ChE-402

Solution to exercise problems

Prof. Kumar Varoon Agrawal

Course syllabus: ChE-402

Instructors

Prof. Kumar Varoon Agrawal	2D films for molecular and ionic separation
Dr. Marina Micari	Design and optimization of separation processes

Teaching Assistants

Stefania Bempeli	Design and optimization of membrane processes for carbon capture
Moein Fazli Mamaghani	Hybrid processes for direct air capture

Intended learning outcome

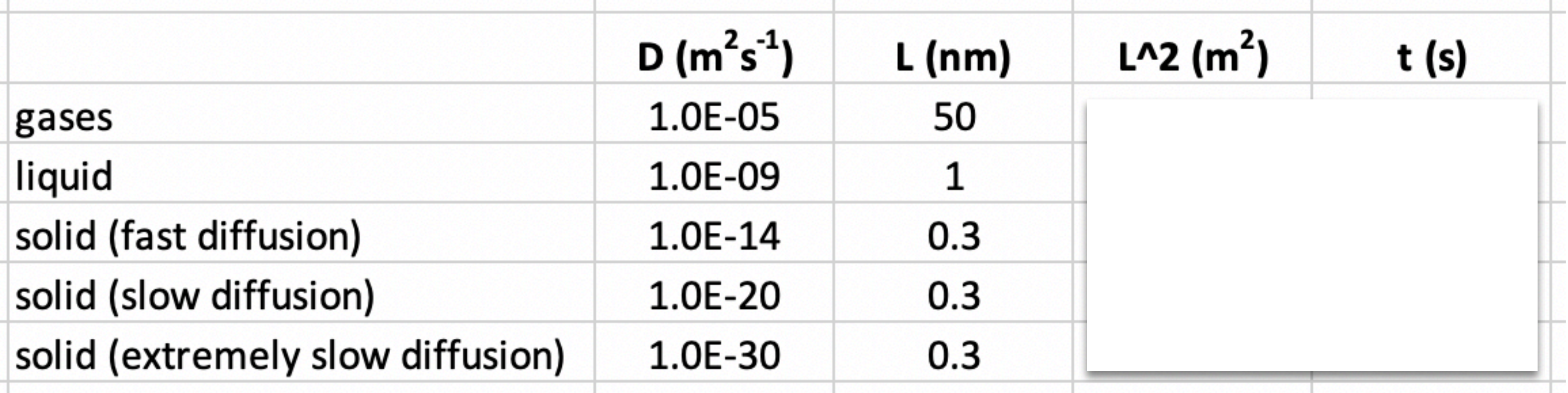
1. Analyze Fick's law of diffusion from molecular hopping point of view.
2. Understand the limits of Fick's law of diffusion.
3. Analyze the origin of diffusion.
4. Inspect diffusion from a single particle perspective (Brownian motion).
5. Inspect diffusion from Einstein's perspective (chemical potential gradient).

Time scale of diffusion

$$t = \frac{L^2}{2D}$$

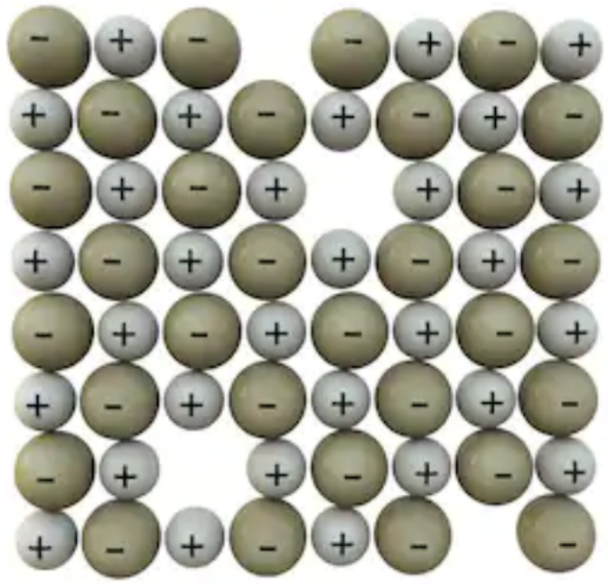
Vapor or gas

Calculate the time scale of diffusion in these systems

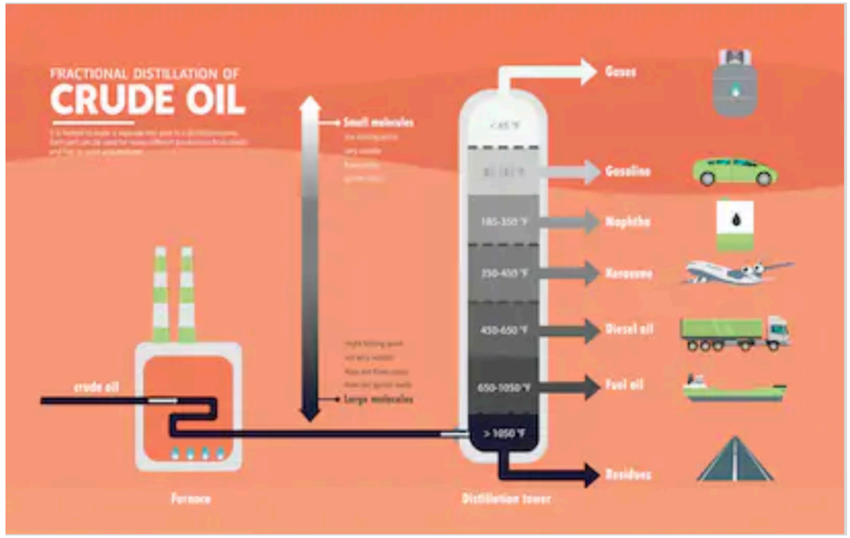


	D (m^2s^{-1})	L (nm)	L^2 (m^2)	t (s)
gases	1.0E-05	50		
liquid	1.0E-09	1		
solid (fast diffusion)	1.0E-14	0.3		
solid (slow diffusion)	1.0E-20	0.3		
solid (extremely slow diffusion)	1.0E-30	0.3		

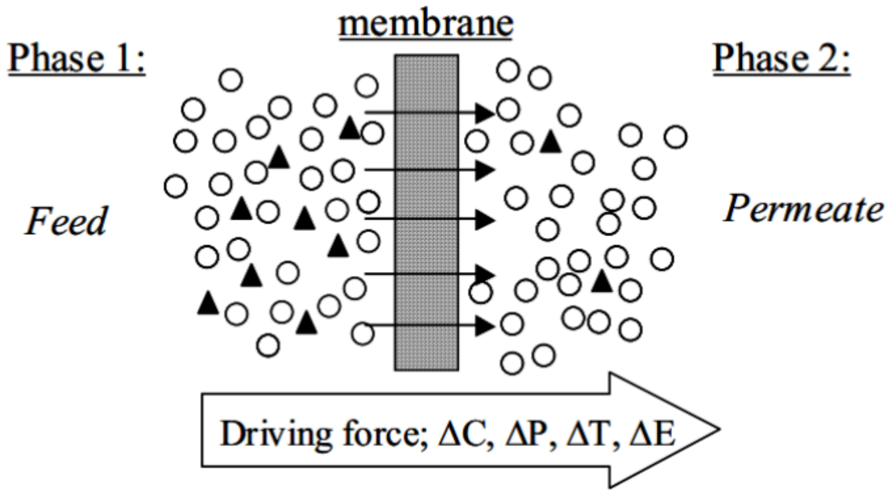
Defects in solid



Why should you learn about diffusion and mass transfer?

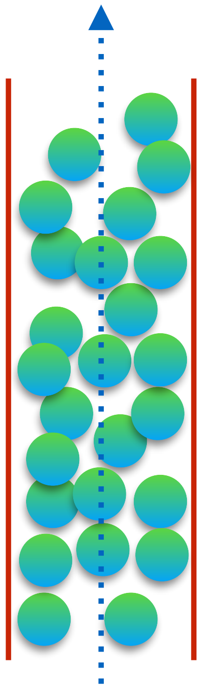


Distillation



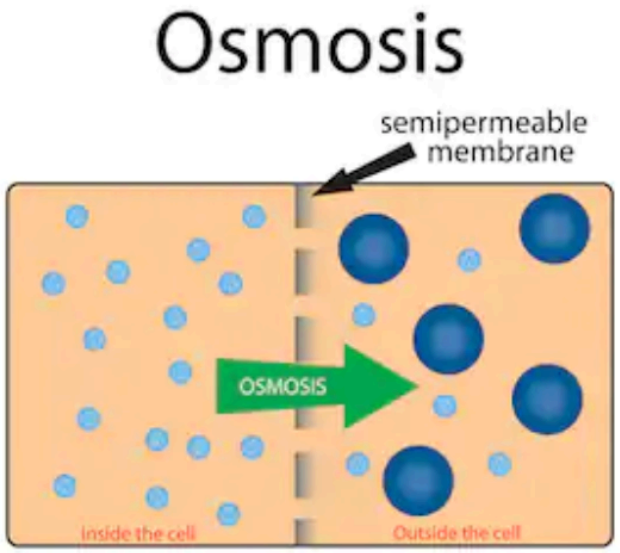
Membranes

Bioreactor



Packed columns
(absorption, reaction)

Air pollution



Drinking water

Some common examples

Fluid-fluid interface

- Distillation
- Bioreactors
- Humidifiers
- Absorbers

Typical design questions for engineers:

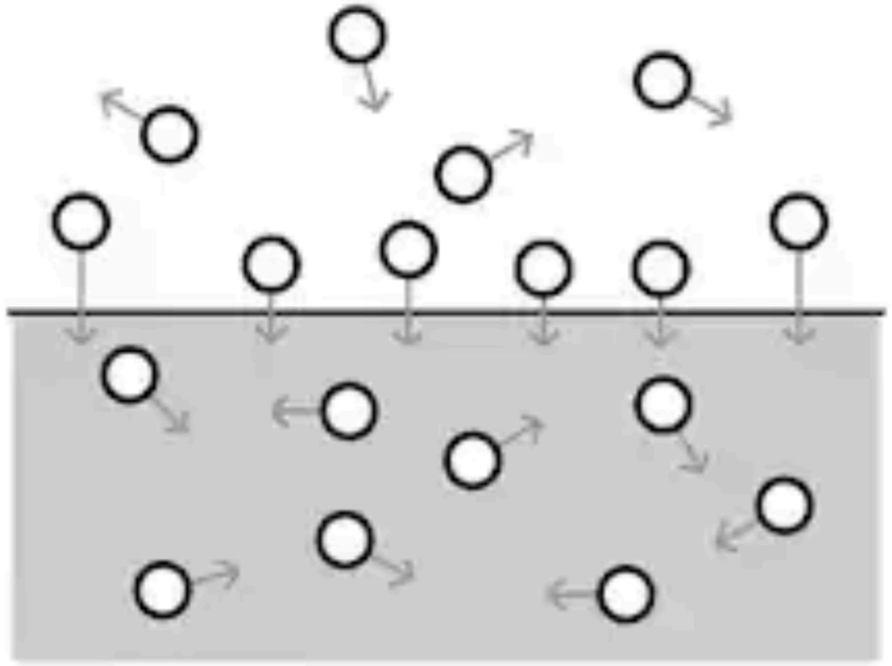
- What is the needed height of contact to reach close to equilibrium?
- What is the role of droplet size?

Governed by fundamental transport property

diffusion

Some common examples

Fluid-solid interface



- Membranes
- Adsorption
- Leaching
- Reaction in porous catalyst
- Corrosion

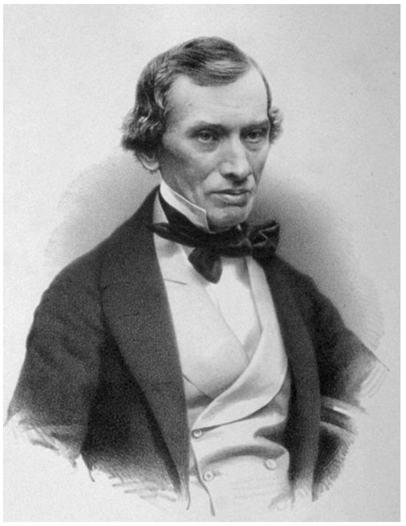
Typical design questions for engineers:

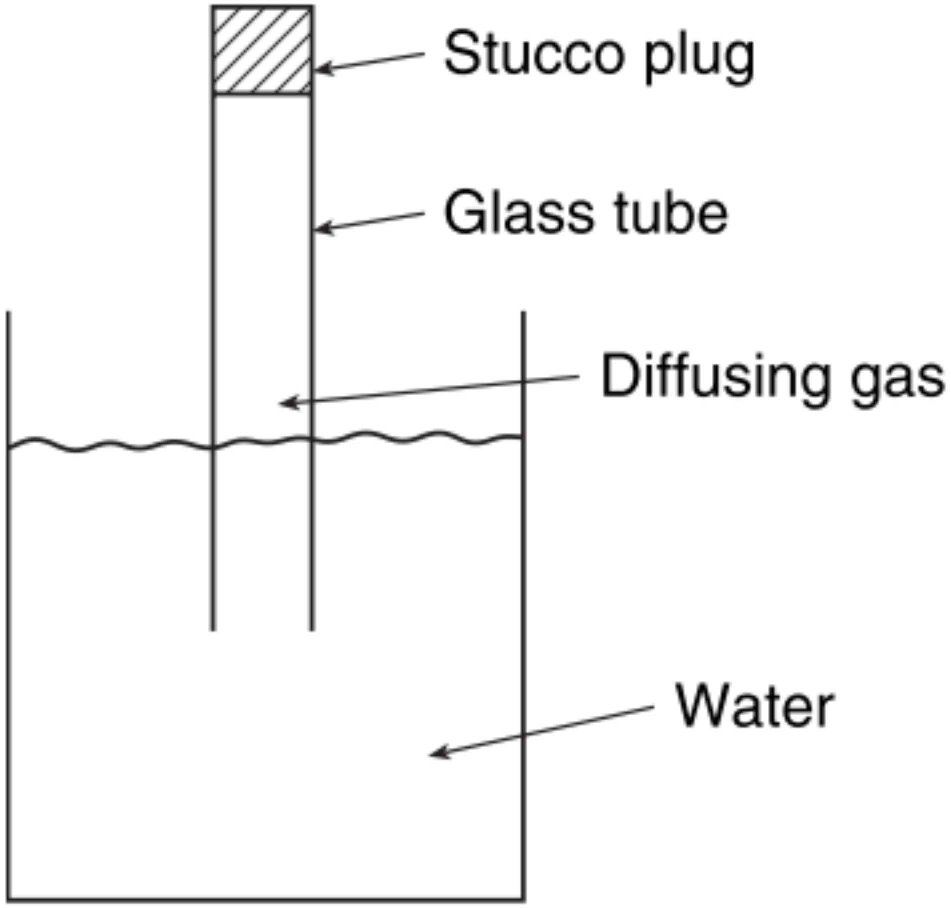
- How fast a fluid can move inside the solid.
- What is the role of porosity in solid.
- What is the role of temperature, pressure, etc.

Governed by fundamental transport property

diffusion

Thomas Graham (1805 - 1869)
Gas diffusion experiments:





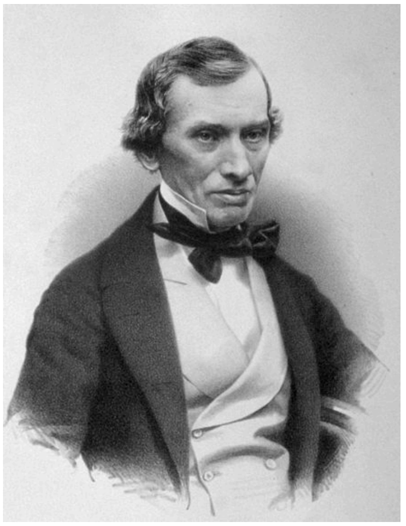
Can you guess what happens to water level in this experiment?

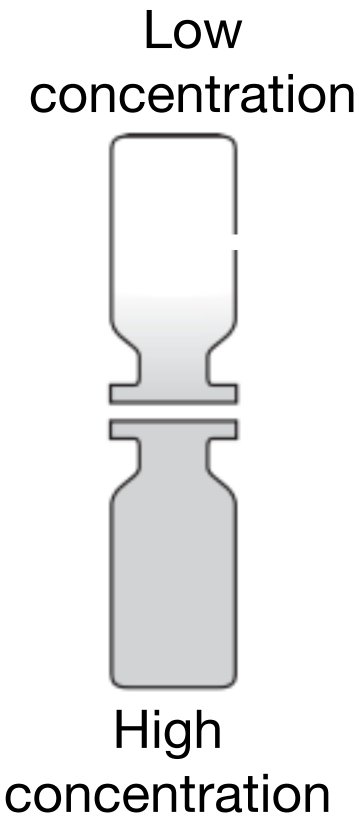
- **Gas pre-filled in the tube diffuses out.**
- **Air diffuses in the tube.**
- **Water level in the tube rises as gas diffuses out.**
- **Net rate measured by water level in the tube.**

Graham's conclusion

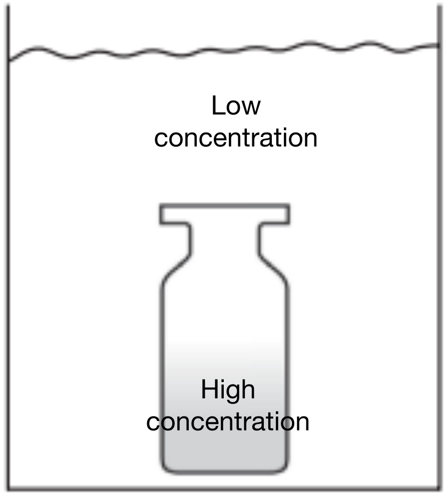
Rate of gas diffusion proportional to $\sqrt{MW}$

Thomas Graham (1805 - 1869) Liquid diffusion experiments:





Experiment 1



Experiment 2

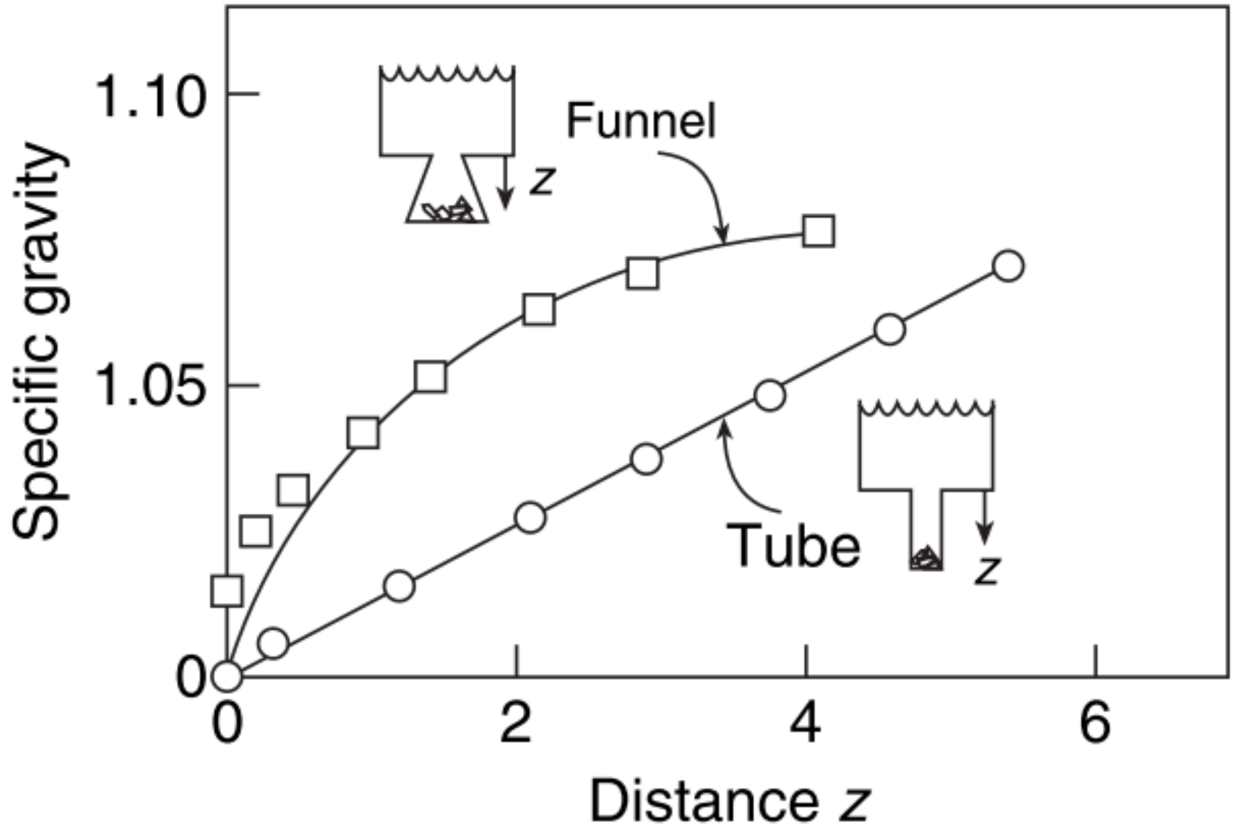
Graham's conclusion

Quantity of diffused material is proportional to quantity of material in the vial.
Diffusion in liquids is <u>several orders of magnitude smaller</u> than that in gas.

Adolf Fick (1829 - 1901)

Postulated an analogy to the Fourier's Law for heat conduction or Ohm's law for electrical conduction

"The diffusion of the dissolved material ... is left completely to the influence of the molecular forces basic to the same law ... for the spreading of warmth in a conductor and which has already been applied with such great success to the spreading of electricity"



Flux

$$Aj_1 = -AD\frac{\partial c_1}{\partial z}$$

Conservation Equation

$$\frac{\partial c_1}{\partial t} = D\left(\frac{\partial^2 c_1}{\partial z^2} + \frac{1}{A}\frac{\partial A}{\partial z}\frac{\partial c_1}{\partial z}\right)$$

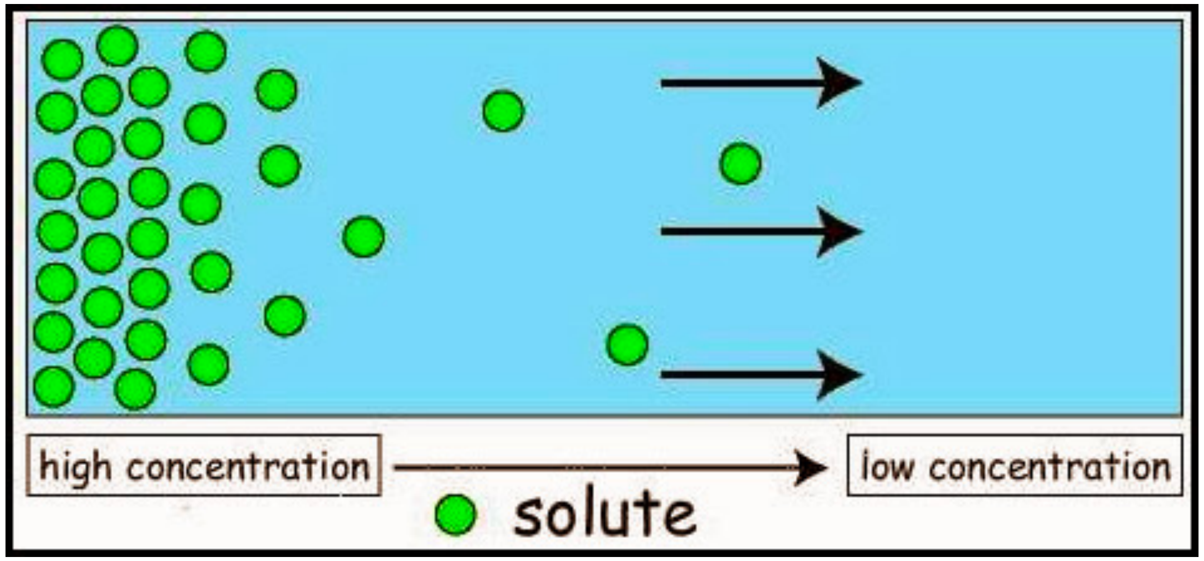
Fick's first and second law

First Law

$$J = -D\frac{\partial c}{\partial z}$$

Why there is a negative sign?

Why there is a negative sign?



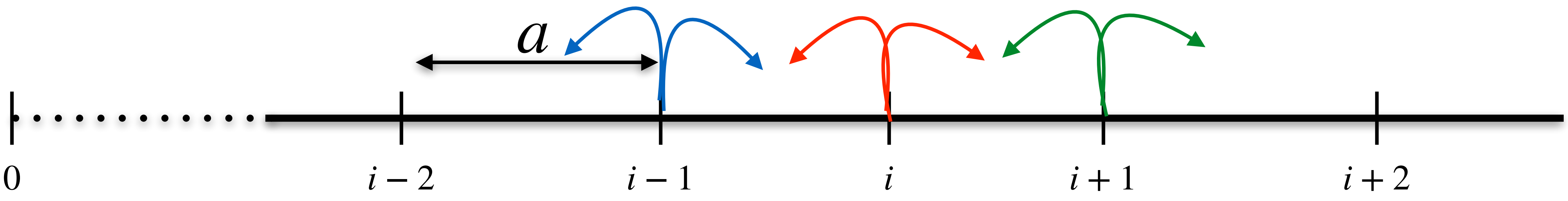
Second Law

$$Rate\ of\ accumulation = \dot{in} - \dot{out}$$

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial z} = D\frac{\partial^2 c}{\partial z^2}$$

Fick’s second law: derivation

Consider a one-dimensional system



N_i = Number of particles at i

$$\Gamma = \text{Jump frequency} = \left(\frac{\text{number of jump}}{\text{time}}\right)$$

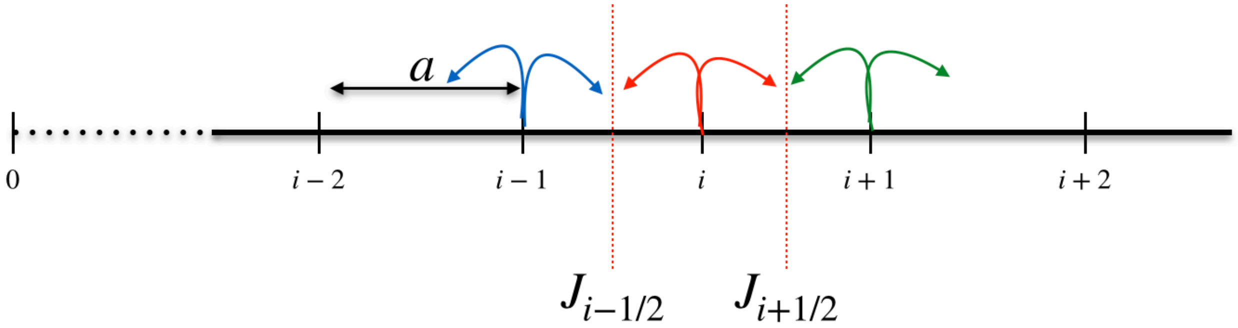
Each particle can jump left or right with frequency Γ

Flux of particles out of spot i $= \Gamma N_i$

Fick's second law: derivation

$$J_{i+1/2} = \frac{\Gamma}{2}N_i - \frac{\Gamma}{2}N_{i+1}$$

$$J_{i-1/2} = \frac{\Gamma}{2}N_{i-1} - \frac{\Gamma}{2}N_i$$



Flux of particles out of spot i $= \Gamma N_i$

$$\dot{N}_i = \frac{\partial N(i,t)}{\partial t} = J_{i-1/2} - J_{i+1/2}$$

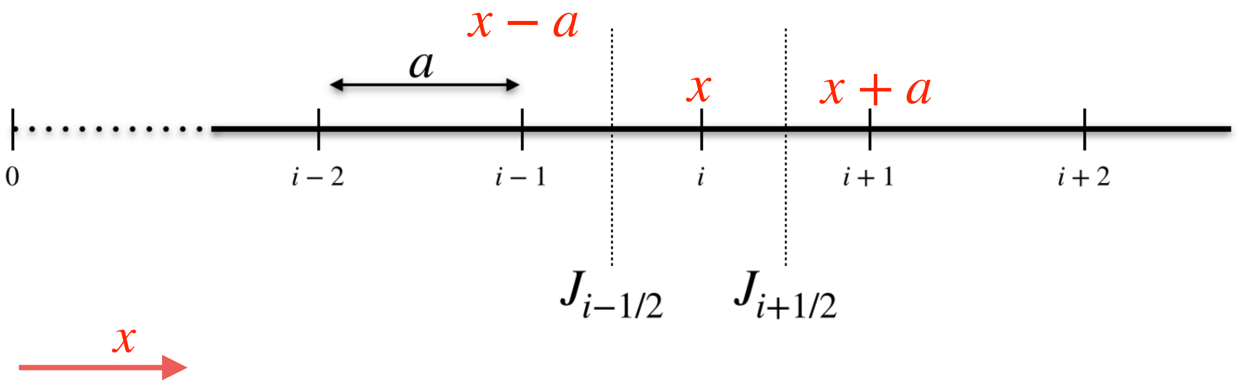
Concentration changes at the position *i* is dictated by these two fluxes

For positive flux, $J_{i-1/2} > J_{i+1/2}$

$$= \left(\frac{\Gamma}{2}N_{i-1} - \frac{\Gamma}{2}N_i\right) - \left(\frac{\Gamma}{2}N_i - \frac{\Gamma}{2}N_{i+1}\right)$$

$$= \frac{\Gamma}{2}N_{i-1} - \Gamma N_i + \frac{\Gamma}{2}N_{i+1} = \frac{\Gamma}{2}\left(N_{i-1} - 2N_i + N_{i+1}\right)$$

Fick's second law: derivation



$$\dot{N}_i = \frac{\partial N(i,t)}{\partial t} = \boxed{\frac{\Gamma}{2}\left(N_{i-1} - 2N_i + N_{i+1}\right)}$$

For small hops

$$\boxed{\lim_{a\to 0}\frac{N_{i-1} - 2N_i + N_{i+1}}{a^2}}$$

$$= \lim_{a\to 0}\frac{N(x-a,t) - 2N(x,t) + N(x+a,t)}{a^2} = \frac{\partial^2 N(x,t)}{\partial x^2}$$

$$\Rightarrow \lim_{a\to 0}\frac{\Gamma}{2}\left(N_{i-1} - 2N_i + N_{i+1}\right) = \frac{\partial N}{\partial t} = \boxed{\frac{\Gamma a^2}{2}}\frac{\partial^2 N(x,t)}{\partial x^2} = \boxed{D}\frac{\partial^2 N(x,t)}{\partial x^2}$$

$$\frac{\partial N}{\partial t} = D\frac{\partial^2 N(x,t)}{\partial x^2}$$

Fick's 2nd law

$$D = \frac{\Gamma a^2}{2}$$

Diffusion in three-dimensions

For 1 dimensional system : $D = \frac{\Gamma a^2}{2}$

For 2 dimensional system (square lattice) : $D = \frac{\Gamma a^2}{4}$

For 3 dimensional system (cubic lattice) : $D = \frac{\Gamma a^2}{6}$

What is the dimension of diffusion coefficient?

$[D] = m^2\ s^{-1}$

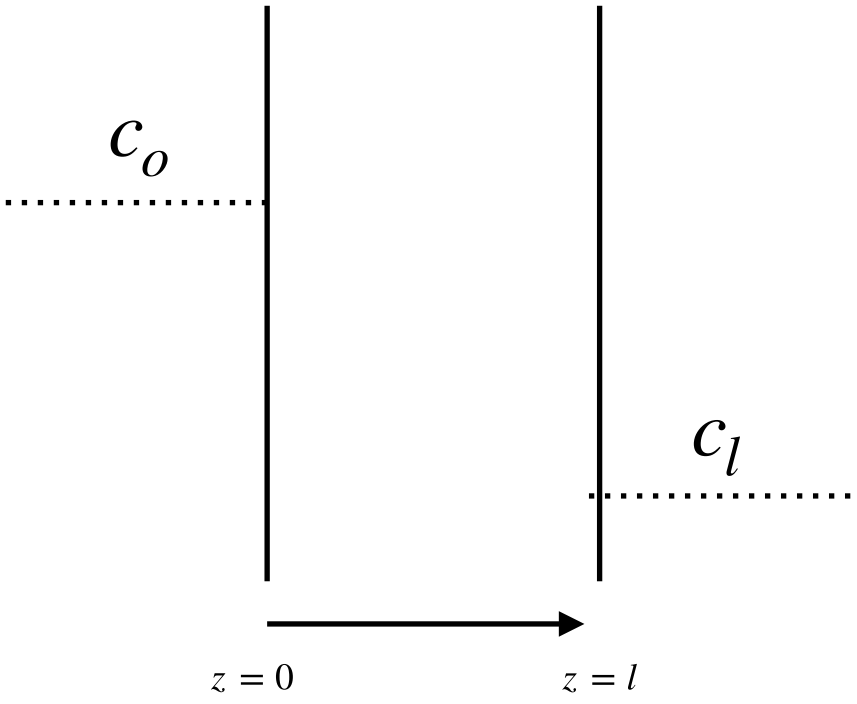
Exercise problems on flux

Exercise problem

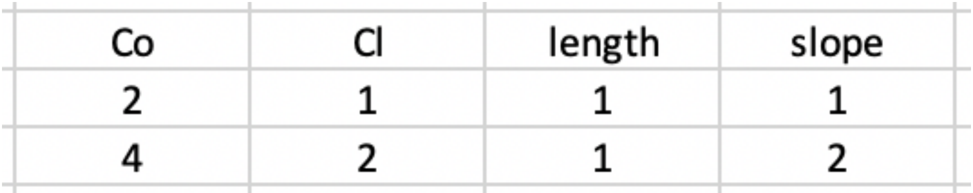
$$J = -D\frac{\partial c}{\partial z}$$

A gas is diffusing from left (z= 0) to right (z= l) with flux J_o. The initial concentration on left is C_o, and on the right is C_l.

What will happen to flux if both C_o and C_l are doubled?



A. $J_{new} = J_o$
B. $J_{new} = 2J_o$
C. $J_{new} = 0.5\ J_o$
D. $J_{new} = 4\ J_o$

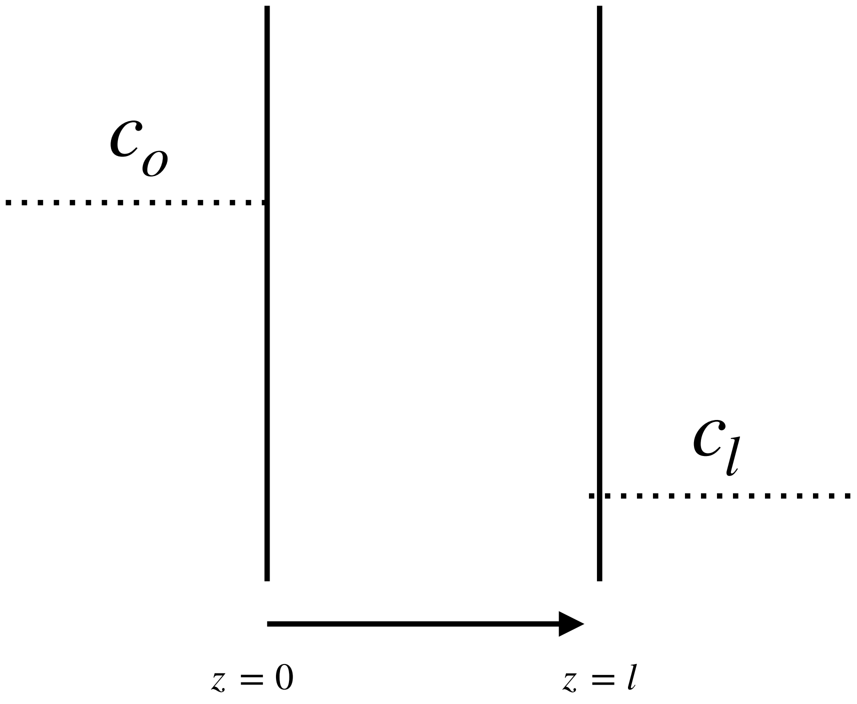


Co	Cl	length	slope
2	1	1	1
4	2	1	2

Exercise problem:

A gas is diffusing from left (z= 0) to right (z= l) with flux J_o. The initial concentration on left is C_o, and on the right is C_l.

What will happen to flux if the distance *l* is cut short to half?



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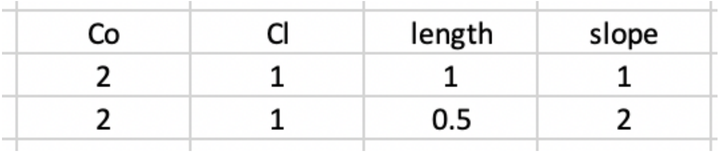
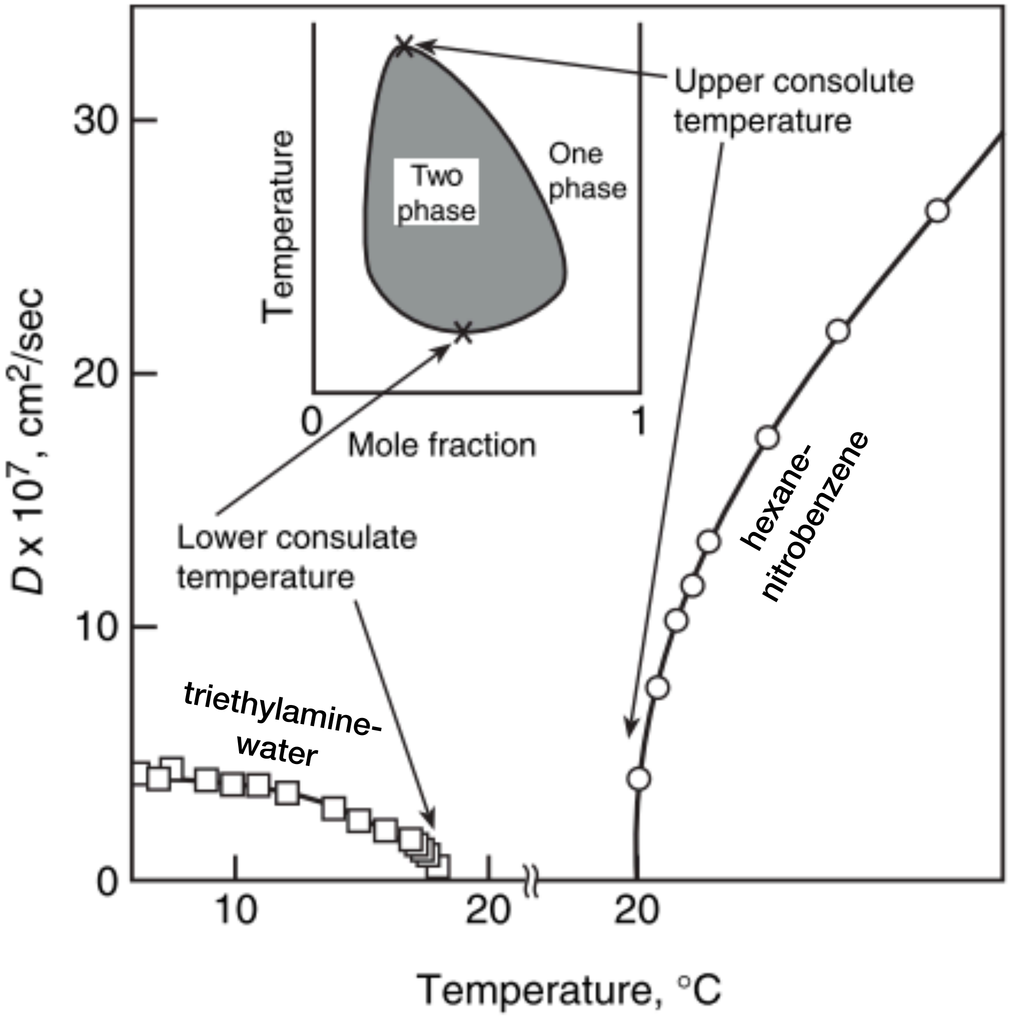


Co	Cl	length	slope
2	1	1	1
2	1	0.5	2

Diffusion will stop even if the concentration gradient is not zero?

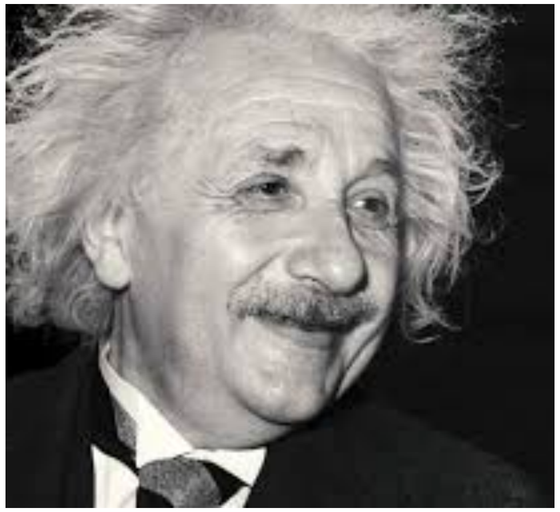
Diffusion coefficient near consolute points



E. L. Cussler, Diffusion: Mass Transfer in Fluid Systems

Limitation of Fick’s laws of diffusion

Diffusion is driven by concentration gradient



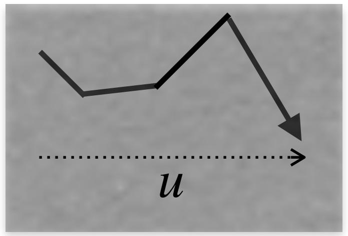
Diffusion is macroscopic manifestation of the tendency to reach equilibrium, therefore, it must be driven by chemical potential gradient

Understanding the driving force for diffusion

- Diffusive flux is essentially a flow driven by force (the gradient of chemical potential).
- If there is a flow, there should be frictional force opposing the flow.

Frictional drag = chemical potential force

High concentration



Low concentration

Friction, f

$$fu = -\frac{d\mu}{dz} \qquad \Rightarrow \qquad u = -\frac{1}{f}\frac{d\mu}{dz}$$

$$\text{flux} = uc = -\frac{c}{f}\frac{d\mu}{dz} \qquad \mu = \mu^o(T,P) + k_BT\ln(\hat{f}/P) \qquad \Rightarrow \quad \frac{d\mu}{dz} = k_BT\frac{d\ln(\hat{f}/P)}{dz}$$

$$\Rightarrow \quad \text{flux} = -\frac{c}{f}\frac{d\mu}{dz} = -\frac{ck_BT}{f}\frac{d\ln(\hat{f}/P)}{dz} = -\frac{ck_BT}{f}\frac{d\ln(\hat{f}/P)}{d\ln c}\frac{d\ln c}{dz} = -\left[\frac{k_BT}{f}\frac{d\ln(\hat{f}/P)}{d\ln c}\right]\frac{dc}{dz} = -D\frac{dc}{dz}$$

$$D = \frac{k_BT}{f}\frac{d\ln(\hat{f}/P)}{d\ln c} = D_o\frac{d\ln(\hat{f}/P)}{d\ln c} \qquad D_o = \frac{k_BT}{f}$$

Diffusivity is inversely proportional to frictional force

<u>Stoke's Einstein Equation</u>

Understanding the driving force for diffusion

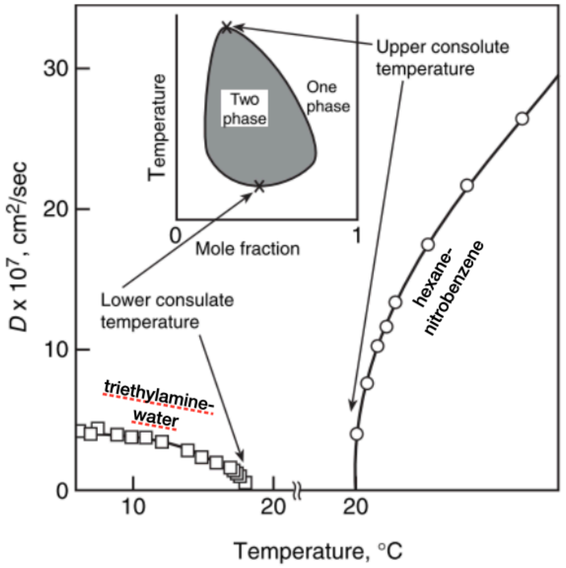
$$D = D_o \frac{d \ln(\hat{f}/P)}{d \ln c}$$

Transport diffusivity

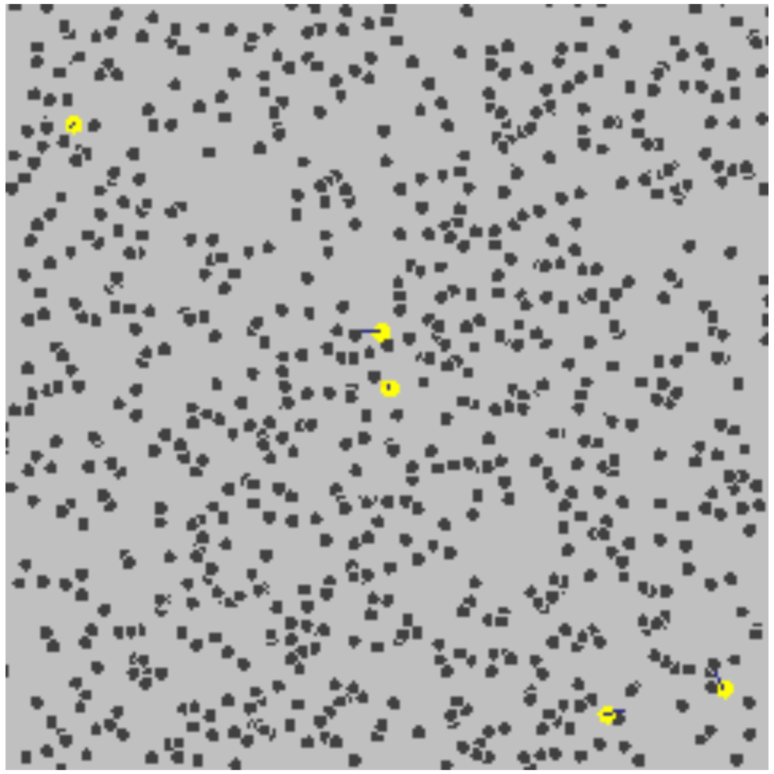
$$D_o = \frac{k_B T}{f}$$

Self-diffusivity or tracer diffusivity

This difference is reflected when one deals with
- Where non-ideal behavior kicks in (e.g., hexane/nitrobenzene).
- Multicomponent systems



Origin of diffusion (molecular perspective): Brownian motion



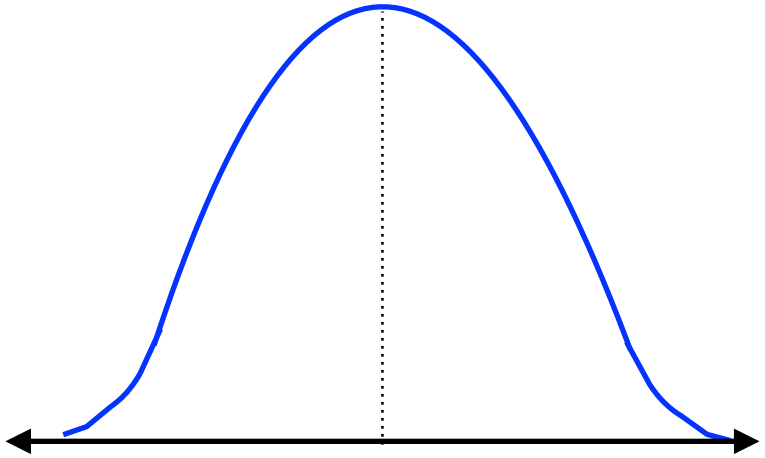
Source: wiki

Robert Brown, 1773-1858

Brownian motion (single-particle perspective)

$$P(z,t) = \frac{1}{\sqrt{4\pi D_o t}} \exp\left(\frac{-z^2}{4D_o t}\right)$$

If you observe a single particle (tracer) as a function of time

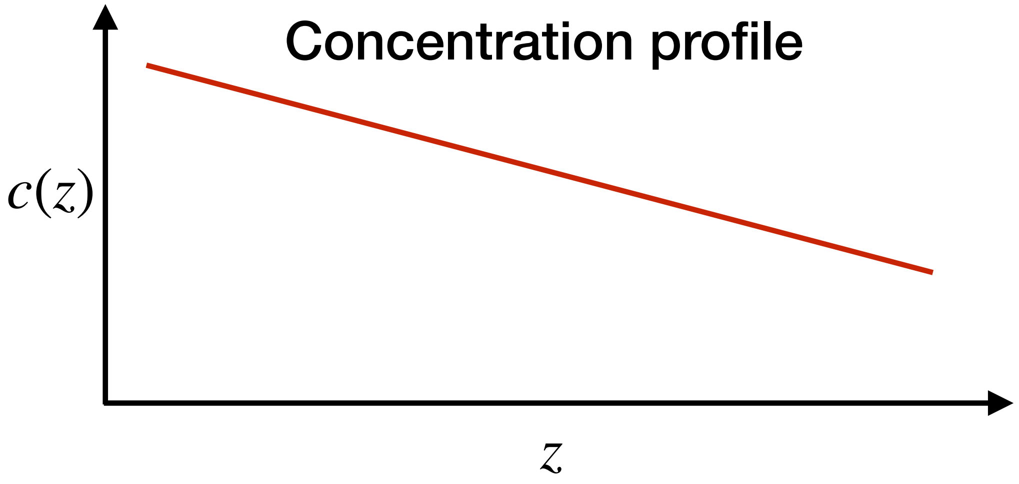


Point spread probability

Making sense of two fundamental concepts: Fick's law and random motion

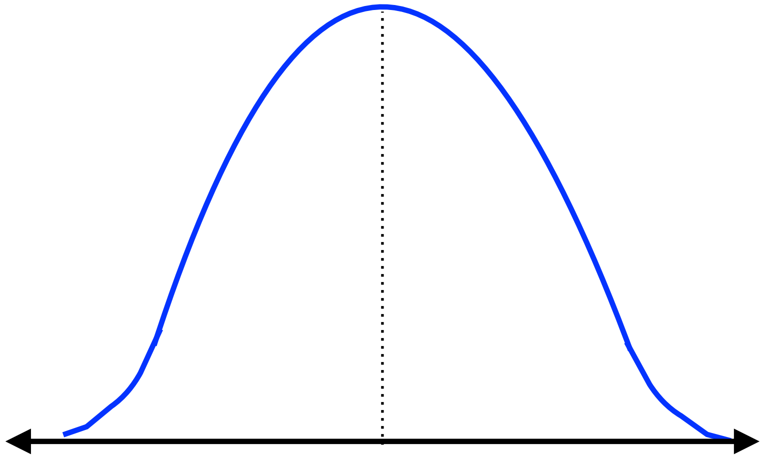
Fick's first law (collective motion)

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



Brownian motion (single-particle perspective)

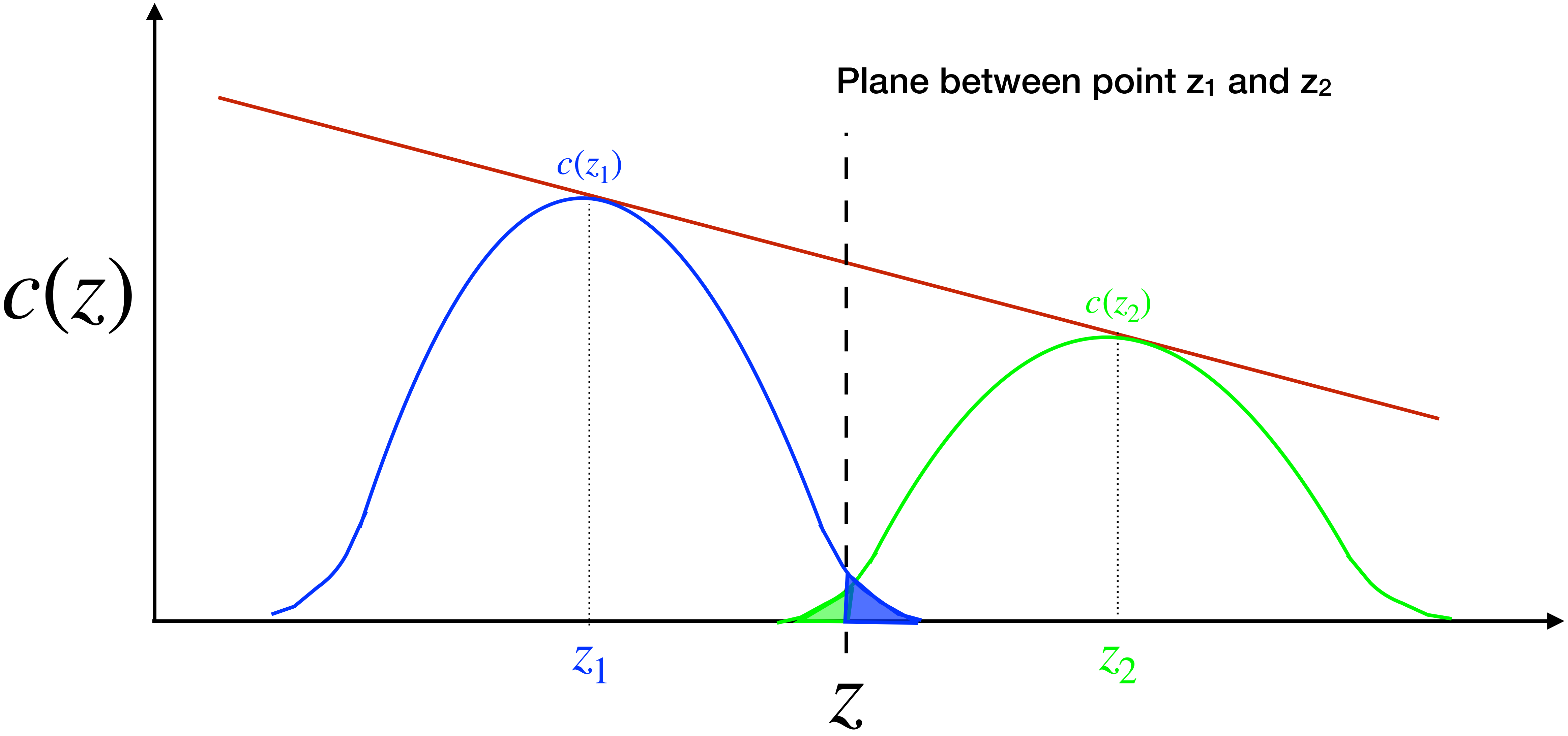
$$P(z,t) = \frac{1}{\sqrt{4\pi D_o t}}\exp\left(\frac{-z^2}{4D_o t}\right)$$



Point spread probability

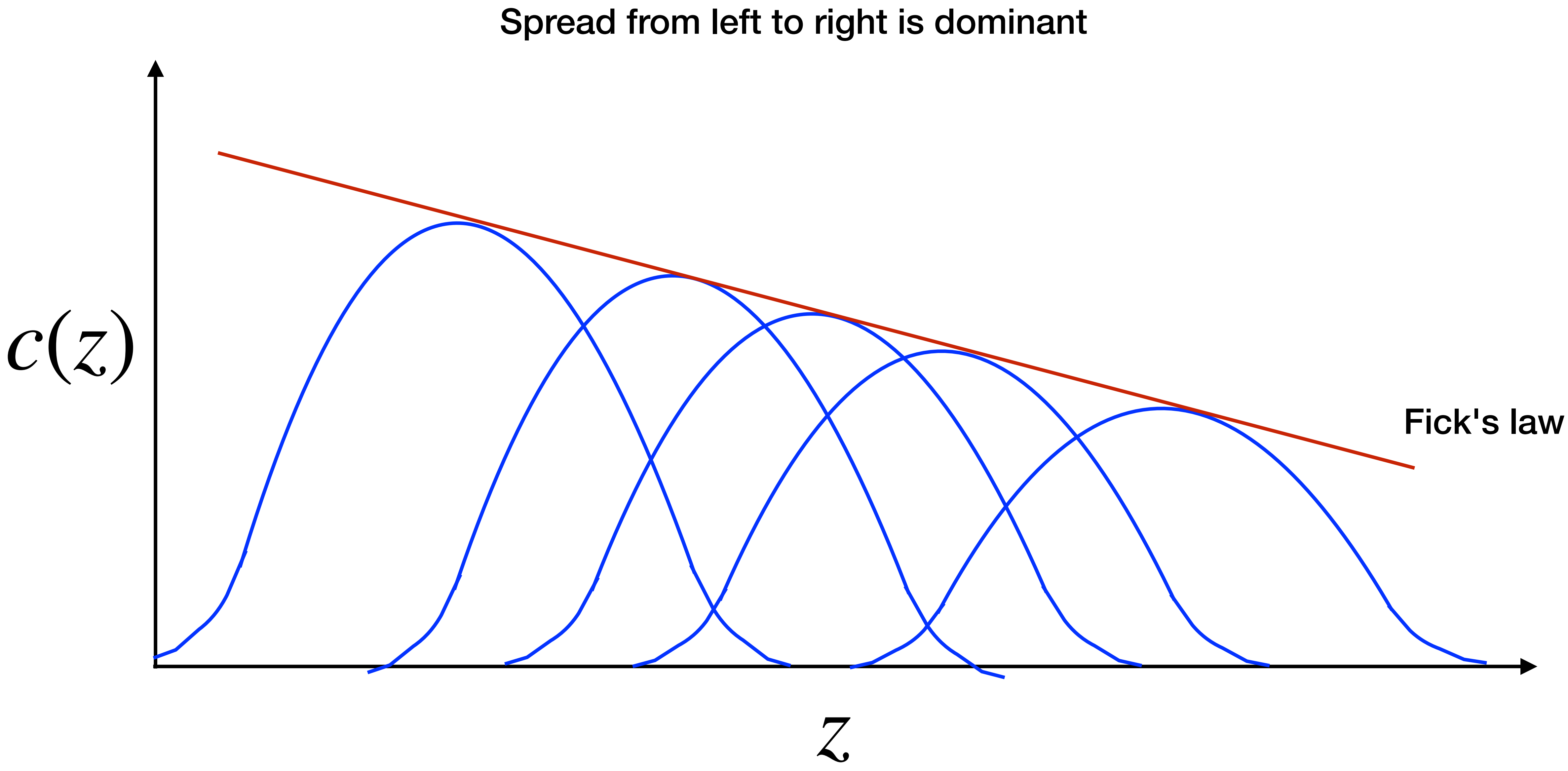
Making sense of Fick's law and random motion

$$c(z,t) \;=\; \frac{c(z_1, t=0)}{\sqrt{4\pi D_o t}} \exp\left(\frac{-(z-z_1)^2}{4D_o t}\right) \qquad c(z,t) \;=\; \frac{c(z_2, t=0)}{\sqrt{4\pi D_o t}} \exp\left(\frac{-(z-z_2)^2}{4D_o t}\right)$$



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

Making sense of Fick’s law and random motion



Diffusion as a random walk: Brownian motion

Brownian motion is diffusion under macroscopic equilibrium

$$J^* = -\mathfrak{D}\frac{\partial c^*}{\partial z}\bigg|_{c=\text{const}}$$

Self-diffusivity flux under slight fluctuation in concentration

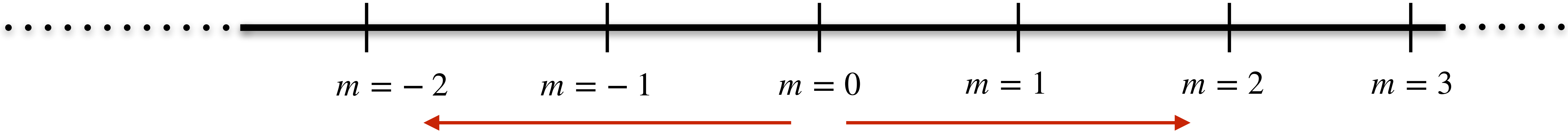
Measurement of self-diffusivity

For 3 dimensional system (cubic lattice) : $$D_0 = \frac{\Gamma a^2}{6}$$

Mean-squared displacement of N particles at time t = $$\left\langle r^2(t) \right\rangle = \frac{1}{N}\Sigma_1^N (x_i(t) - x_i(0))^2 = 6D_o t$$

Mean-squared displacement of random walker

Consider our one-dimensional system again



Starting from origin a particle can hop right or left with equal probability

Probability to find a particle at position z, after time t is given by a gaussian function

$$P(z,t) = \frac{1}{\sqrt{4\pi D_o t}} \exp\left(\frac{-z^2}{4D_o t}\right)$$

$$\langle z^2(t) \rangle = \int z^2 P(z,t) dz = 2D_o t$$

For 1 dimensional system

$$\langle r^2(t) \rangle = 6D_o t$$

For 3 dimensional system

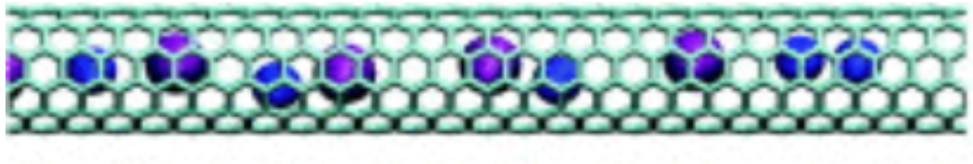
Mean square displacement profile can be a signature for type of diffusion

Fickian diffusion

$$\langle z^2(t) \rangle = 2D_0 t$$

$$\langle z^2(t) \rangle \propto t$$

Single-file diffusion



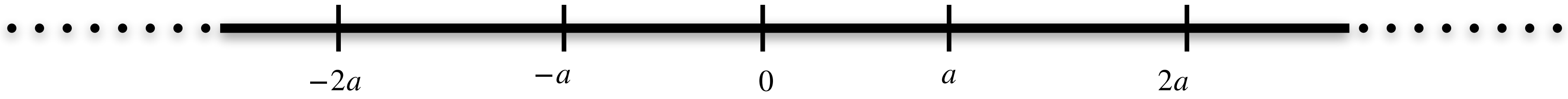
$$\langle z^2(t) \rangle = \sqrt{\frac{2D(\theta)t}{\pi\Gamma}}$$

$$\langle z^2(t) \rangle \propto \sqrt{t}$$

Single-file-diffusion is much slower than that of Fickian

Exercise problem 1

Let's look at one-dimensional space divided across several hopping sites.
Initially there are no particles.
At time t = 0, you place 10000 particles at 0.
Calculate number of particles at 0, -a and a, -2a and 2a after 1 s.



$$\Gamma = 100 \ \text{hop/s}$$
$$a = 1 \ \text{length unit}$$

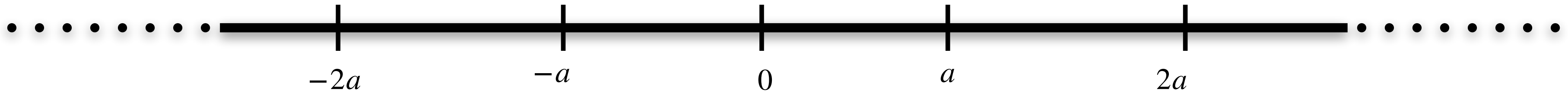
$$D = \frac{\Gamma a^2}{2}$$

$$P(z,t) = \frac{1}{\sqrt{4\pi D_o t}} \exp\left(\frac{-z^2}{4D_o t}\right)$$

$$N(z,t) = \frac{N_o(t=0,z_0)}{\sqrt{4\pi D_o t}} \exp\left(\frac{-z^2}{4D_o t}\right)$$

Exercise problem 2

Continuation of previous problem:
Initially there are no particles.
At time t = 0, you place 100000 particles at 0 and 10000 particles at 2a to make a negative concentration gradient along the x-direction.
Calculate the direction of particle flow at the position a (midway between 0 and 2a) after 1 s.
Calculate the net directional flow of particle (from left to right) at the position a after 1s.



$\Gamma = 100$ hop/s
$a = 1$ length unit

$$D = \frac{\Gamma a^2}{2}$$

$$N(z,t) = \frac{N_o(t=0, z_0)}{\sqrt{4\pi D_o t}} \exp\left(\frac{-z^2}{4D_o t}\right)$$

Exercise problem 3

A gas molecule, He, is diffusing in a one dimensional channel, 1 µm away from the end of channel. Assuming the diffusion coefficient, D_o, to be 10^{-8} cm^2 s^{-1}, calculate the time that it take He to reach the end of channel.

$$\langle r^2(t) \rangle = 2D_o t$$

For 1D diffusion