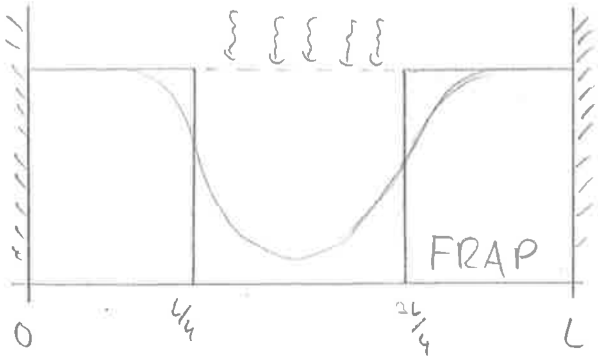
Diffusion constants

2018-10-04 ①

$$\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2}$$

Initial condition: $P(x,0) = c$



Boundary conditions: (BC):

$$\left.\frac{\partial P}{\partial x}\right|_{x=0} = \left.\frac{\partial P}{\partial x}\right|_{x=L} = 0$$

(no flux)

our prev solution

$$P(x,t) = \frac{1}{\sqrt{4\pi D t}} e^{-\frac{(x-x_0)^2}{4Dt}}$$

does not fulfill the BC.

alternative Ansatz: $P(x,t) = f(x)\, g(t)$

$$f(x)\dot{g}(t) = g(t) D f''(x)$$

$$\Rightarrow \quad \frac{\dot{g}(t)}{g(t)} = D\frac{f''(x)}{f(x)} = -\lambda$$

LHS depends on t, RHS on x $\Rightarrow$ constant!

$$\Rightarrow \quad f(x) = a\cos\left(\sqrt{\tfrac{\lambda}{D}}\,x\right) + b\sin\left(\sqrt{\tfrac{\lambda}{D}}\,x\right)$$

$$g(t) = c\, e^{-\lambda t}$$

a, b, c, λ need to be determined by IC & BC

$$\left.\frac{\partial P}{\partial x}\right|_{x=0} = g'(0) = 0 \quad \Rightarrow \quad b = 0$$

$$g'(L) = 0 \quad \Rightarrow \quad \sin\left(\sqrt{\tfrac{\lambda}{D}}\,L\right) = 0 \quad \Rightarrow \quad \sqrt{\tfrac{\lambda}{D}}\,L = n\pi \qquad n = 0, 1, 2, 3 \ldots$$

$\Rightarrow \lambda_n = D\dfrac{n^2\pi^2}{L^2}$ $\Rightarrow$ BC give rise to a discrete set of allowed values !?

$\Rightarrow$ general solution

$$P(x,t) = \sum_n a_n e^{-\frac{Dn^2\pi^2}{L^2}t} \cos\frac{n\pi x}{L}$$

$\Rightarrow$ a_n are determined by IC

(What does this solution remind you of?)

To determine the a_n, remember

$$\int_0^L \cos\left(\frac{n\pi x}{L}\right)\cos\left(\frac{m\pi x}{L}\right)dx = \begin{cases} 0 & \text{if } n \neq m \\ L/2 & \text{if } n = m \end{cases}$$

$$\int_0^L dx\, P(x,0)\cos\left(\frac{n\pi x}{L}\right) = c\int_0^{L/4} dx \cos\frac{n\pi x}{L} + c\int_{3L/4}^{L} dx \cos\frac{n\pi x}{L}$$

$$= \frac{cL}{n\pi}\left(\sin\frac{n\pi}{4} - \sin\frac{3n\pi}{4}\right) = a_n\frac{L}{2}$$

$$\Rightarrow a_n = \frac{2c}{n\pi}\left(\sin\frac{n\pi}{4} - \sin\frac{3n\pi}{4}\right)$$

$a_0 = \frac{c}{2}$

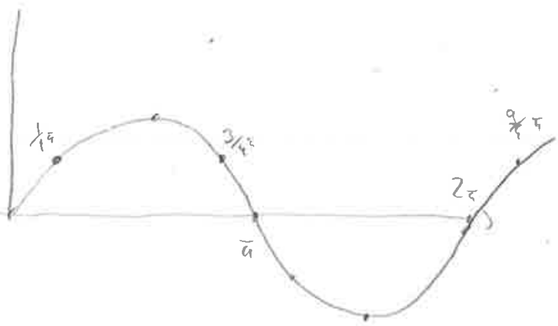
$a_1 = 0$

$a_2 = \frac{2c}{\pi}$

$a_3 = 0$

$a_4 = 0$

$a_5 = 0$



how many modes do we need?

- high modes decay fast

  $\Rightarrow$ if interested in later times, $n = 0, 2, 6$ might be enough

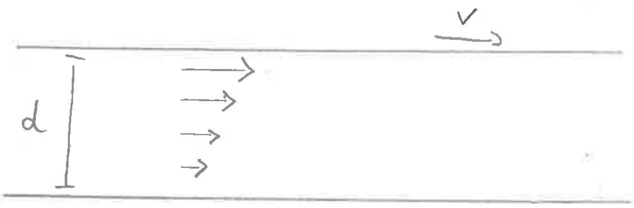
- FRAP experiment

$$P\left(\tfrac{L}{2}, t\right) \approx c\left[\frac{1}{2} - \frac{2}{\pi} e^{-\frac{4D\pi^2}{L^2}t} + \cdots\right]$$

What determines diffusion coefficients

- the bigger, the slower $\longrightarrow$ r [length]
- diffusion is thermal motion $\longrightarrow$ kT [energy]
- viscosity $\longrightarrow$ $\eta \left[\frac{\text{force} \cdot \text{time}}{\text{length}^2}\right]$

Excurs: what is viscosity?



consider two plates that move relative to each other with velocity v

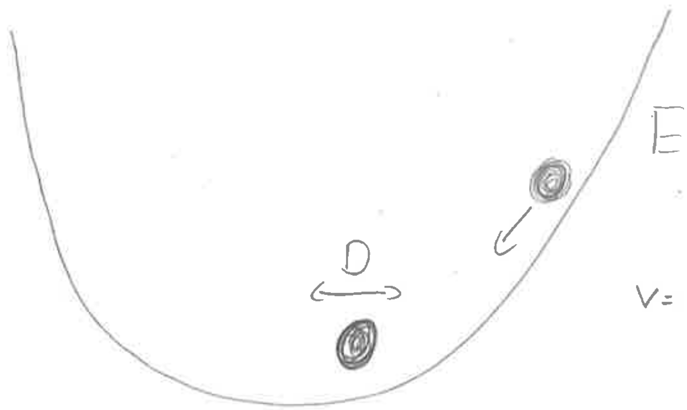
$$F = \underset{\text{viscosity}}{\eta} \; \underset{\text{area}}{A} \; \underset{\text{velocity gradient}}{\frac{v}{d}} \quad \Rightarrow \quad [\eta] = \left[\frac{\text{Force} \cdot \text{time}}{\text{length}^2}\right]$$

- how do you combine r, kT & η to yield units of a diffusion constant?

$$\left[\frac{kT}{\eta}\right] = \frac{\text{Force} \cdot \text{length} \cdot \text{length}^2}{\text{Force} \cdot \text{time}} = \frac{\text{length}^3}{\text{time}}$$

$$\Rightarrow \left[\frac{kT}{r\eta}\right] = \frac{\text{length}^2}{\text{time}} \Rightarrow D \sim \frac{kT}{r\eta}$$

- how do we make this hand-waving argument more precise?



$$E = \frac{a x^2}{2}$$

$$v = -\mu \frac{\partial E}{\partial x} \qquad \mu = \text{mobility}$$

$$\Rightarrow \dot{P}(x,t) = D \frac{\partial^2 P}{\partial x^2} - v \frac{\partial P}{\partial x}$$

$$\Rightarrow \text{at steady state:} \quad D \frac{\partial P}{\partial x} = -\mu \frac{\partial E}{\partial x} P$$

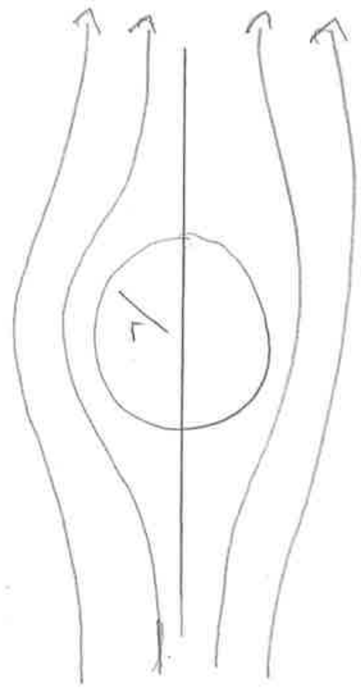
$$\Rightarrow P \approx e^{-\frac{\mu E}{D}} \sim e^{-E/kT}$$

$$\Rightarrow D = \mu kT$$

Einstein relation

- μ is calculated via the Stokes-formula

$$\mu = \frac{1}{6\pi\eta r}$$



$$\boxed{\Rightarrow D = \frac{kT}{6\pi\eta r}}$$

Stokes-Einstein relation

- viscosity of water $\eta_0 = 10^{-3}\,\frac{Ns}{m^2} = 10^{-15}\,\frac{Ns}{\mu m^2} = \frac{10^{-3}\,pNs}{\mu m^2}$
- cytosol: $\eta = 3\eta_0$

$$D = \frac{kT}{6\pi\eta r} \approx \frac{4\,pNnm}{20\cdot 3\cdot 10^{-3}\,\frac{pNs}{\mu m^2}}\,\frac{1}{r} = \frac{\mu m^3}{15\,s\,r}$$

- a 2nm protein $\Rightarrow$ $D = \frac{\mu m^2}{15s\;0.002} \approx \frac{30\,\mu m^2}{s}$