

ChE-402

Diffusion and Mass Transfer



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

Shaoyu Wang

Synthesis of porous two 2D materials for selective diffusion of gases

Jiaming Tian

Synthesis of high-temperature catalyst for electrolysis

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

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

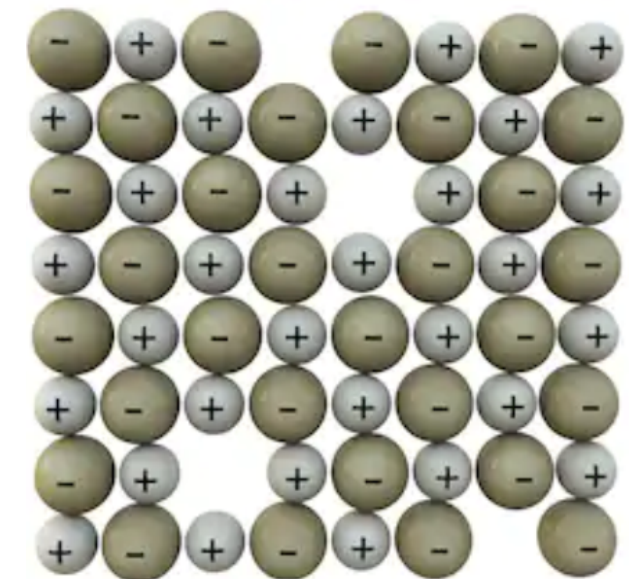
Calculate the time scale of diffusion in these systems

	D (m ² s ⁻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		

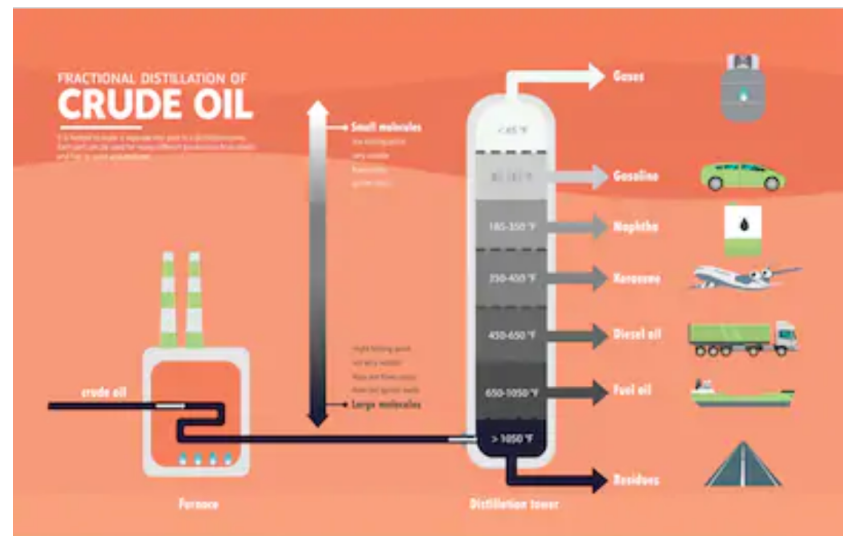
Vapor or gas



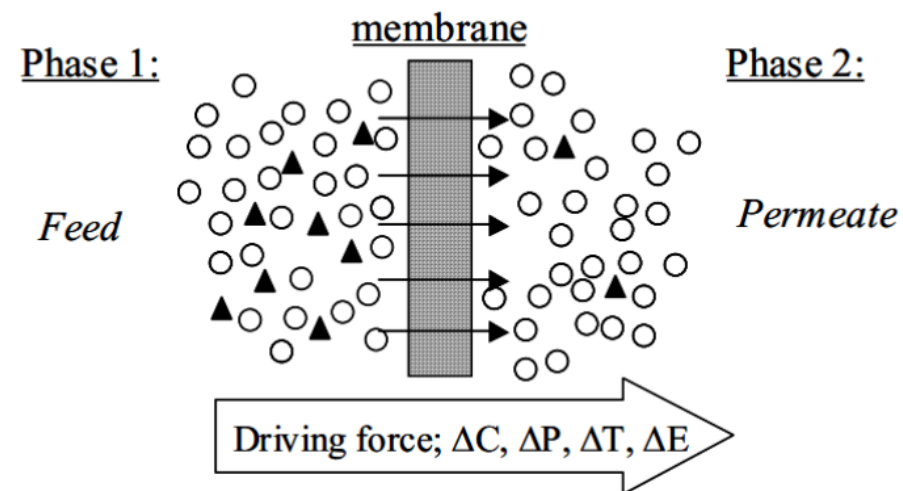
Defects in solid



Why should you learn about diffusion and mass transfer?



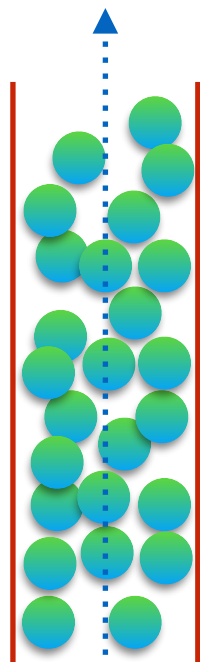
Distillation



Membranes



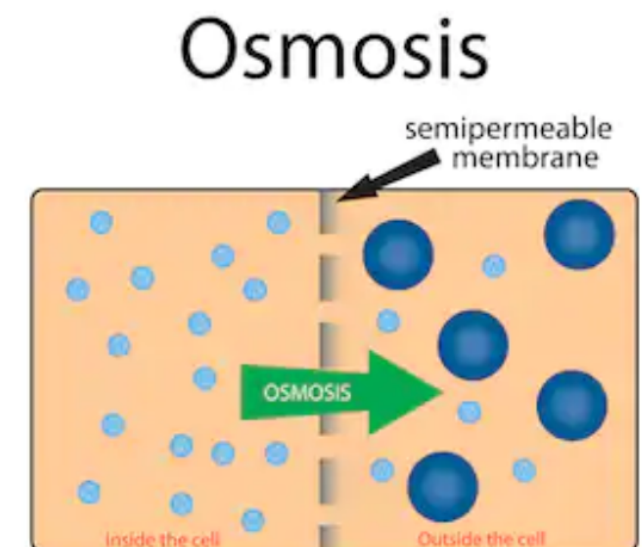
Bioreactor



Packed columns
(absorption, reaction)



Air pollution



Drinking water

Some common examples

Fluid-fluid interface



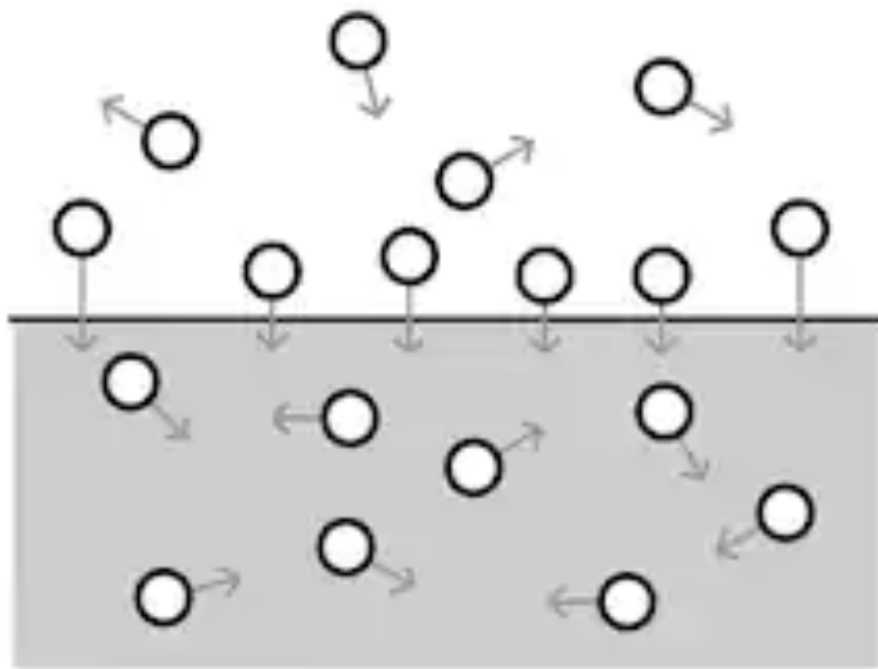
- ✦ Distillation
- ✦ Bioreactors
- ✦ Humidifiers
- ✦ Absorbers

Typical design questions for engineers:

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

Some common examples

Fluid-solid interface



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

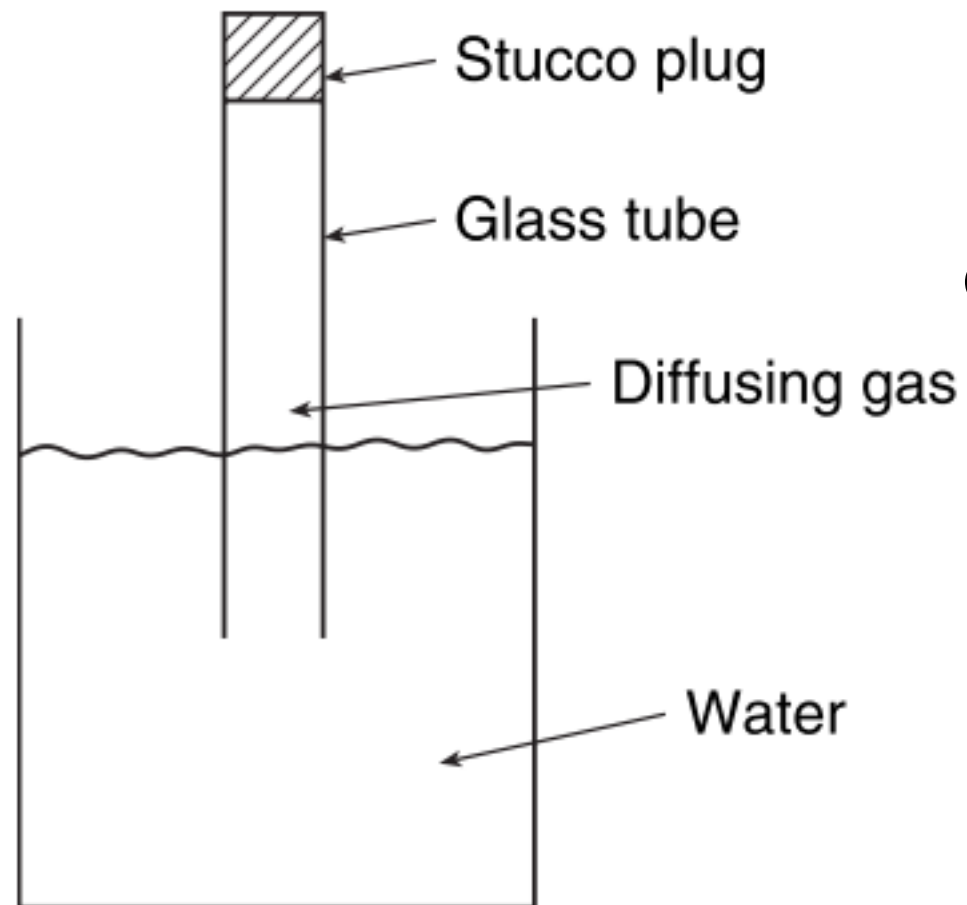
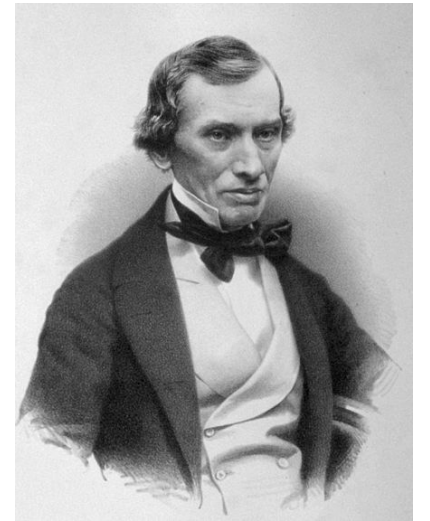
Typical design questions for engineers:

- ✦ 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:



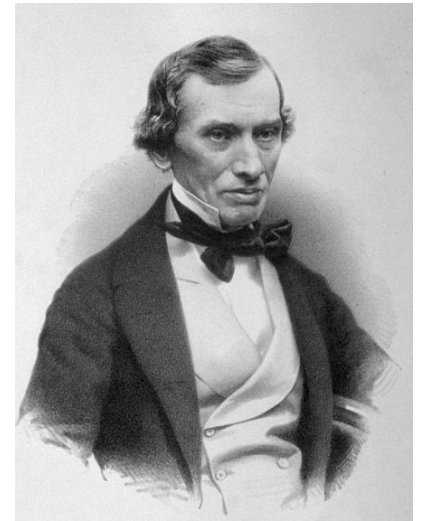
Can you guess what happens to water level in this experiment?

Graham's conclusion

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

Thomas Graham (1805 - 1869)

Liquid diffusion experiments:

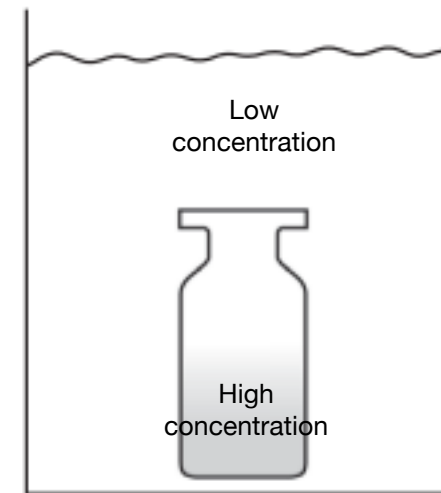


Low
concentration



High
concentration

Experiment 1

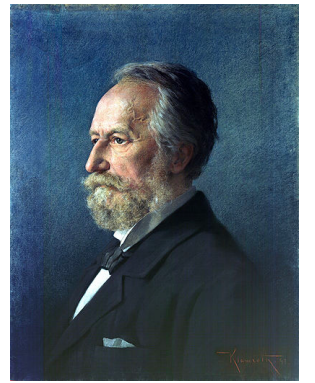


Experiment 2

Graham's conclusion

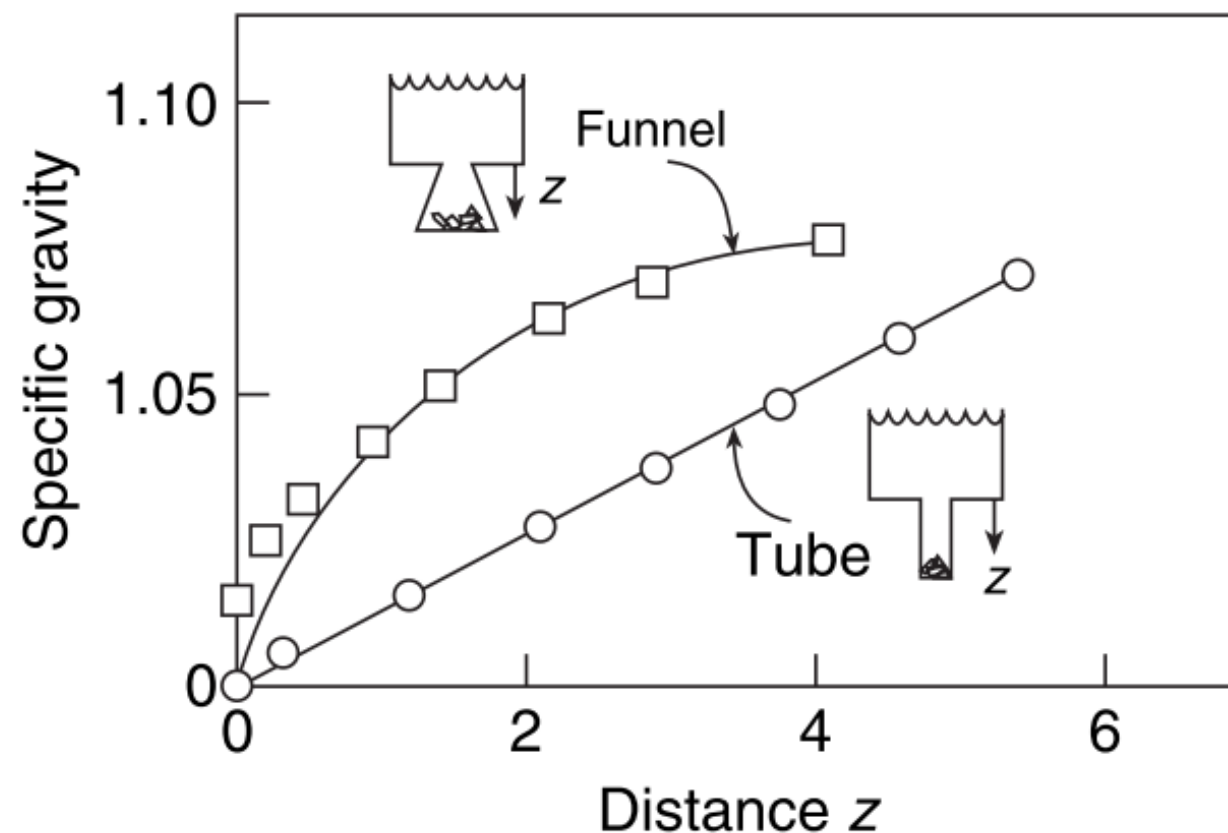
Quantity of diffused material is proportional to quantity of material in the vial.
Diffusion in liquids is several orders of magnitude smaller than that in gas.

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

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

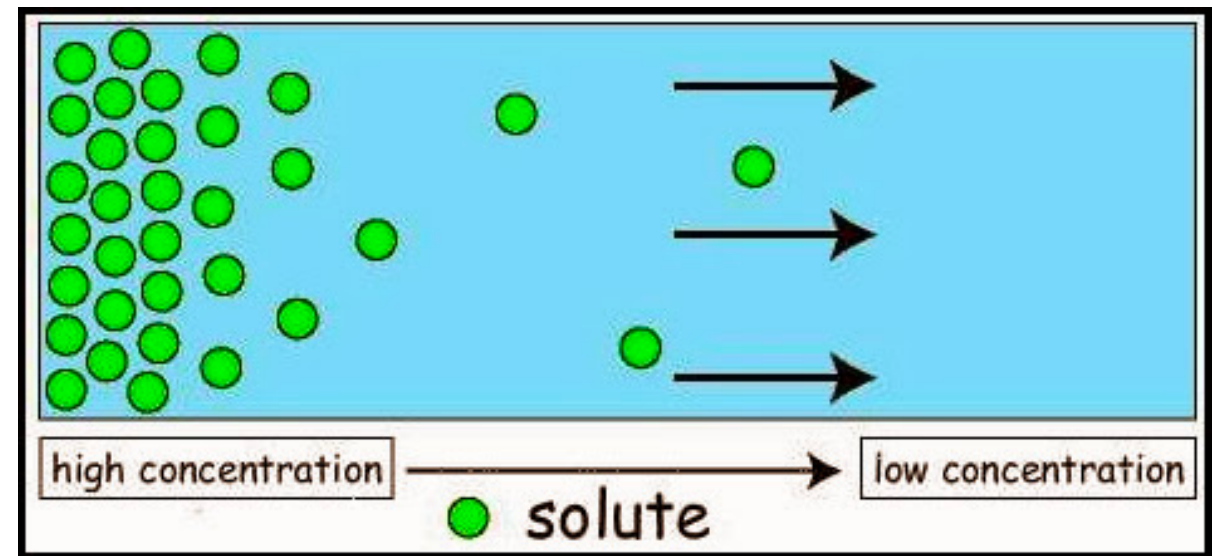
Fick's first and second law

First Law

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

Why there is a negative sign?

Why there is a negative sign?



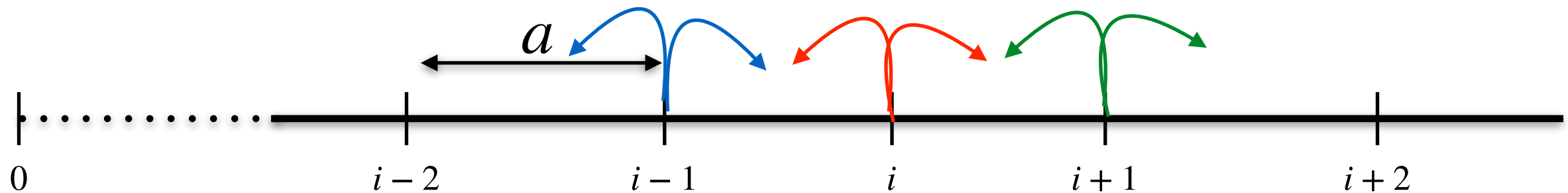
Second Law

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

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

Fick's second law: derivation

Consider a one-dimensional system



N_i = Number of particles at i

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

Each particle can jump left or right with frequency Γ

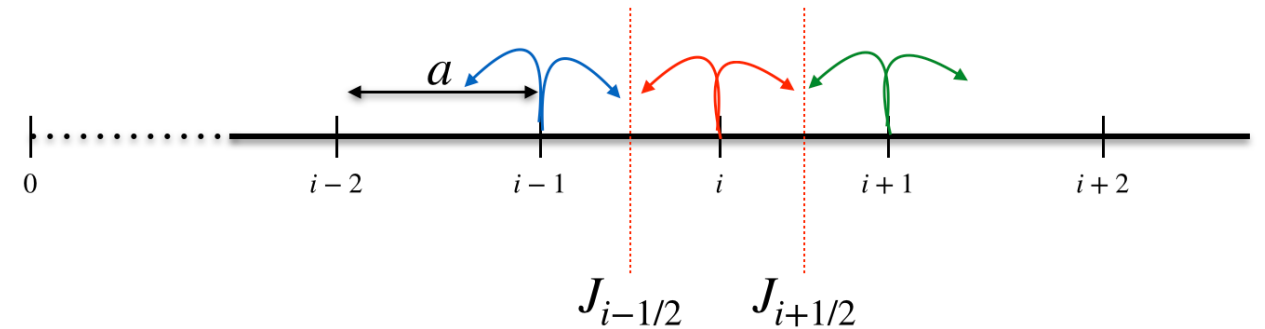
Flux of particles out of spot i = ΓN_i

Fick's second law: derivation

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

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

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



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

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

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

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

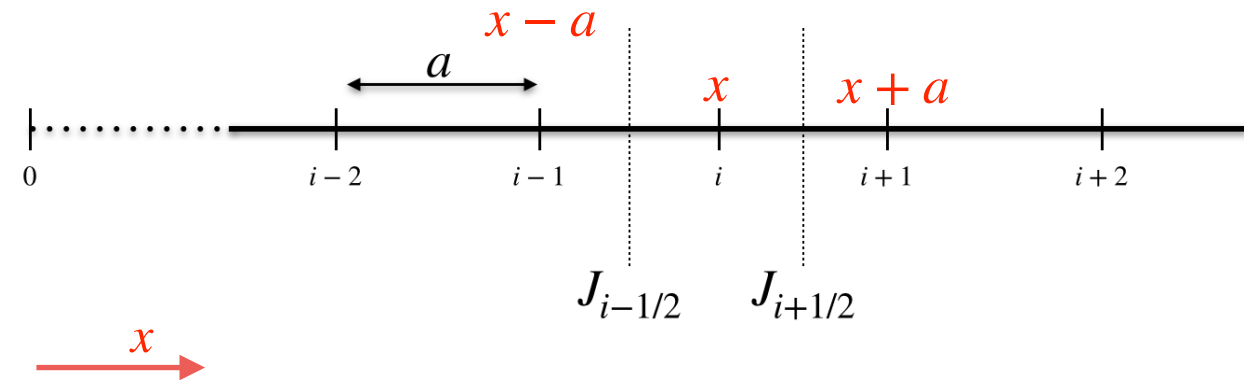
$$= \frac{\Gamma}{2}N_{i-1} - \Gamma N_i + \frac{\Gamma}{2}N_{i+1} = \frac{\Gamma}{2} (N_{i-1} - 2N_i + N_{i+1})$$

Fick's second law: derivation

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

For small hops

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



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

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

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

Fick's 2nd law

EPFL

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

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?

Exercise problems on flux

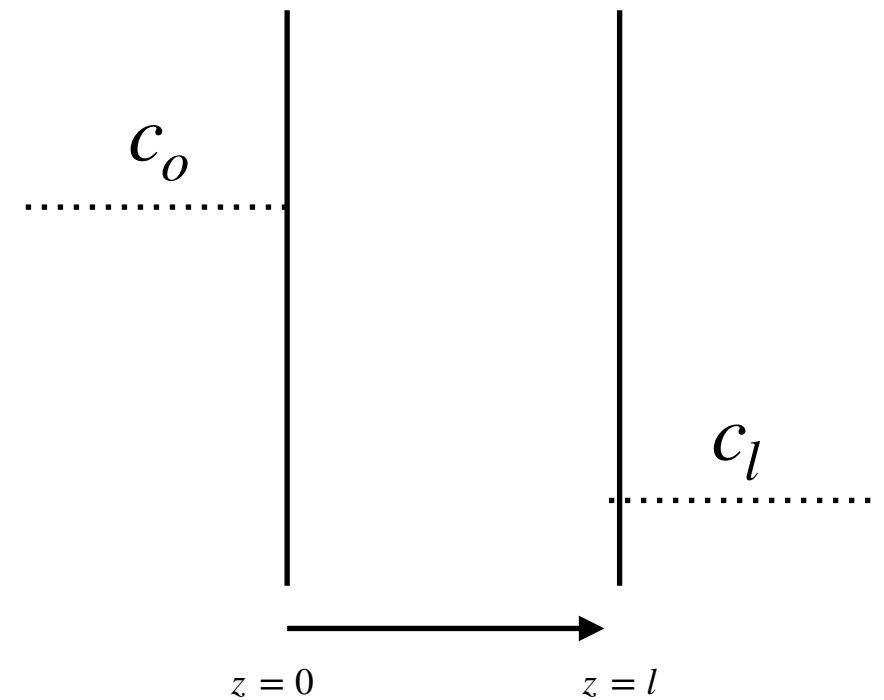
Exercise problem

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

A gas is diffusing from left ($z=0$) to right ($z=l$) with flux J_0 . The initial concentration on left is C_0 , and on the right is C_l .

What will happen to flux if both C_0 and C_l are doubled?

- A. $J_{\text{new}} = J_0$
- B. $J_{\text{new}} = 2J_0$
- C. $J_{\text{new}} = 0.5 J_0$
- D. $J_{\text{new}} = 4 J_0$

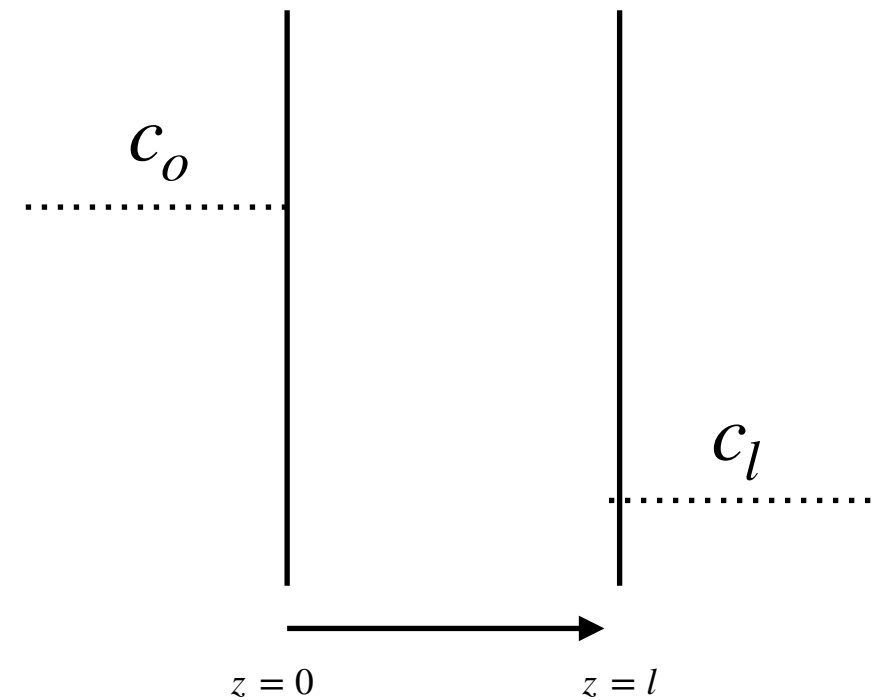


Exercise problem:

A gas is diffusing from left ($z=0$) to right ($z=l$) with flux J_0 . The initial concentration on left is C_0 , and on the right is C_l .

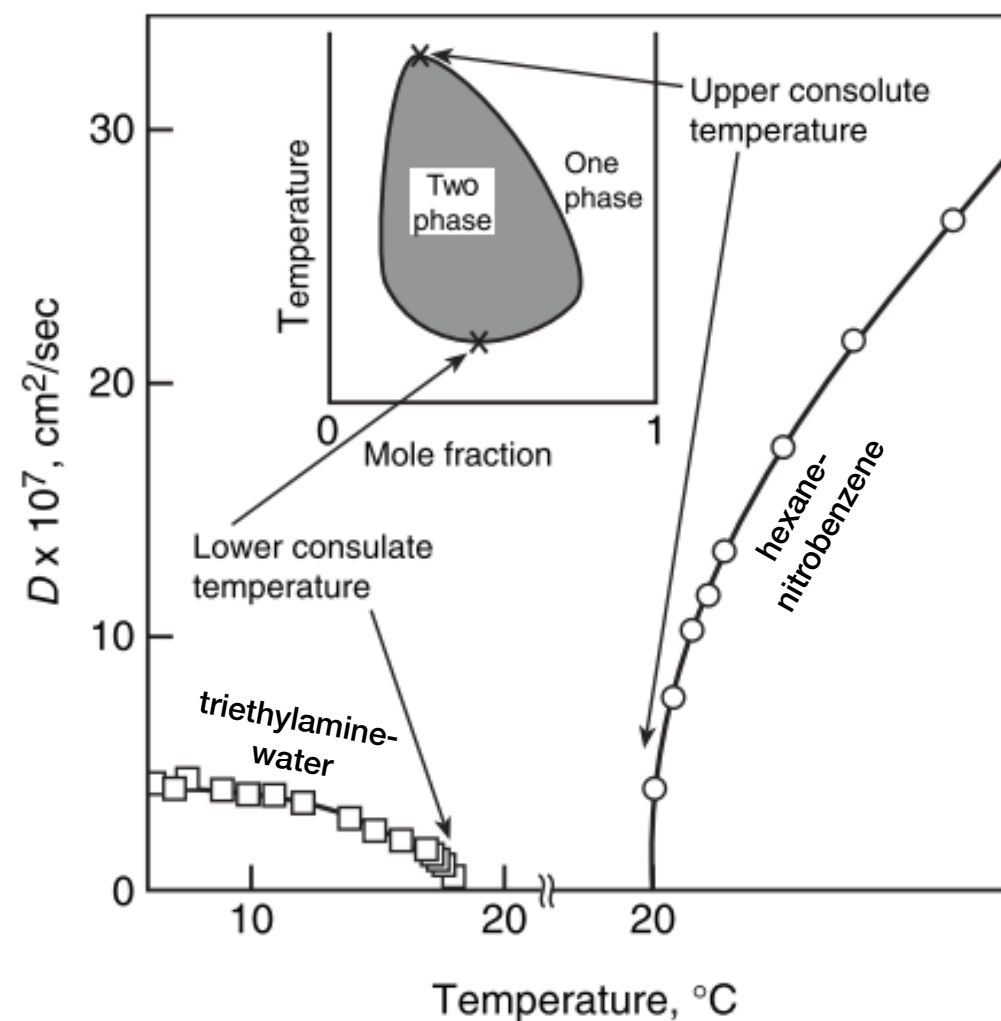
What will happen to flux if the distance l is cut short to half?

- A. $J_{\text{new}} = J_0$
- B. $J_{\text{new}} = 2J_0$
- C. $J_{\text{new}} = 0.5 J_0$
- D. $J_{\text{new}} = 4 J_0$



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

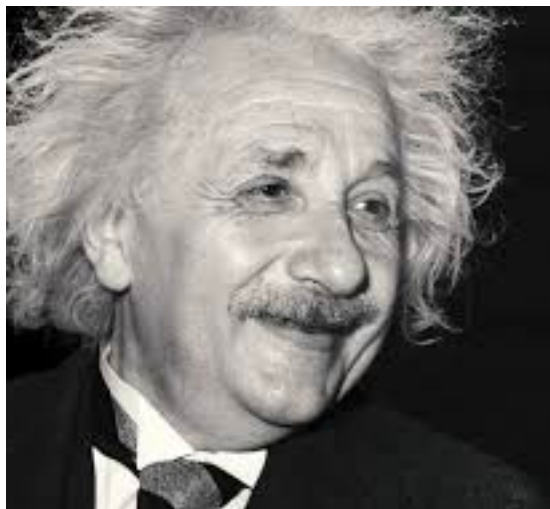
Diffusion coefficient near consolute points



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

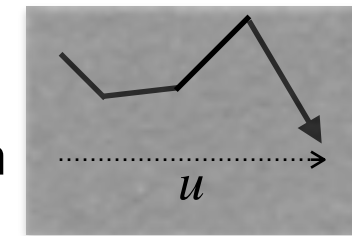
Understanding the driving force for diffusion

- 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

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

High
concentration



Low
concentration

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

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

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

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

Diffusivity is inversely proportional to frictional force

Stoke's Einstein Equation

Understanding the driving force for diffusion

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

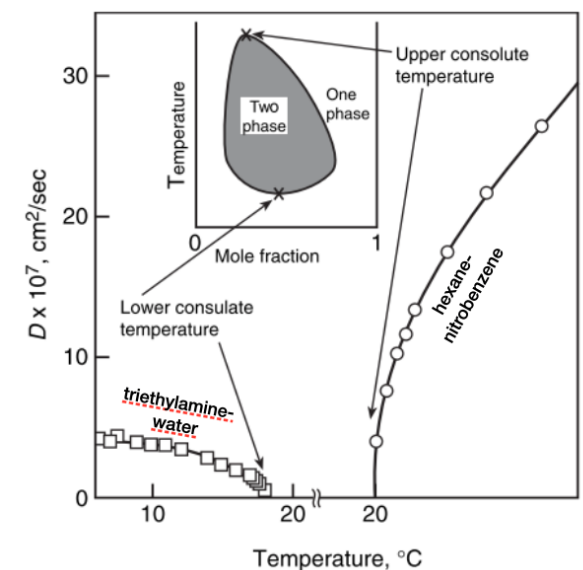
Transport diffusivity

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

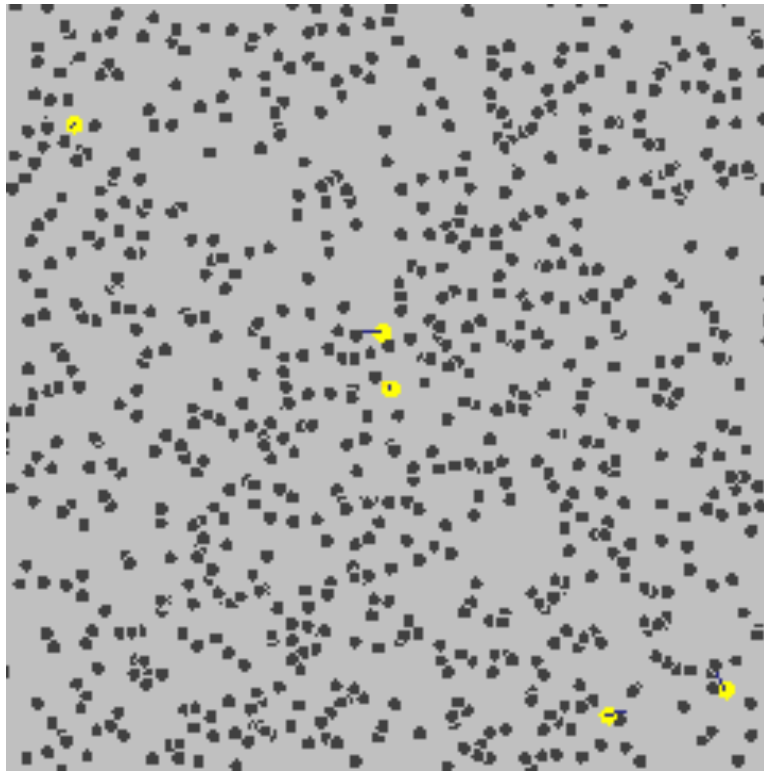
Self-diffusivity or tracer diffusivity

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



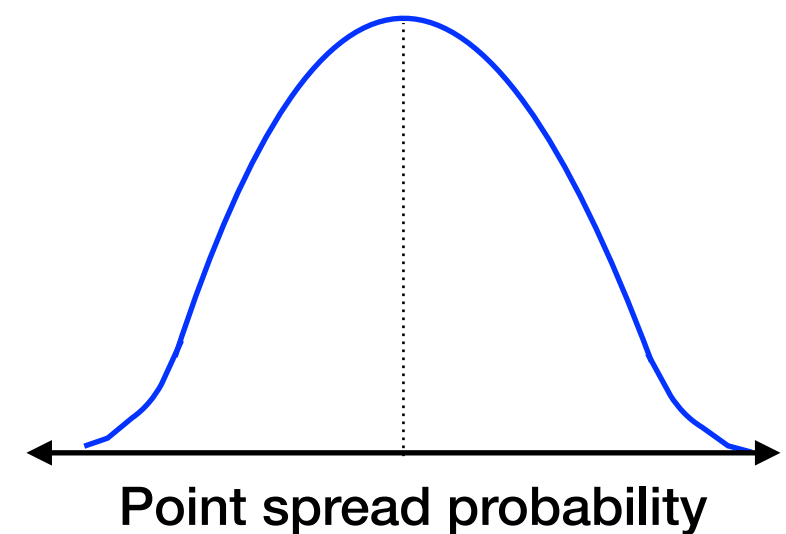
Robert Brown, 1773-1858

Source: wiki

Brownian motion (single-particle perspective)

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

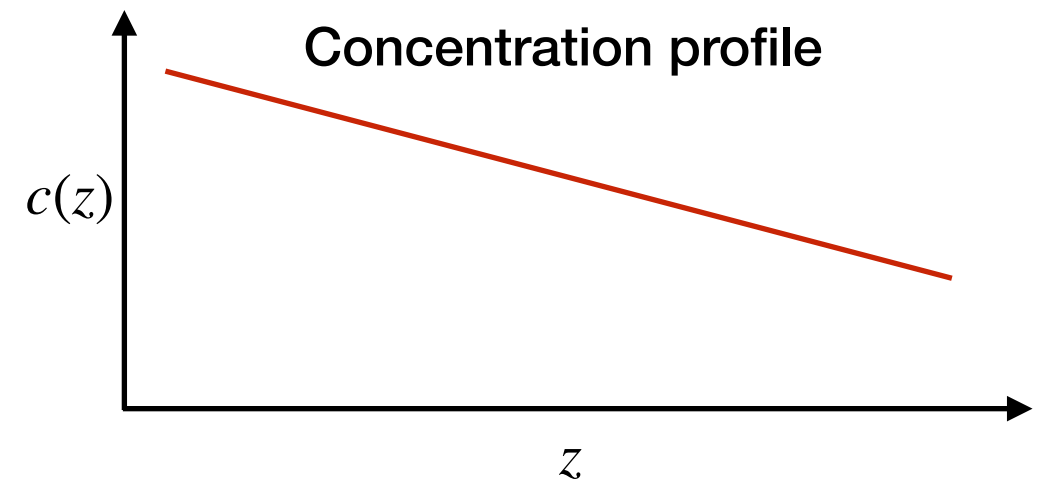
If you observe a single particle (tracer) as a function of time



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

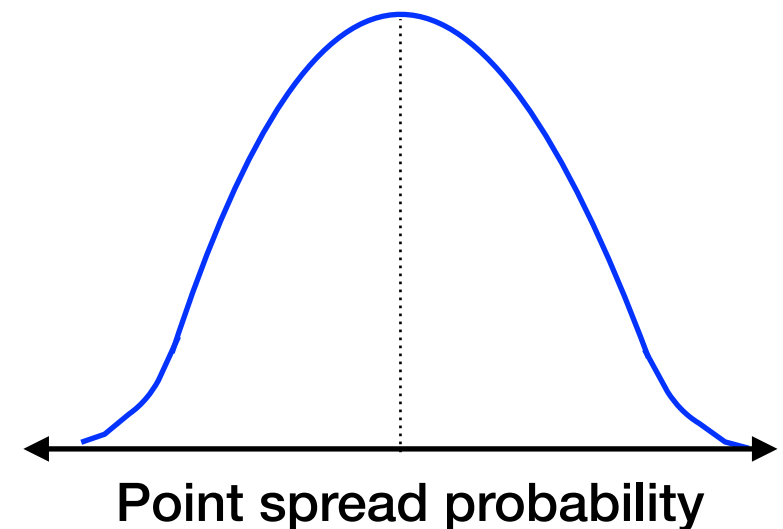
Fick's first law (collective motion)

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



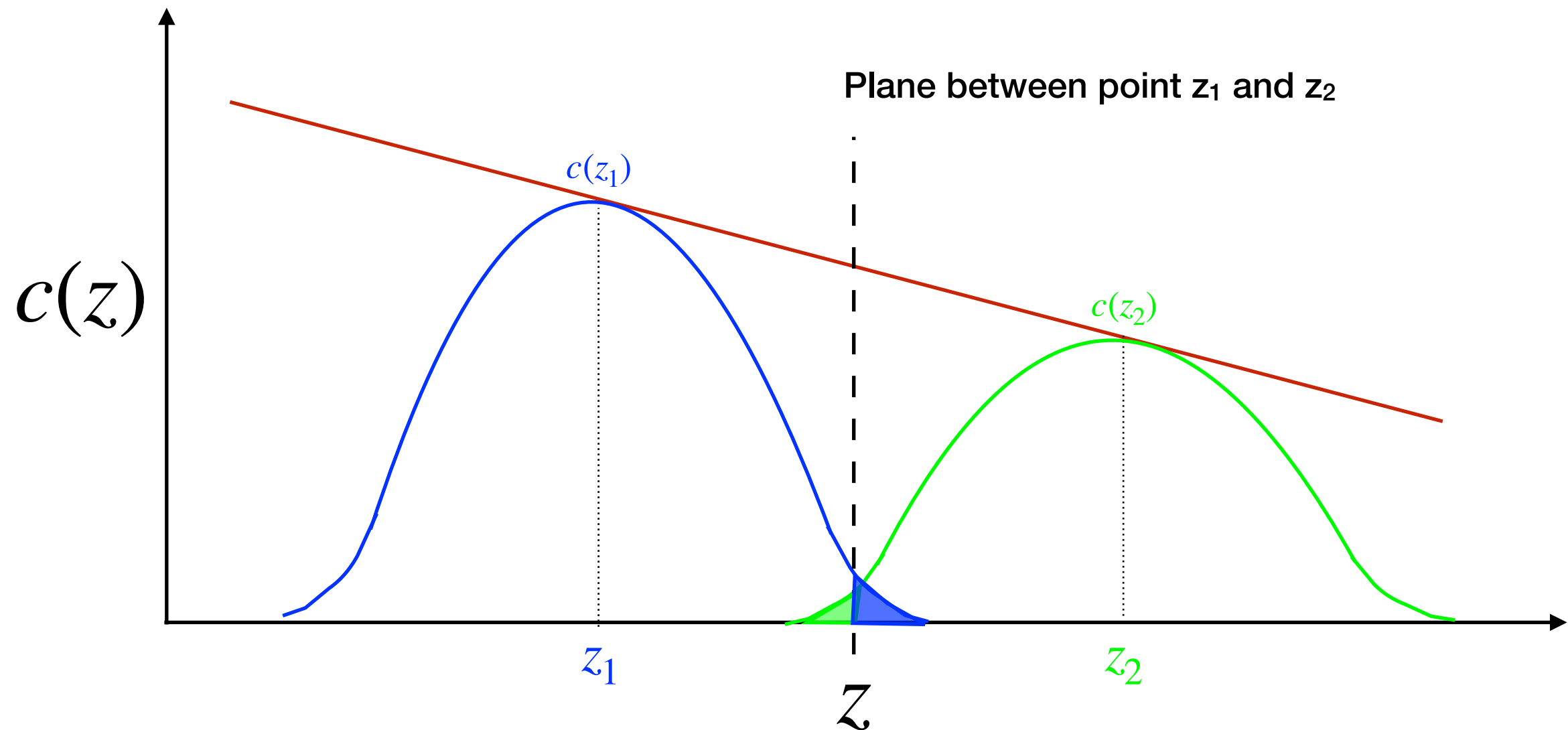
Brownian motion (single-particle perspective)

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



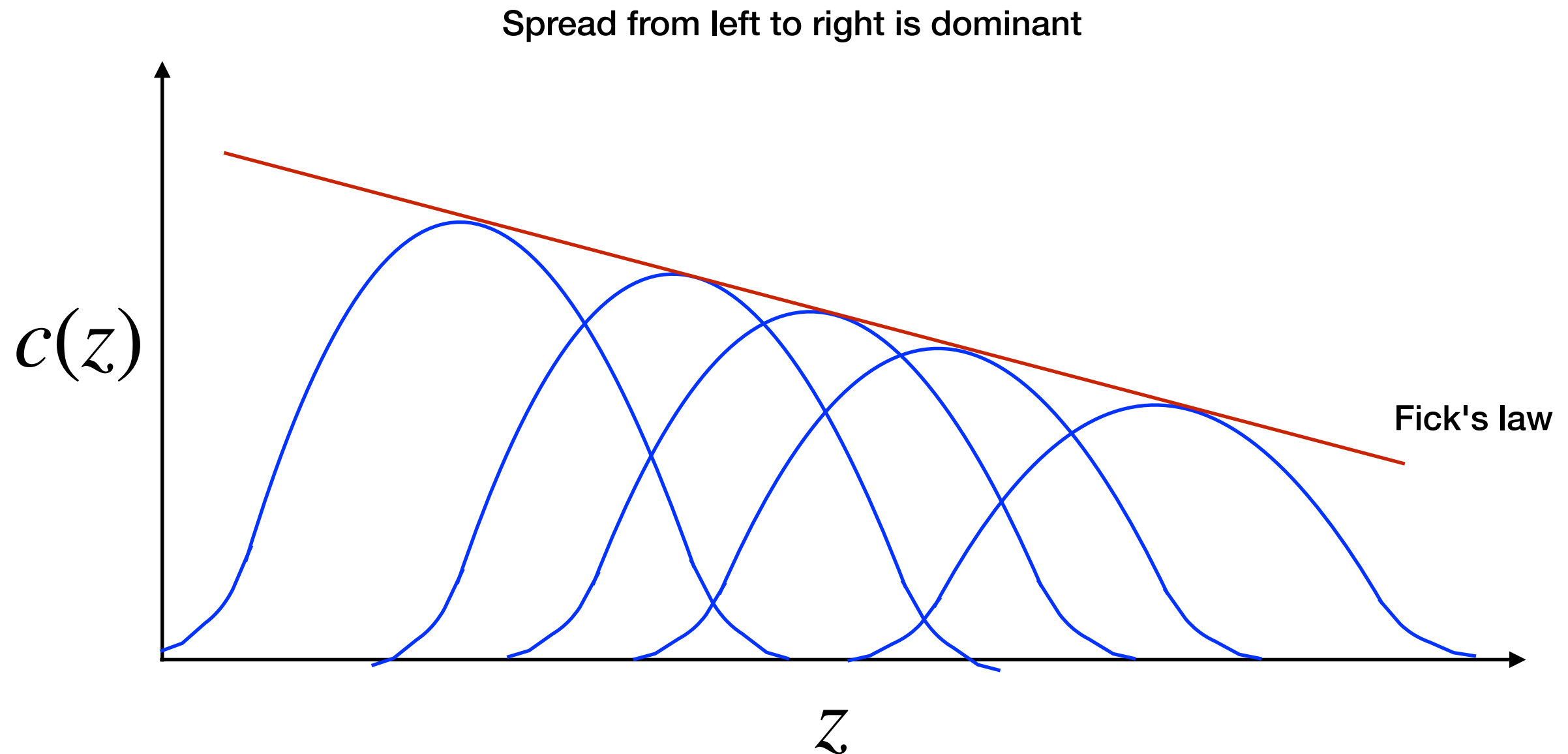
Making sense of Fick's law and random motion

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



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

Making sense of Fick's law and random motion



Diffusion as a random walk: Brownian motion

Brownian motion is diffusion under macroscopic equilibrium

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

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 = $\langle r^2(t) \rangle = \frac{1}{N} \sum_1^N (x_i(t) - x_i(0))^2 = 6D_0 t$

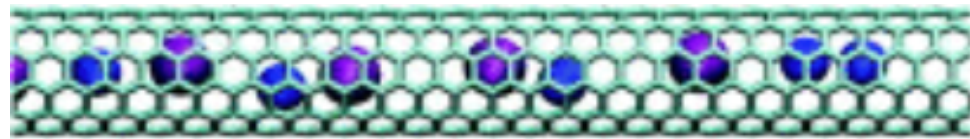
Mean square displacement profile can be a signature for type of diffusion

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

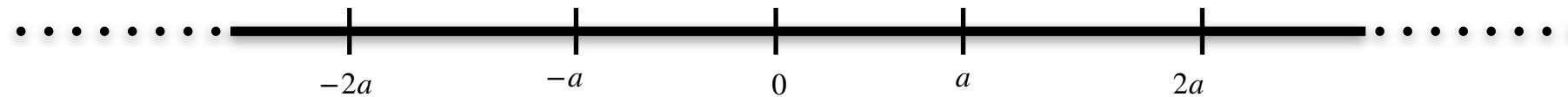
In class exercise 1

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.



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

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

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

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

In class exercise #2

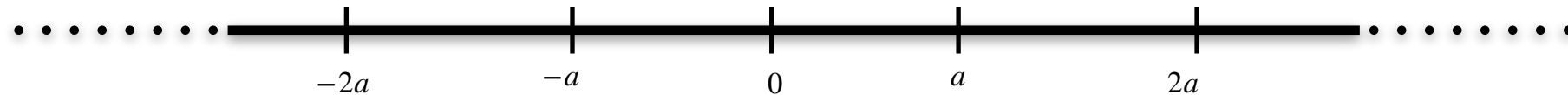
Continuation of previous problem:

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 1 s.



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

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

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

In class exercise #3: self-diffusion

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 $10^{-8} \text{ cm}^2 \text{ s}^{-1}$, calculate the time that it take He to reach the end of channel.

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

For 1D diffusion