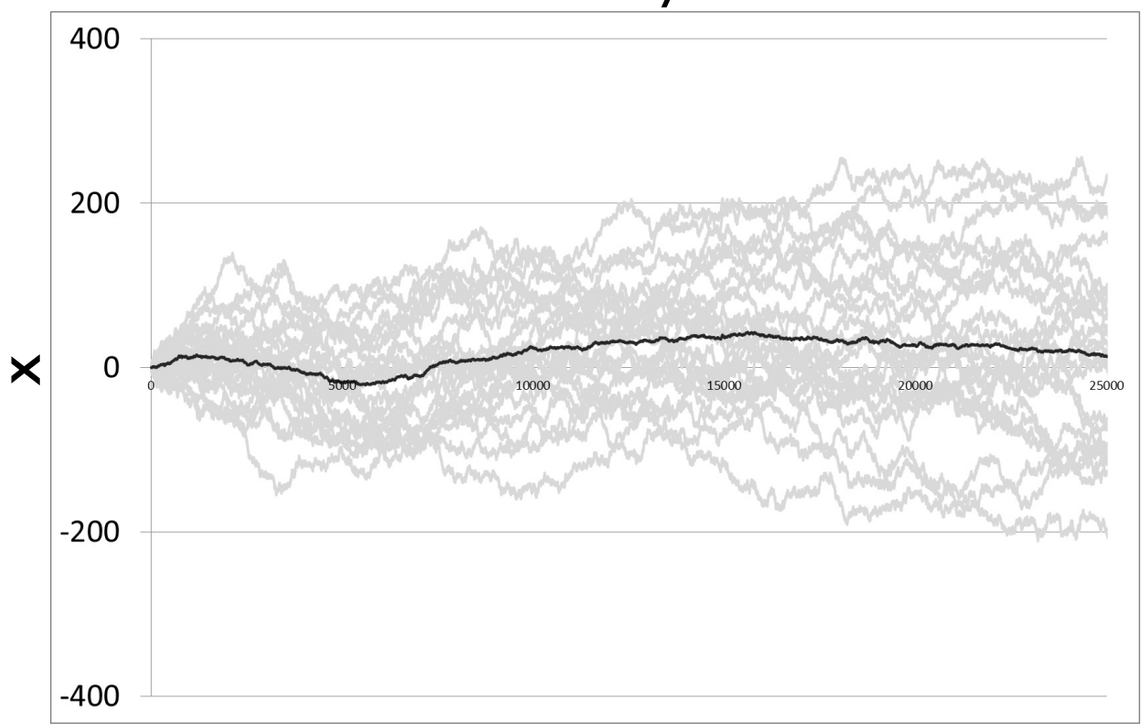
Random walks: distance vs time

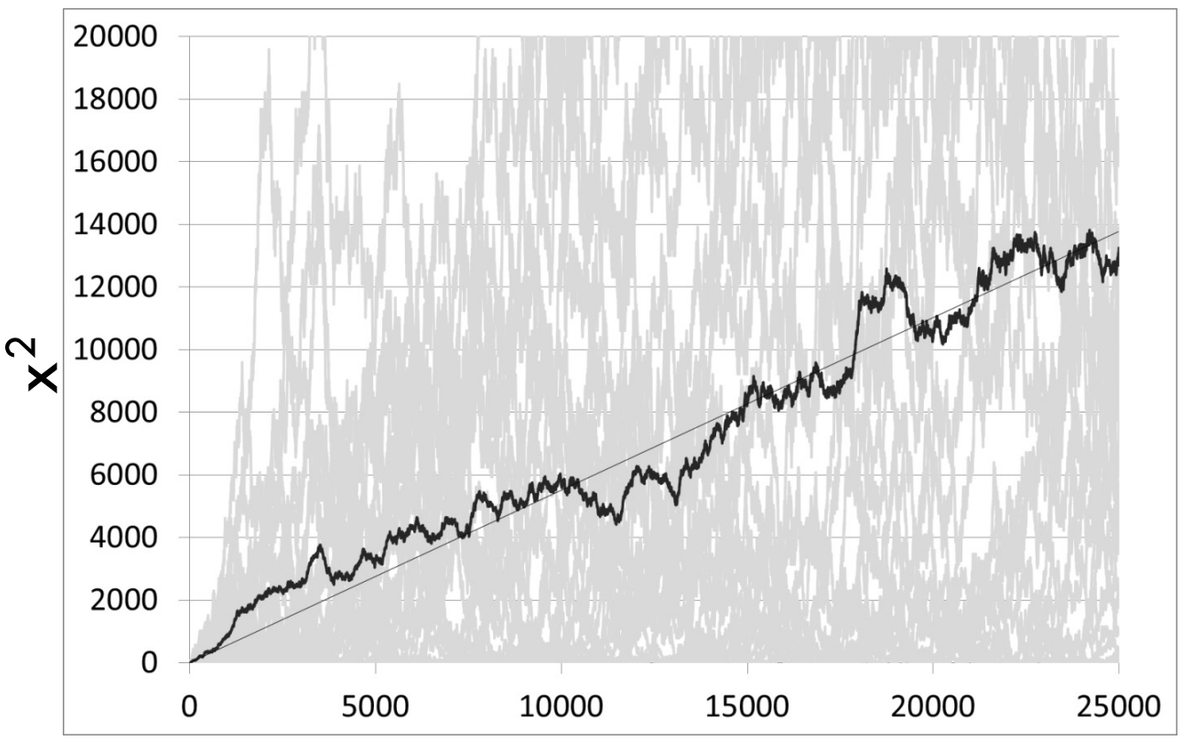
- The actual position of a particular particle undergoing a particular walk is unpredictable, but its probability distribution can be quantified accurately.



Random walks: distance vs time

- When many particles are executing random walks, the behaviour of the ensemble becomes predictable.
- The average stays around 0, but if you first square the values before you average, the result trends linearly with time.





Diffusion coefficients in 1d, 2d, 3d

The diffusion coefficient, *D,* (units $m^2\ s^{-1}$)
is defined via the average square displacement $\langle(\Delta x)^2\rangle$

In *one dimension*, (e.g. a thin pore),
the relevant equation is: $D = \frac{\langle(\Delta x)^2\rangle}{2\Delta t}$

In *two dimensions* (e.g. on a membrane),
the relevant equation is: $D = \frac{\langle(\Delta s)^2\rangle}{4\Delta t}$ because $(\Delta s)^2 = (\Delta x)^2 + (\Delta y)^2$

In *three dimensions* (e.g. in solution),
the relevant equation is: $D = \frac{\langle(\Delta s)^2\rangle}{6\Delta t}$ because $(\Delta s)^2 = (\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2$

These three important relationships, thus, allow one to calculate the average RMS ("root mean squared") displacement of a particle with time from measurements of its diffusion coefficient, or vice-versa. $\sqrt{\langle(\Delta s)^2\rangle}$

Diffusion coefficients in real systems

- This diffusion coefficient can be related to the properties of the chemical system (by Albert Einstein, 1905)

$$D = \frac{kT}{f}$$

where k is the Boltzmann constant, T is the absolute temperature, and f is known as the friction coefficient.

- The friction coefficient in turn can be:
  - Estimated from the statistical mechanics of solutions, e.g.

    Stokes' Law: $f = 6\pi\eta r$

    for a spherical particle in a fluid with viscosity η
  - Measured experimentally, e.g.

    Applying an electric field across a charged particle and measuring the time, τ it takes to reach 63.2% of terminal velocity $f = m/\tau$

Diffusion

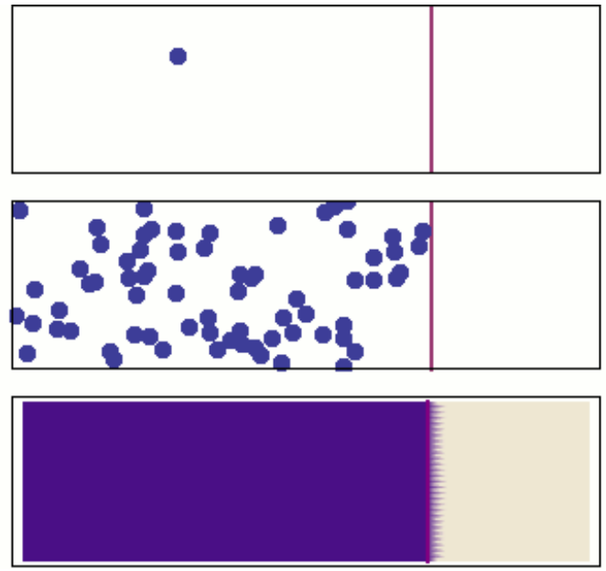
Q3

Diffusion is the transport of matter which arises because of concentration differences.

- Diffusion occurs in a particular *direction*. However, the motion of the diffusing particles is Brownian, i.e. *random*.

  How can this be?

- We now need to look at the macroscopic behaviour of a collection instead of the microscopic motion of a single particle.
- The net effect of the random motion is that the concentration throughout the vessel equalizes. Therefore, macroscopically there is a net movement of matter from the high concentration to the low concentration, although at a microscopic level the motion of each particle is completely random.



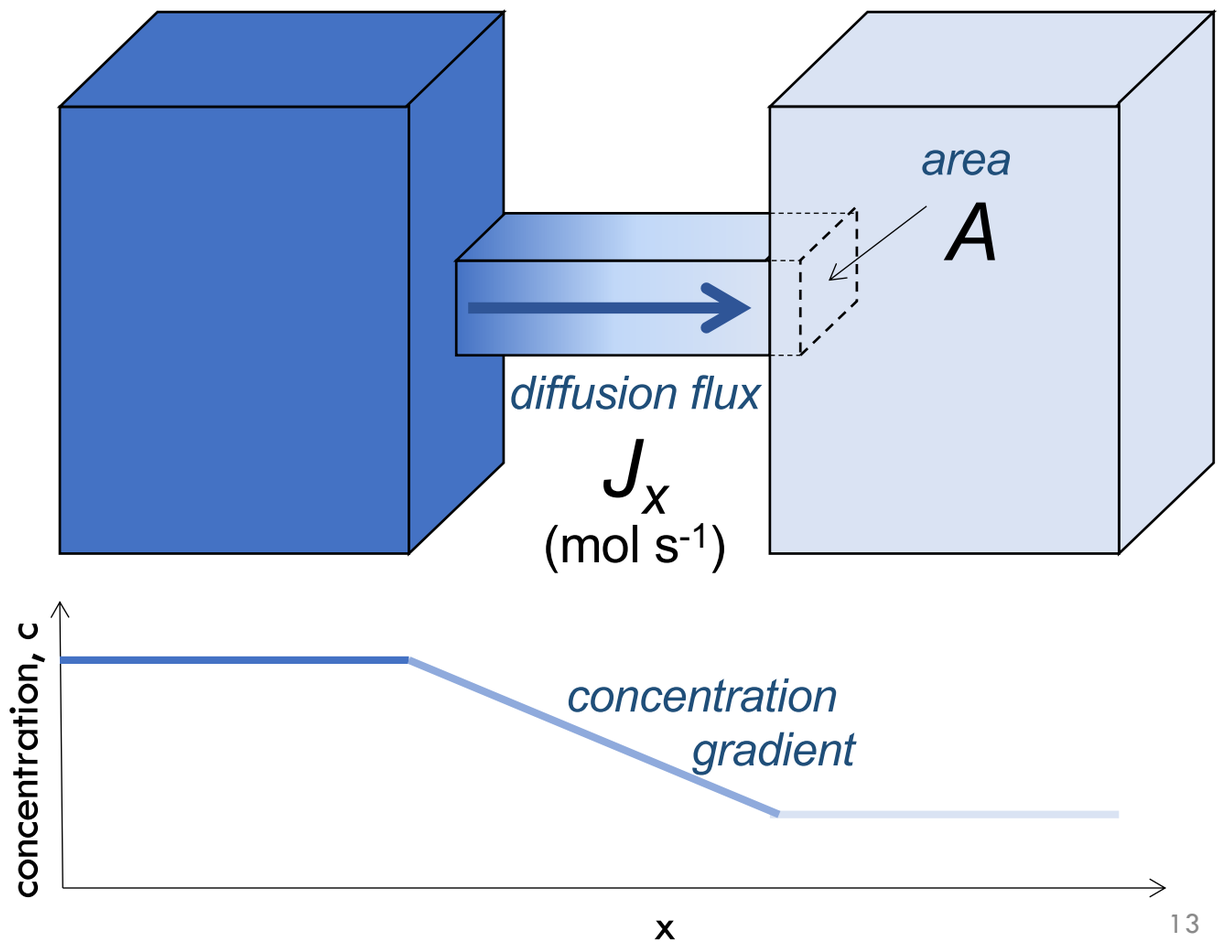
https://commons.wikimedia.org/wiki/File:DiffusionMicroMacro.gif

Diffusional transport on a concentration gradient

- To describe the diffusion process we define the *diffusion flux*, J_x, (mol s^{-1}) as the net amount of substance moving across a surface perpendicular to the *x* direction per time interval.
- According to Fick (1855), the flux is proportional to the surface area, *A*, over which the substance is diffusing and the concentration gradient, $-(dc/dx)$:

$$J_x = -DA\left(\frac{dc}{dx}\right)$$

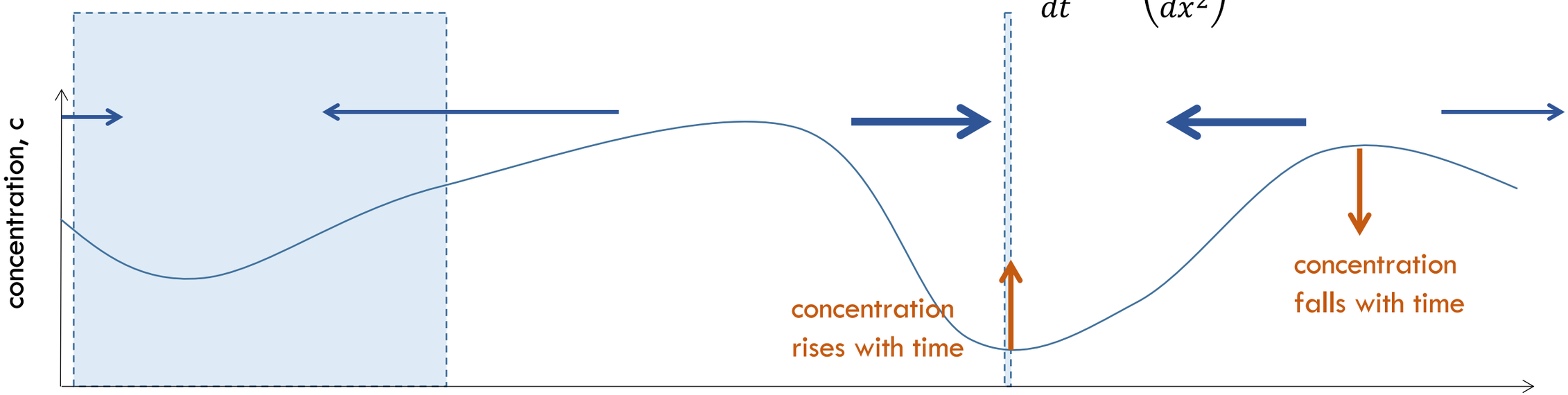
- This equation is known as *Fick's 1st Law.*



Fick's second law

- From the first Law, the flux of material flowing into and accumulating in a region depends on the concentration gradients at either end.
- But to get the rate of change of concentration at a specific point, Fick uses differentials:

$$\frac{dc}{dt} = D\left(\frac{d^2c}{dx^2}\right)$$



Dimensionality and random walks

By the end of this lecture, we have understood the following "joke":

- A drunk man will find his way home. (2d random walks are recurrent)
- A drunk bird may get lost forever. (3d random walks are transient)

Shizuo Kakutani

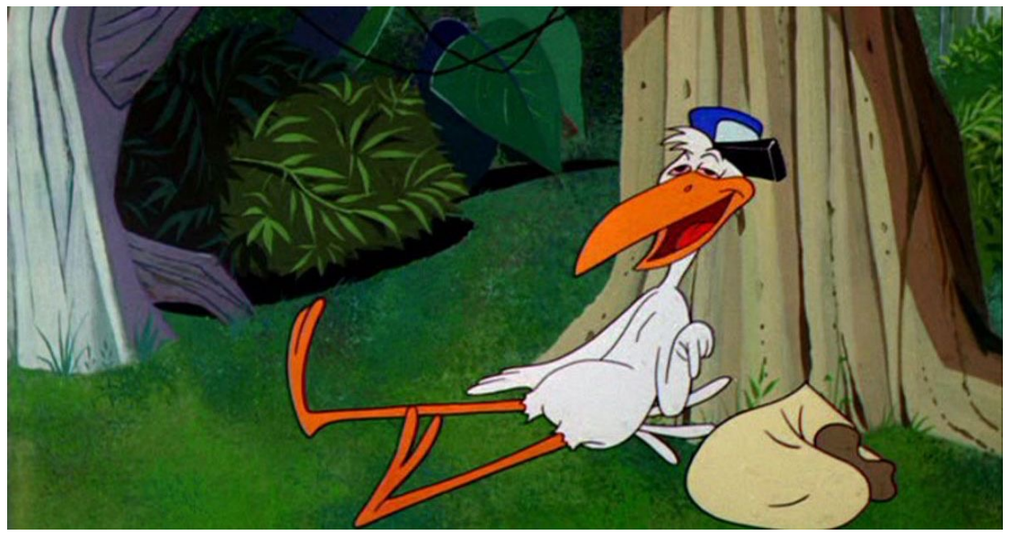


Image: Warner Bros.

Learning outcomes

After this lecture you should be able to

- Describe the random walk model of Brownian motion
- Explain the difference between recurrence and transience, and how it depends on the dimensionality of the system
- Describe a consequence of 3d transience in chemical systems
- Relate the diffusion coefficient to the temperature and physical properties of the particle and solution
- Use microscopic and macroscopic language to explain how diffusion arises from random motion
- Relate the root-mean-squared displacement of a particle to the diffusion coefficient and time period
- Use Fick's laws to numerically predict particle fluxes and concentration changes

Further Reading

- https://www.math.ucla.edu/~biskup/PDFs/PCMI/PCMI-notes-1
- https://onlinelibrary.wiley.com/doi/pdf/10.1002/app.1976.070200926
- https://en.wikipedia.org/wiki/Fick%27s_laws_of_diffusion