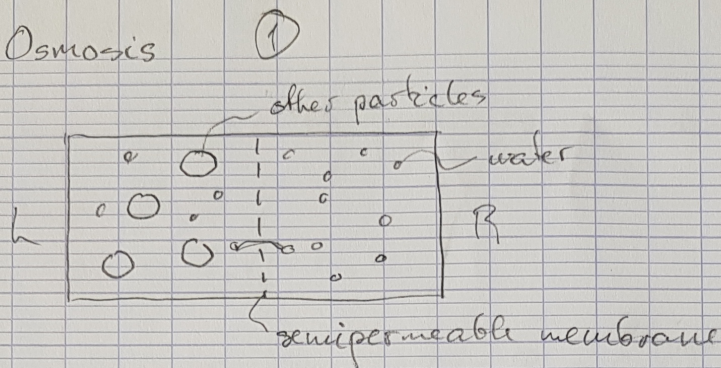


Osmosis



What will happen?

?

How can we model this?

?

$$\begin{aligned}
 N_{w,L} &= N_{w,R} \\
 N_{p,L} &> N_{p,R} \\
 V_L &= V_R = \frac{V}{2} \\
 P_L &= P_R
 \end{aligned}$$

Initially equal

* Only water molecules are free to move. How do they distribute? $S_{L,R}$?

From intuition & ideal gas:
Largest S when equal distribution
in the volume

* \Rightarrow Equilibrium of water on right & left side
 $P_{w,L} = P_{w,R}$

* Particles not in equilibrium on L & R

What is the effect?

* Dilute solution \Rightarrow non interacting particles

Osmosis (2)

* Non-interacting particles \approx Ideal gas model

Left side:

$$\Rightarrow P_L V_L = N_P kT$$

$$P_L - P_R = \Delta P = P_P = C_P kT, \quad C_P = \frac{N_P}{V_L}$$

Can this shockingly simple argument be true?

Van't Hoff equation

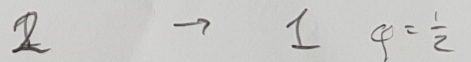
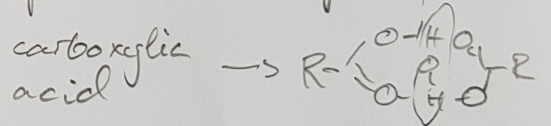
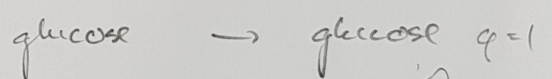
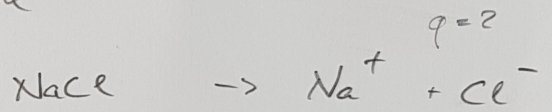
$$\Delta P = \phi_i C_i kT$$

C_i = solute concentration

ϕ_i = dimensionless number

ϕ_i = how many particles in solution from one solute particle

$$C_P = \phi_i C_i$$



It is actually the number of "ideal gas" particles that account

Numbers: Physiological saline solution: Eyes, blood, ...

$$C = \frac{9 \text{ g NaCl}}{1 \text{ l H}_2\text{O}}$$

How do I calculate C_P ?

Periodic table: Na: 23
Cl: 35

What units?

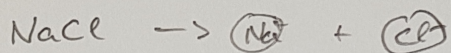
$$\left[\frac{\text{g}}{\text{mol}} \right]$$

$$P = \frac{nRT}{V}$$

$$R = 8.3 \text{ J/Kmol}$$

Osmosis (3)

$$C = \frac{9 \text{ g}}{(23+35) \text{ g/mol} \cdot \text{l}} = 15,5 \frac{\text{mol}}{\text{l}}$$



$$C_p = 2C = 0,31 \frac{\text{mol}}{\text{l}}$$

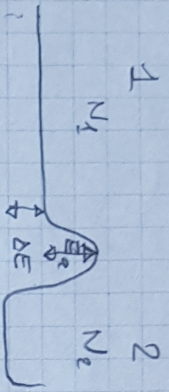
$$P = CRT = 0,31 \cdot 8,3 \cdot 300 \frac{\frac{\text{mol} \cdot \text{J}}{\text{l} \cdot \text{Kmol}}}{10^{-3} \text{ m}^3}$$

$$\approx 9 \cdot 8 \cdot 10^{-1+2+3} \text{ Pa}$$

$$\approx 7,2 \cdot 10^5 \text{ Pa} = 7,2 \text{ bar}$$

more than in tyres of a racing bike!

Reaction rates (1)



Boltzmann factors

$$\frac{P_1}{P_2} = \frac{e^{-E_1/kT}}{e^{-E_2/kT}} = e^{-\Delta E/kT} = \frac{N_{1,eq}}{N_{2,eq}}$$

Rate

$$\Gamma_{1 \rightarrow 2} = A N_1 e^{-E_1/kT}$$

$$\Gamma_{2 \rightarrow 1} = B N_2 e^{-(E_1 + \Delta E)/kT}$$

\propto how many can jump over the E_a

$$\Gamma_{1 \rightarrow 2} = \Gamma_{2 \rightarrow 1}$$

$$\frac{A N_1}{B N_2} = \frac{e^{-(E_1 + \Delta E)/kT}}{e^{-E_1/kT}} = e^{-\Delta E/kT}$$

$\Rightarrow A = B$

$$N_1^0 = N_1 \Gamma_{12} - N_2 \Gamma_{21}$$

$$N_2^0 = -N_1 \Gamma_{12} + N_2 \Gamma_{21}$$

Fixed N_{tot}

$$N_1^0 = N_1 \Gamma_{12} - (N_{tot} - N_1) \Gamma_{21} = 0$$

eq

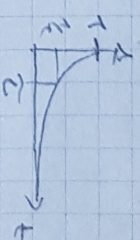
$$N_1 = 0 \Rightarrow N_{tot} (\Gamma_{12} + \Gamma_{21}) - N_{tot} \Gamma_{21} = 0$$

$$N_1 (\Gamma_{12} + \Gamma_{21}) - N_{tot} \Gamma_{21} = 0$$

$$(N_1 - N_{tot}) (\Gamma_{12} + \Gamma_{21}) = \frac{dN_1}{dt} = \frac{d(N_1 - N_{tot})}{dt}$$

(2)

$$\Rightarrow \frac{N_1(t) - N_{1,eq}}{N_1(0) - N_{1,eq}} = e^{-(\Gamma_{12} + \Gamma_{21})t}$$



NVT: natural free energy

NVE $dE = T dS = p dV + \mu dN$ TDI

for NVT $dX = (\) dT + (\) dV + (\) dU$

$$d(TS) = T dS + S dT$$

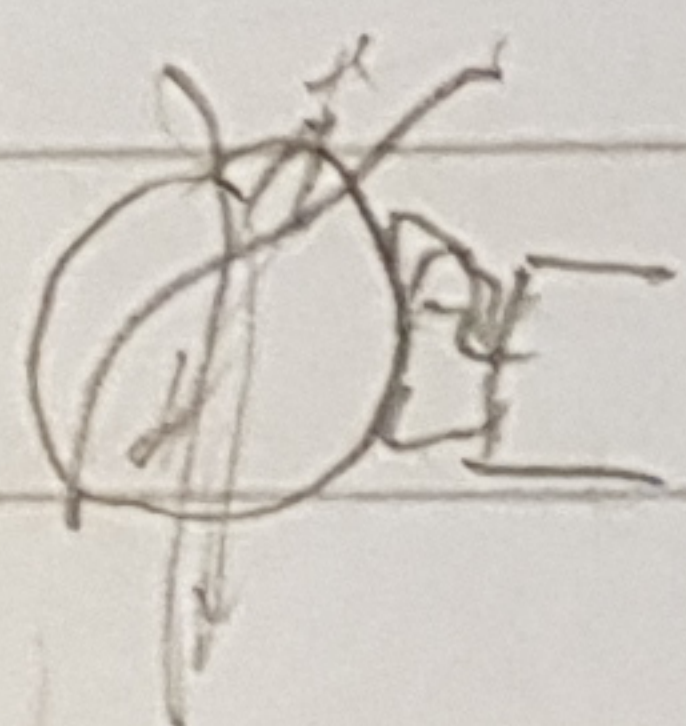
$$\Rightarrow dE - d(TS) = S dT - p dV + \mu dN$$

Helmholtz $\Rightarrow dF, F = E - TS$

17.09.2019

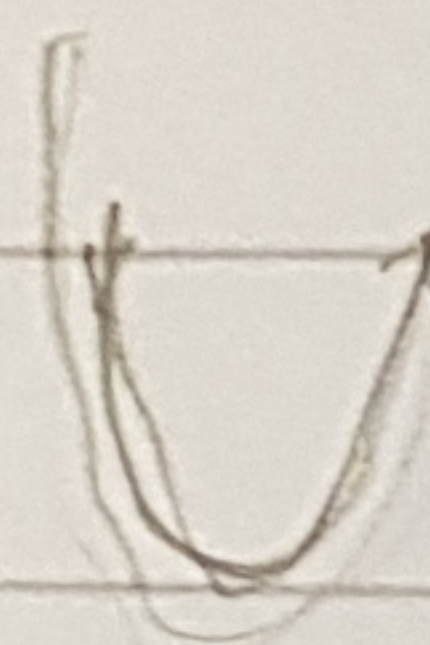
Problem 6.6

Red blood cell cytoskeleton



harmonic oscillator:

$$E = \frac{1}{2} m v^2 + \frac{1}{2} k x^2$$



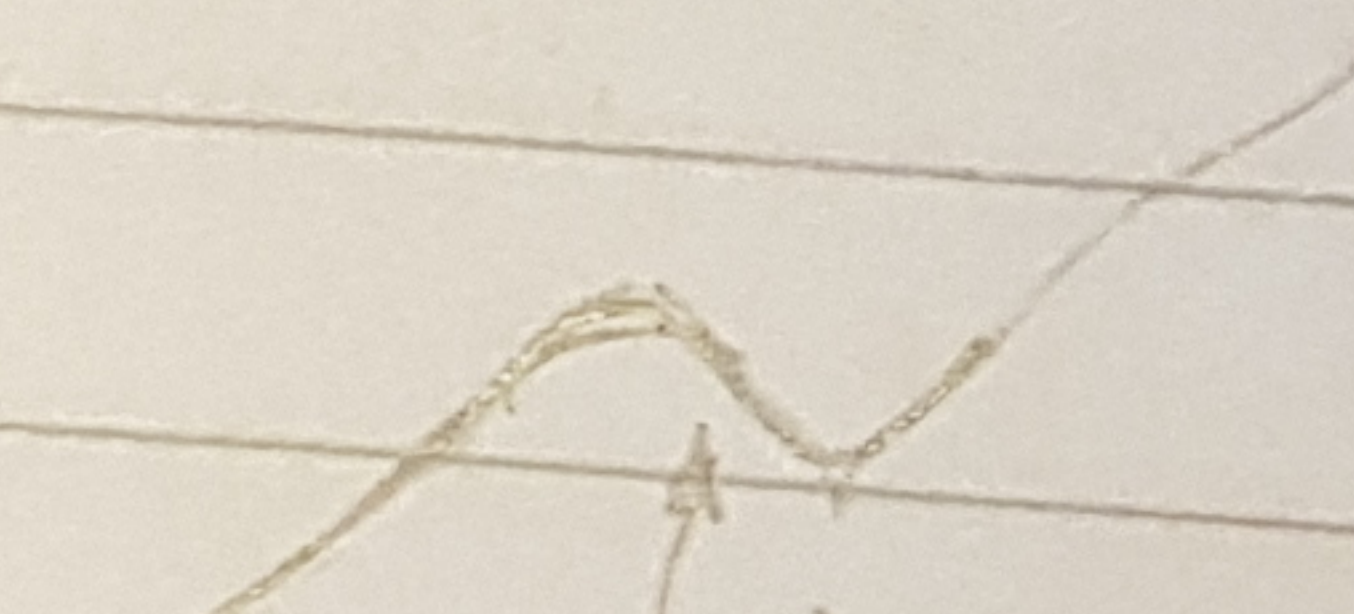
Equipartition principle $\frac{1}{2} k x^2 = \frac{1}{2} k T$

$$\Rightarrow k = \frac{k_B T}{\langle x^2 \rangle} = \frac{1.38 \cdot 10^{-23} \text{ m}^2 \text{ kg}^{-1} \text{ s}^{-2} \cdot 300 \text{ K}}{(3.5 \cdot 10^{-8} \text{ m})^2}$$

- micro -6
- nano -9
- pico -12
- femto -15

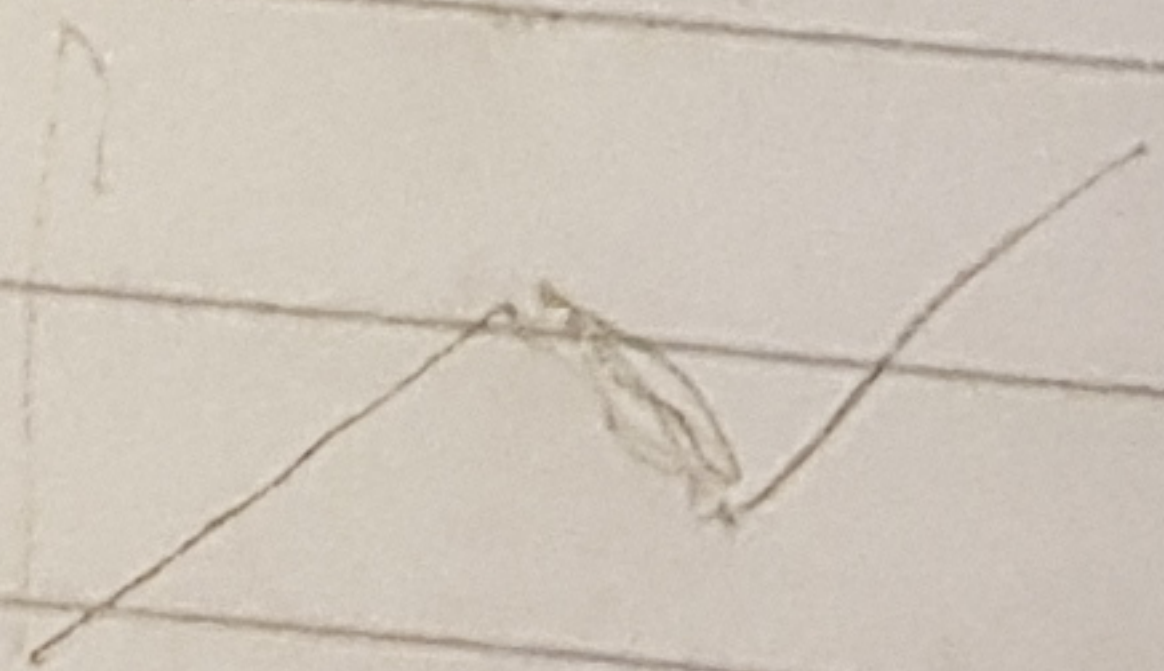
$$3.4 \cdot 10^{-21+15} \frac{\text{N}}{\text{m}} = 3.4 \cdot 10^{-6} \frac{\text{N}}{\text{m}} = 3.4 \text{ fN} = 0.0034 \text{ nN}$$

Problem 6.7



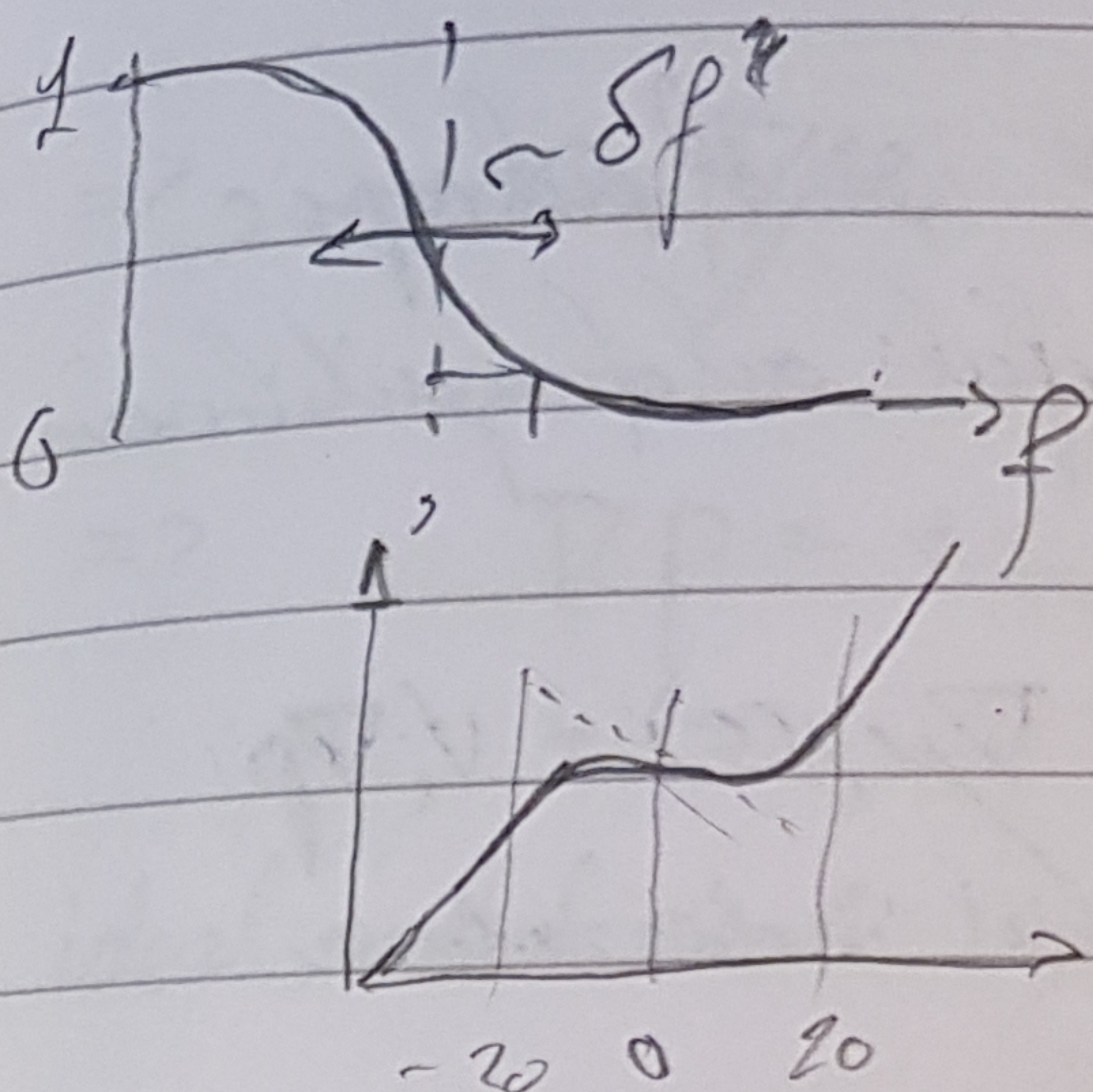
trapdoor like unfolding protein of E. coli

1 single pit of hemocytia



$$P(\varphi) = \frac{1}{1 + e^{-(\Delta F - p \Delta V) / k_B T}}$$

From time averaging



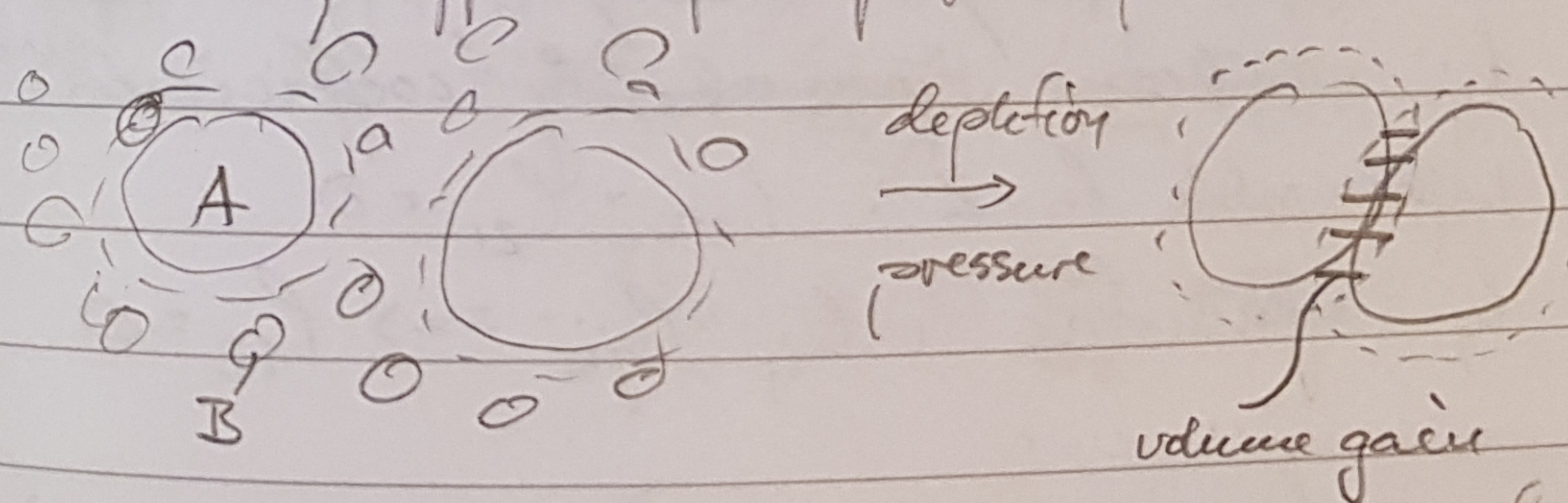
Ergodic hypothesis

$$\langle x \rangle_{\text{time}} = \langle x \rangle_{\text{ensemble}}$$

Only -20 & 20

Try later 6.8, 6.9, 6.10 7.5

Assembling effect of depletion pressure



Ordering: making pairs = reducing number of particles \cdot S reduced!
 More particles = more disorder $\frac{\partial S}{\partial N_A} > 0$

Volume gain: $P = T \left(\frac{\partial S}{\partial V} \right)_{N, E} > 0$
 $\frac{\partial S}{\partial V} > 0$ more volume = more disorder
S increased!

Increased reaction rate when molecules brought together
 but action??

17.07.2012

We now know that Δp is of entropic origin. But to get a useful out of equilibrium description

isothermal system $\nabla \mu_i = \nabla \mu_i(c) + v_i \nabla p$
 $v_i = \left(\frac{\partial V}{\partial n_i} \right)_{p, T, n_{j \neq i}}$ - partial molar volume

2-comp. system 1 = water 2 = solute

$J_1 = -l_{11} \nabla \mu_1 = -l_{12} \nabla \mu_2$ Onsager

$J_2 = -l_{21} \nabla \mu_1 - l_{22} \nabla \mu_2$

l_{ij} - membrane "permeability" coefficients

impermeable to 2: $l_{22} = l_{21} = 0$

l_{ij} - symmetric: $l_{ij} = l_{ji} \Rightarrow l_{12} = 0$

$\Rightarrow J_1 = -l_{11} \nabla \mu_1 = -l_{11} (\nabla \mu_1(c) + v_1 \nabla p)$

Osmotic pressure: max at $J_1 = 0 \Rightarrow \nabla p = - \frac{\nabla \mu_1(c)}{v_1}$

Ideal solution: $c_1 v_1 \approx 1 \Rightarrow \nabla p = -c_1 \nabla \mu(c)$

Gibbs-Duhem $SdT - Vdp + \sum_i n_i d\mu_i = 0$

$\Rightarrow c_1 \nabla \mu_1 = -c_2 \nabla \mu_2$

$\Rightarrow \nabla p = +c_2 \nabla \mu_2$

ideal solution: $\mu_i = \mu_{oi} + RT \ln c_i$
 $\nabla \mu_2 = RT \nabla \ln c_2 = RT \frac{\nabla c_2}{c_2}$

Equil. $\Delta p = RT \Delta c_2$

Non-equil flux $J_1 = -l_{11} (-\nabla \mu_1 + v_1 \nabla p)$
 $= -l_{11} \left(-\frac{c_2}{c_1} \nabla \mu_2 + \frac{1}{c_1} \nabla p \right)$

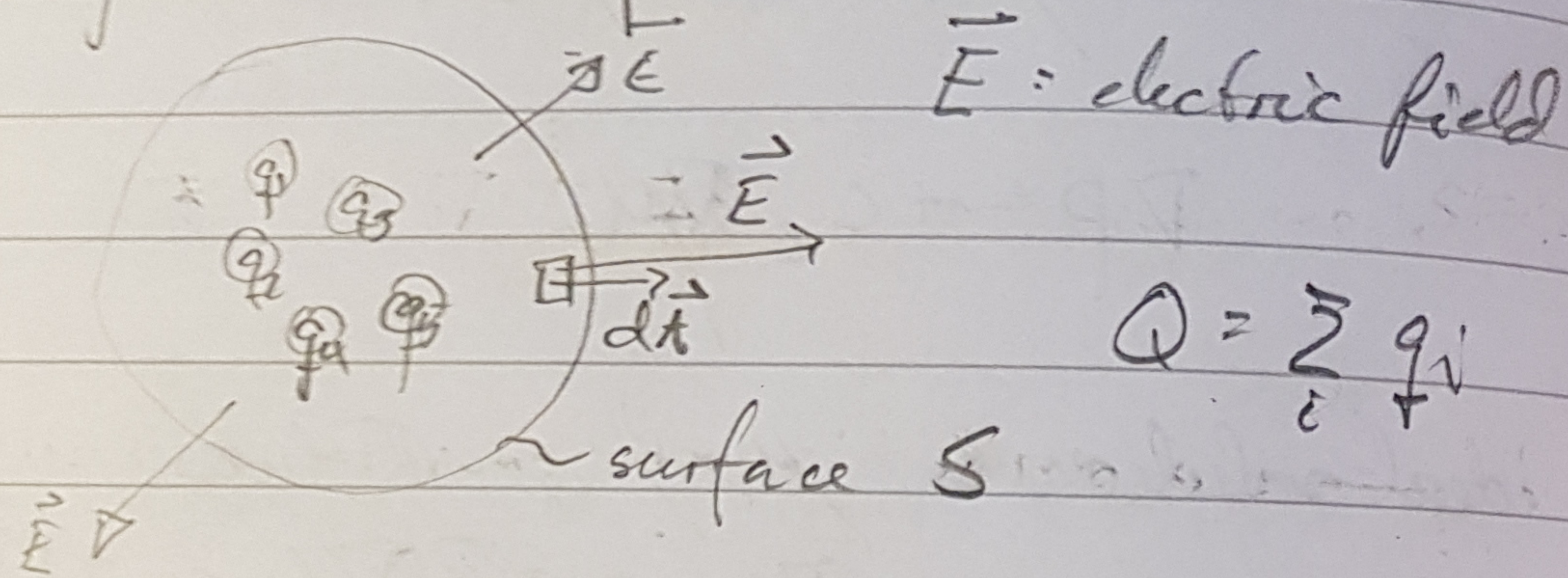
$= -\frac{l_{11}}{c_1} \left(-c_2 RT \frac{\nabla c_2}{c_2} + \nabla p \right)$

$= -\frac{l_{11}}{c_1} (\Delta p - RT \Delta c_2)$

Nelson: $l_{11} = \text{filtration coefficient}$

17.09.2019

Charges & electric fields



Electric flux out of surface equals charge inside

$$\Phi_E = \iint_S \vec{E} \cdot d\vec{A} = \frac{Q}{\epsilon} \quad \epsilon - \text{permittivity}$$

$$\epsilon_w = 80 \cdot \epsilon_0, \quad \epsilon_0 = \text{vacuum / air}$$

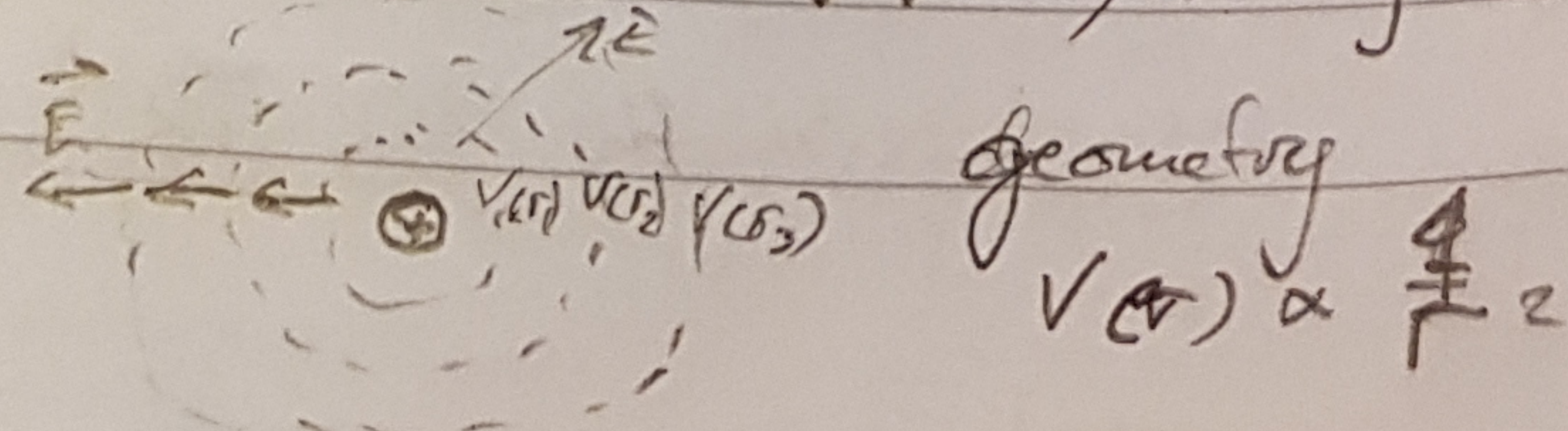
(Due to polarizability of water)

Divergence theorem
vector calculus

$$\iint_S \vec{F} \cdot d\vec{A} = \iiint_V \nabla \cdot \vec{F} dV$$

$$\Rightarrow \nabla \cdot \vec{E} = \frac{\rho}{\epsilon}, \quad \rho = \frac{q}{V} \quad \boxed{\text{Gauss law}}$$

Electrical potential V: $\vec{E} = -\nabla V, \quad V = -\int$



Coulombs law $V = \frac{1}{4\pi\epsilon} \frac{q}{r^2}$

\Rightarrow Poisson equation $\nabla \cdot \vec{E} = -\nabla^2 V = \frac{\rho}{\epsilon}$

Boltzmann distribution of ions in an external potential $V(\vec{r})$

$$E_i = z_i e V(\vec{r})$$

$$n_i(\vec{r}) = n_i^\infty e^{-\frac{z_i e V(\vec{r})}{kT}}$$

$n_i(\vec{r})$ - concentration at \vec{r} of ions of species i

$n_i^\infty = n_i(r \rightarrow \infty)$ where $V=0$

$$\rho(\vec{r}) = \sum_i n_i(\vec{r}) z_i e$$

$$\nabla^2 V = -\frac{\rho}{\epsilon} = -\frac{1}{\epsilon} \sum_i n_i^\infty z_i e e^{-\frac{z_i e V(\vec{r})}{kT}}$$

$$e^{-x} \approx 1 - x, \quad x \ll 1$$

$$\Rightarrow \nabla^2 V = -\frac{1}{\epsilon} \sum_i n_i^\infty z_i e + \frac{1}{\epsilon} \sum_i n_i^\infty z_i^2 e^2 \frac{V}{kT}$$

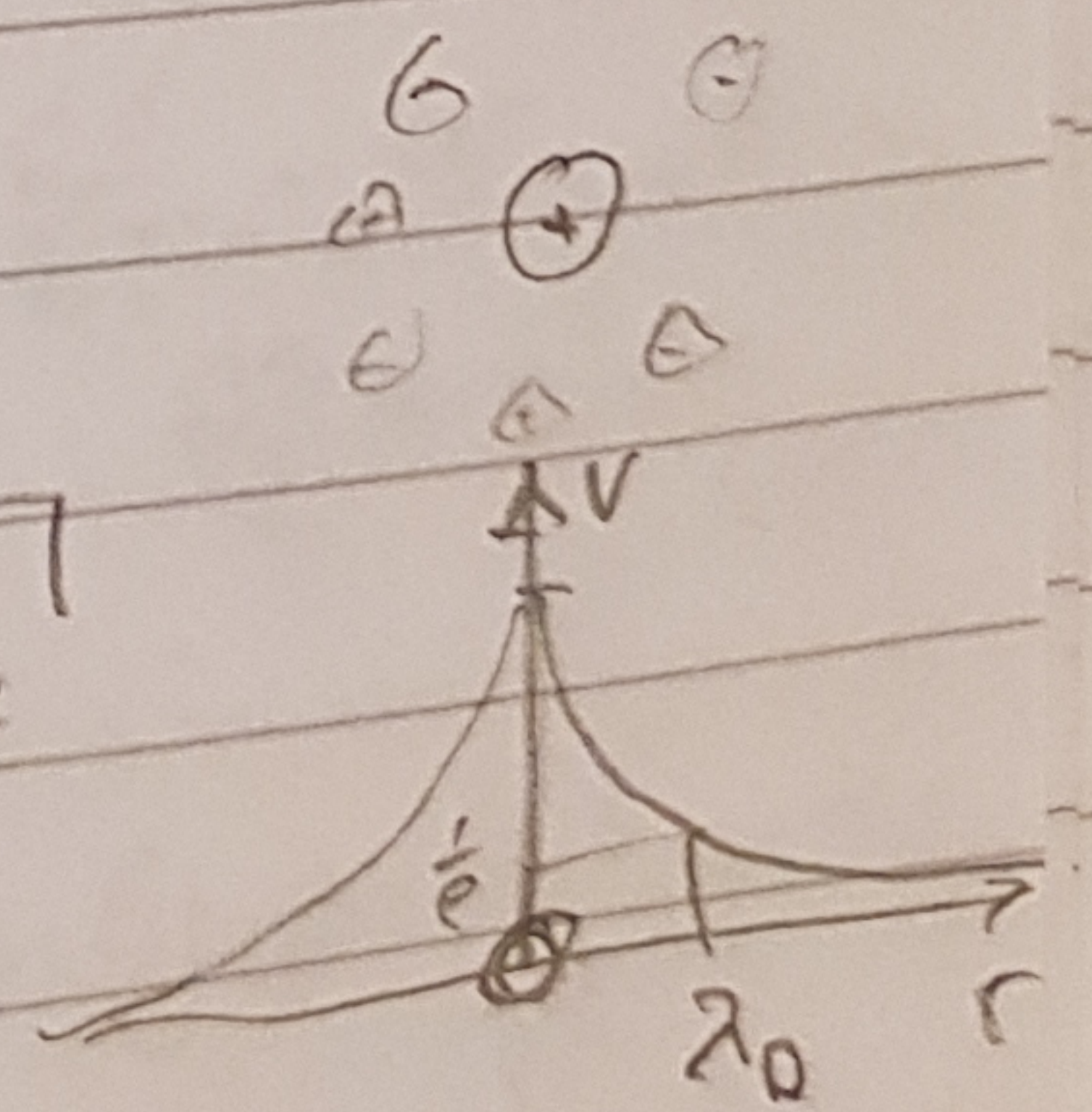
$$\nabla^2 V = -\frac{V}{\lambda_D^2}$$

Debye length

$$\lambda_D = \sqrt{\frac{\epsilon kT}{\sum_i n_i^\infty z_i^2 e^2}}$$

screening length

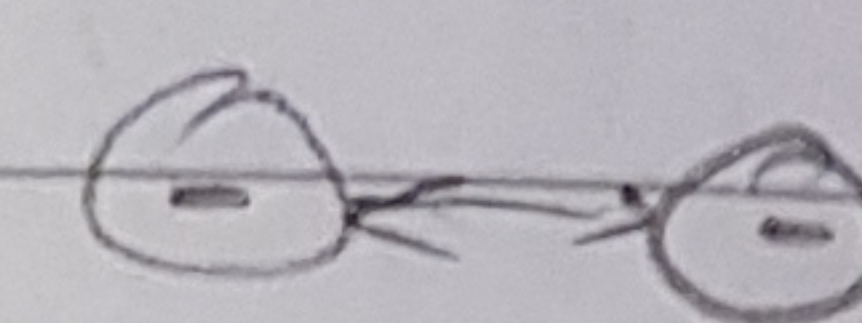
low conc. n_i^∞ λ_D large
 high - n_i^∞ λ_D small



$$\lambda_D = \sqrt{\frac{\epsilon_0 \epsilon_r kT}{4\pi \sum_i n_i z_i^2 e^2}}$$

Bjerrum $\lambda_B = \frac{e^2}{4\pi \epsilon kT}$ $kT = \frac{e^2}{4\pi \epsilon \lambda_B}$

λ_B how close ions get at kT . $\epsilon_0 \epsilon_r \frac{e^2}{4\pi \epsilon r} = e \cdot V =$ energy



Debye-Hückel equation: Flat surface, $\frac{V}{kT} \ll 1$

$$\Psi(x) \approx \Psi_0 e^{-x/\lambda_D}$$

Important for transport, forces, el. signals
el. response of cells...

22.09.2019

A bilayer membrane can have 1 charge (e) per head group $\frac{\sigma_q}{e} = 0.7 \text{ nm}^{-2}$
10 μm spherical cell $\approx 10^9$ charges

But does this not push the headgroups away from each other?

Hydrogen bonds

ΔU	$\text{H}_2\text{O}-\text{H}_2\text{O}$ in vapour	$10 \sim 9kT$
\oplus	covalent	$\Delta U \sim 90-350kT$
$\downarrow \epsilon$	vdW attraction	$\Delta U \sim 0.6-1.6kT$
	net energy cost: breaking H-bond + reforming new	$\Delta U \sim 1-2kT$

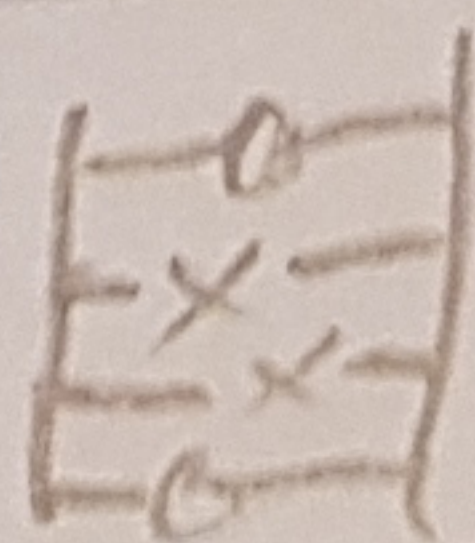
Ice: global order \rightarrow water local order

Cohesive forces larger: Too slow to melt
 $\frac{\Delta H}{RT} \sim 15$ not 10

Order is enhanced locally $\therefore \frac{15}{2} \approx \frac{\Delta H}{RT}$

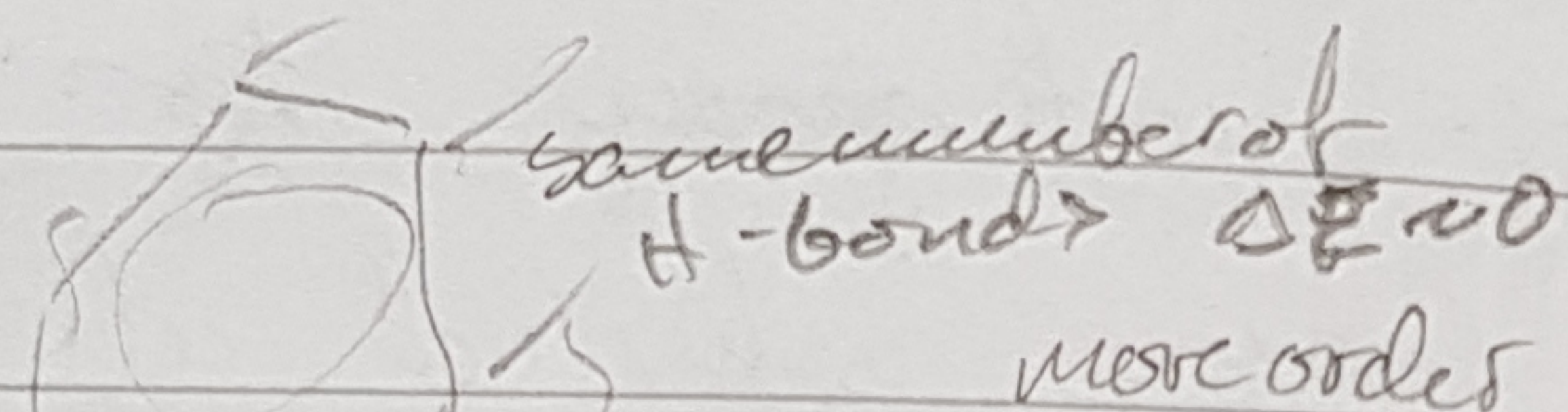
Short range of H-bond: Only perfect matching

zips DNA



solubility in H_2O \propto - free energy cost of molecule in H_2O

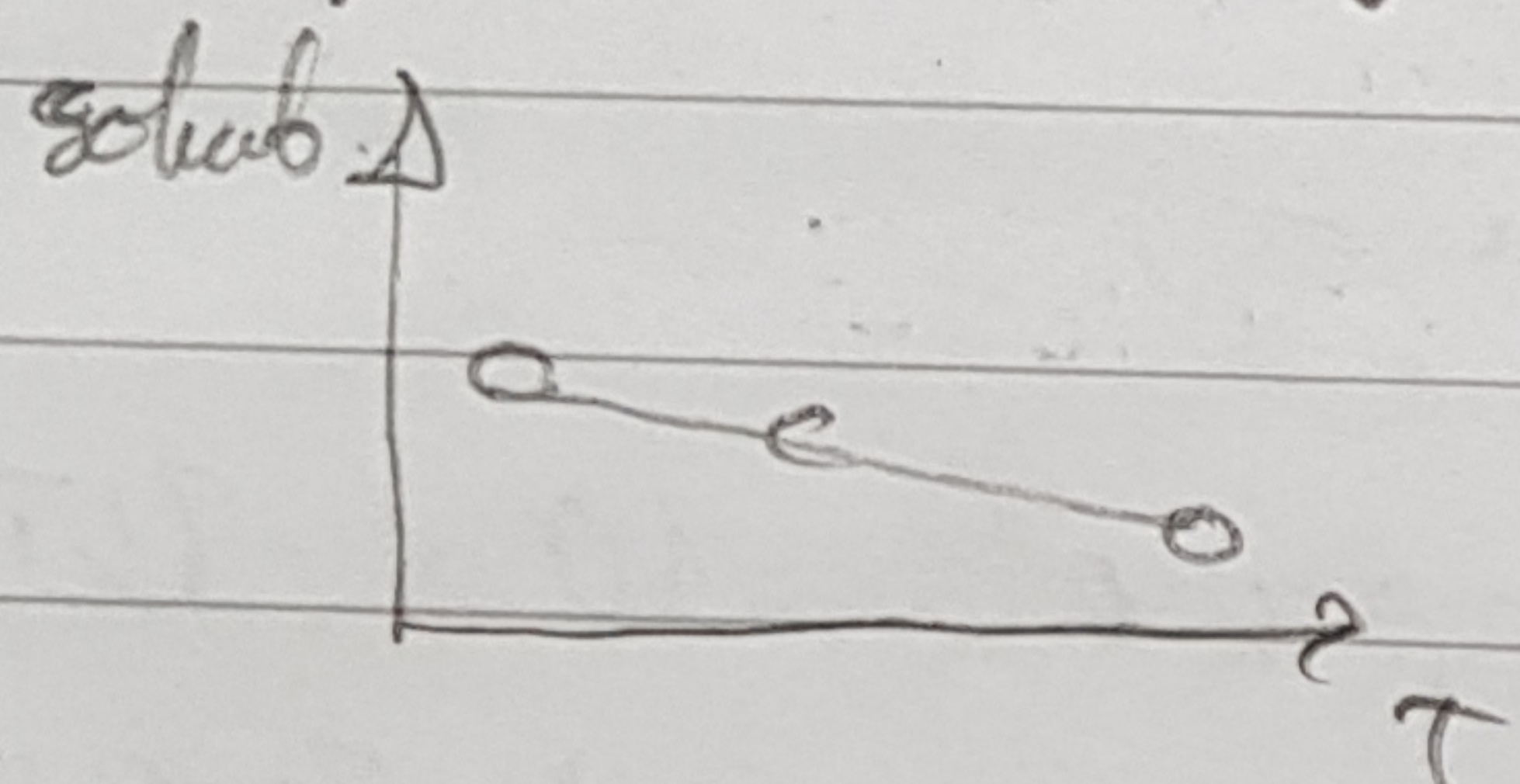
Clathrate cage



\Rightarrow less orientation \leftarrow freedom $\rightarrow \Delta S$

$\Rightarrow F = E - TS$

\Rightarrow Hydrophobicity.



$\Delta S < 0, TA \Rightarrow (-T\Delta S) \uparrow$

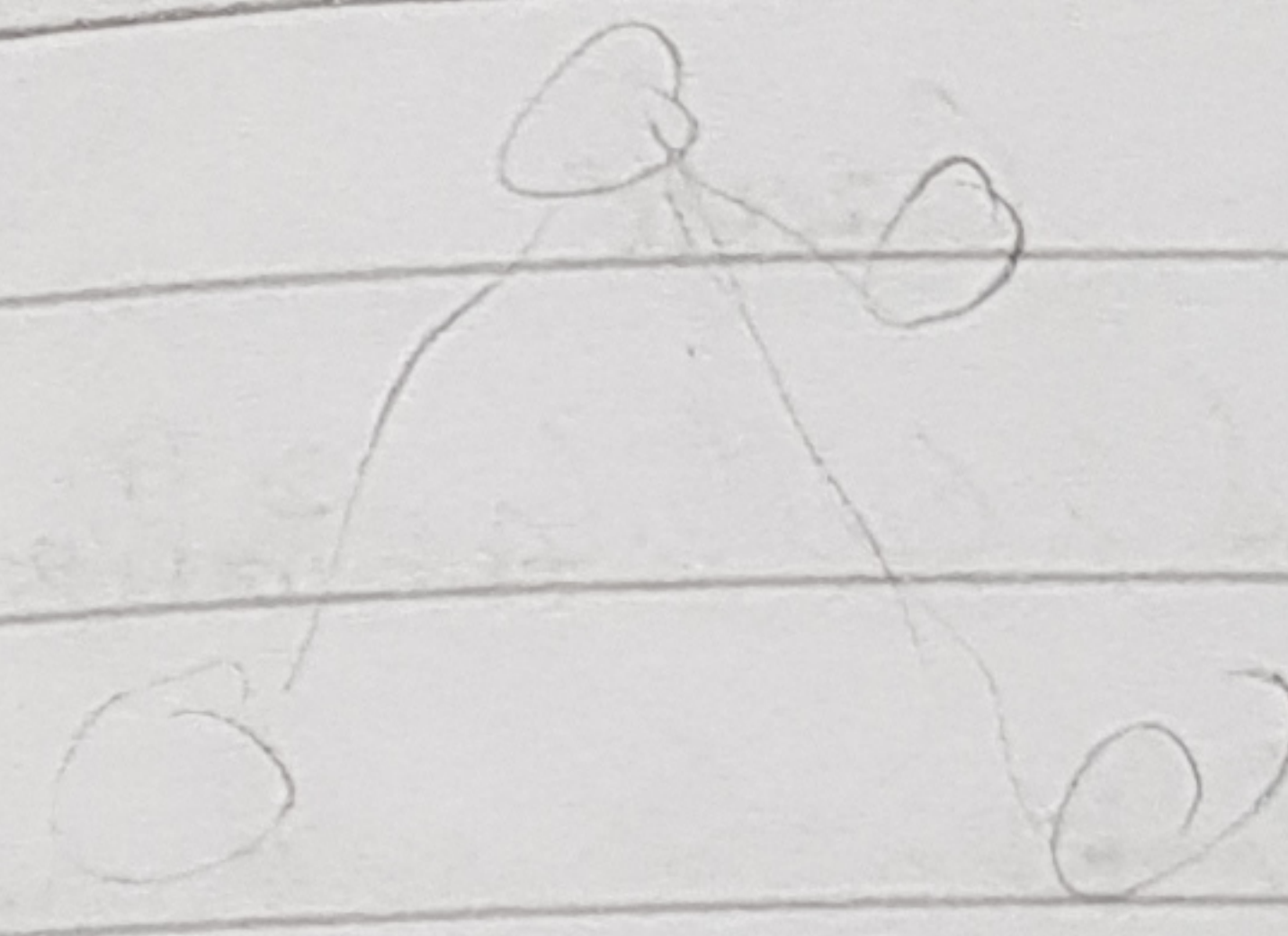
\Rightarrow larger energy cost of solution at higher energy

$\Rightarrow \frac{\partial C_{sol}}{\partial T} < 0 \Rightarrow$ Entropic contrib. outweighs ΔE

Entropic free energy cost of dissolving non-polar molecules \propto area of molecule

* Large objects (surfaces) \therefore number of H-bonds less $\Rightarrow \Delta E > 0$

Your lesson 7H



cut by flat surface.

$\Rightarrow \approx 1$ H-bond per molecule

$1 kT$ per molecule

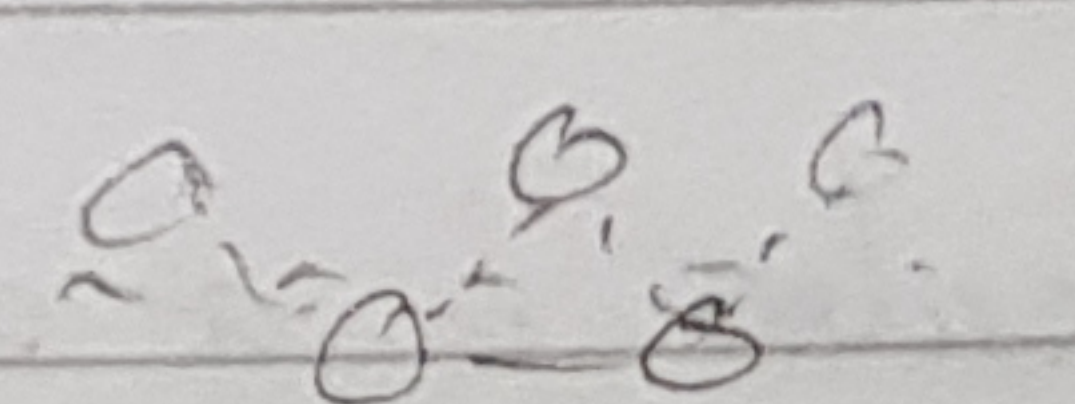
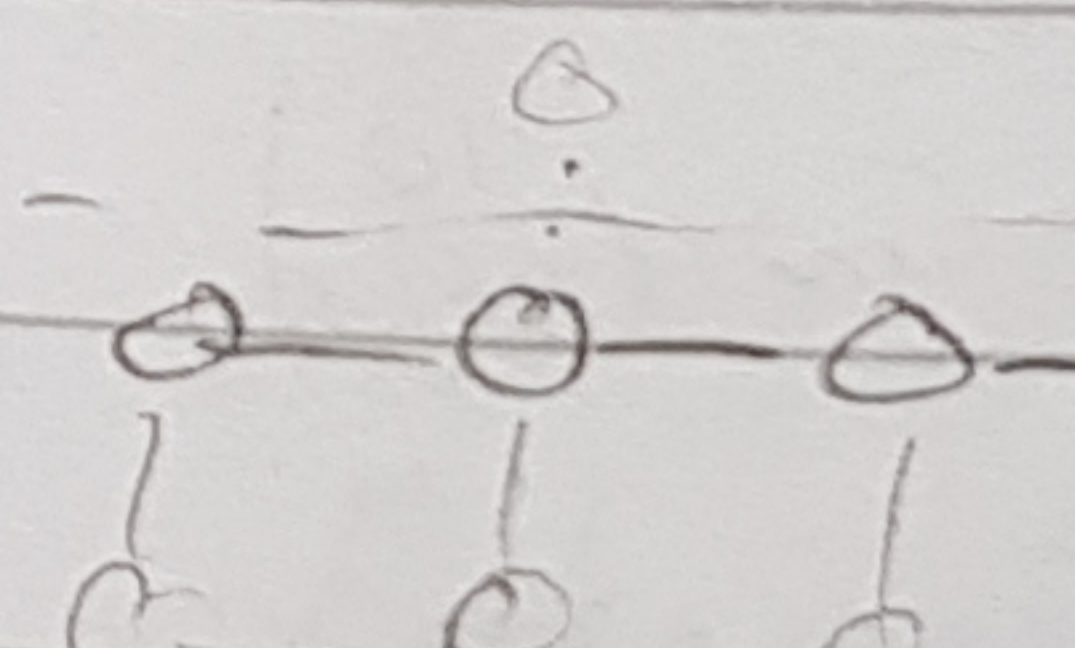
How many molecules per surface area?

$M_n = 18 \frac{g}{mol}, V = 10^{-6} \frac{m^3}{m^3}$

$\rho_m = \frac{10^6 \frac{mol}{m^3}}{18 \frac{m^3}{mol}} = \frac{10^6 \cdot 6 \cdot 10^{23}}{18 \frac{m^3}{mol}} = \frac{1}{3} \cdot 10^{29} \frac{mol}{m^3} = 33 \text{ nm}^{-3}$

\Rightarrow Area per molecule $A_m = (33 \text{ nm}^{-3})^{-\frac{2}{3}} = 0,1 \text{ nm}^{-2}$

$\frac{kT}{A_m} = \frac{4,1 \text{ pN nm}}{0,1 \text{ nm}^{-2}} = 41 \frac{pN}{nm} = 41 \cdot 10^{-3} \frac{N}{m} = 0,04 \frac{J}{m^2}$



Mean: 1 bond per molecule

$\sigma dW \approx 0 \approx 1 k_B T \Rightarrow \sigma \approx \frac{1 kT}{A_m} \approx 0,04 \frac{J}{m^2}$

Not affected by H-bonds?

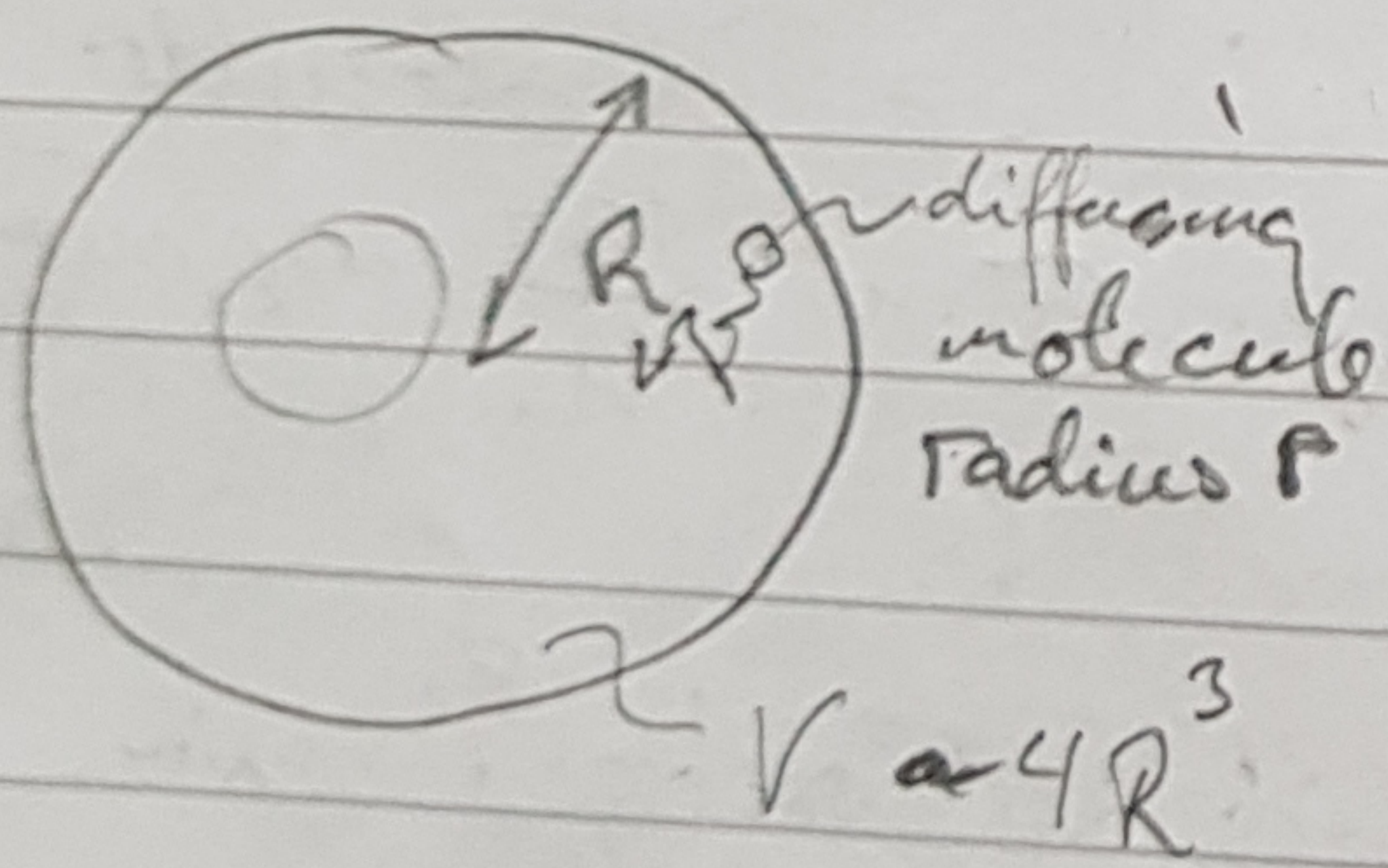
Or balance energy and ordering?

Plan → onsdag Ex 10 Gauke
 Hoffmeister ex 9 Gauke
 Uke 40 + 41 forbered Cellular Polts
 Uke 42: Cellular Polts

Why cells are microscopic?

MSD $\langle r^2 \rangle = \langle x^2 + y^2 + z^2 \rangle = 3 \langle x^2 \rangle = 6Dt$
 $\Rightarrow \tau = \frac{L^2}{6D}$

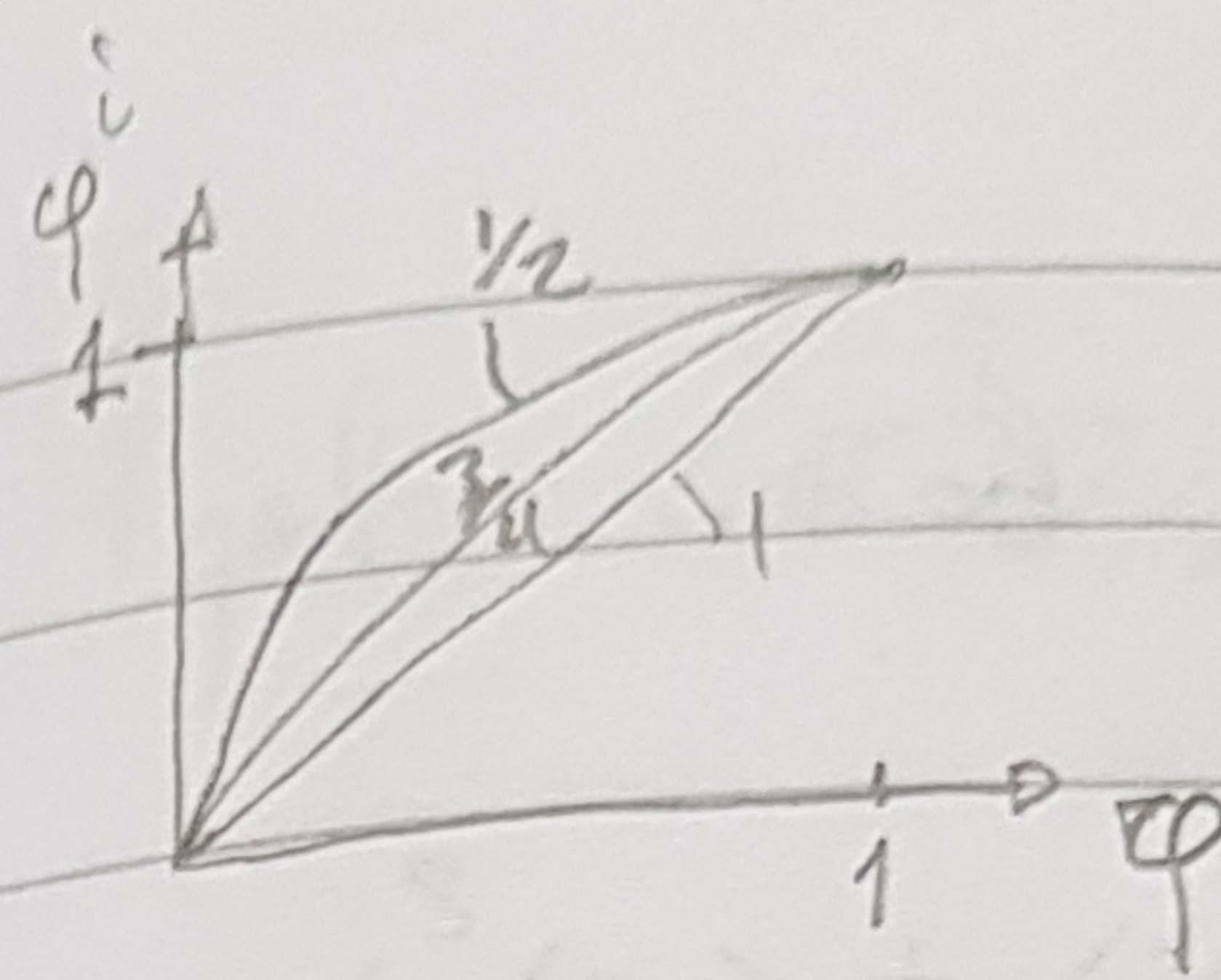
n - # macromolecules in a cell ($n \sim 10^{10}$)



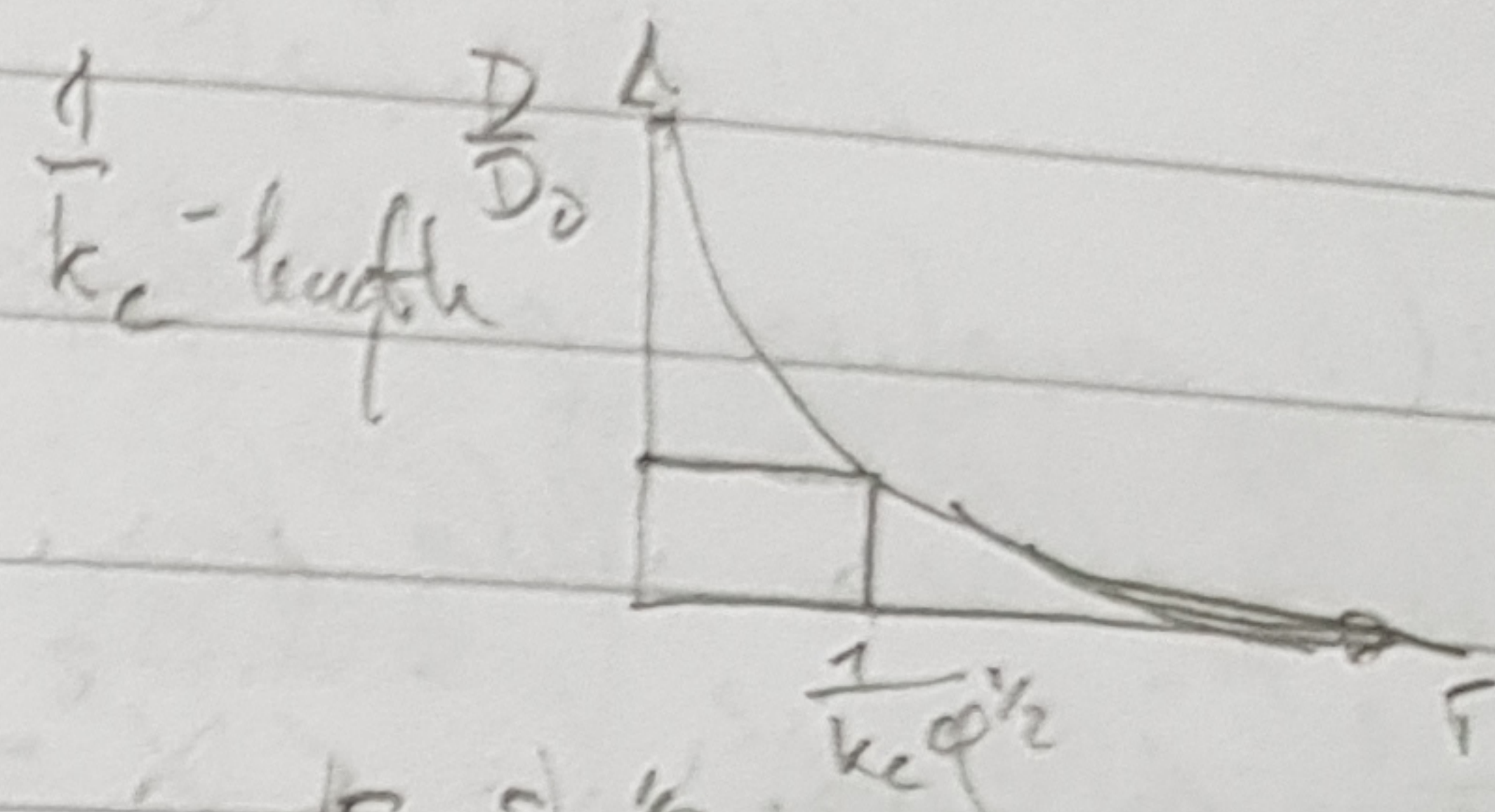
- viscosity
- hydrodyn. interactions
- contact / crowding

Packing fraction $\phi = \frac{nv}{V} = n \left(\frac{r}{R}\right)^3$
 $\phi \ll 1 \quad D_0 \approx \frac{kT}{6\pi\eta r}$

Crowding $D = D_0 e^{-\alpha r}$, $R^2 = k_c \phi^\gamma$, $\gamma = \left\{ \frac{1}{2}, \frac{3}{4}, 1, 2 \right\}$
 in cell $\gamma = \frac{1}{2}$



$\frac{D}{D_0} = e^{-k_c r \phi^{1/2}}$

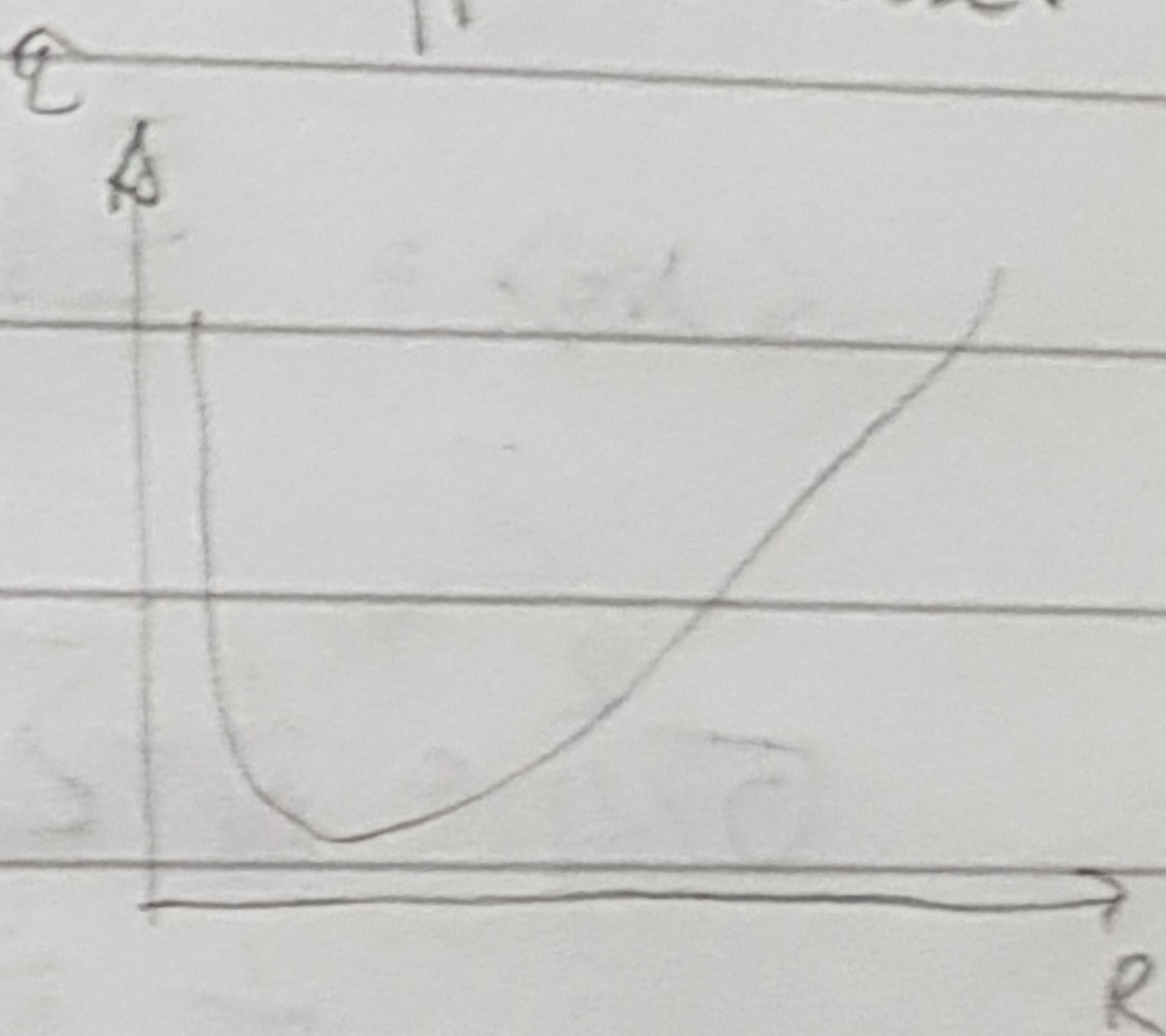


Obstruction theory
 (Experimentalist's theory)
 $\phi^{1/2} = n \left(\frac{r}{R}\right)^{3/2}$

$\frac{D}{D_0} = e^{-\left(\frac{r+r}{r}\right)^{1/2} \phi}$

$\eta \sim 3 \mu\text{Pas}$
 = effective vis.

$\tau(R) = \frac{R^2}{6D_0} e^{-\alpha(r)n \left(\frac{r}{R}\right)^{3/2}}$



minimum: $R_{\min} = \left(\frac{3}{2}\right)^{2/3} n^{1/3} r \Rightarrow \phi_{\min} = 0.4$

Eukaryote: $2R_{\min} = 2 \cdot 6 \cdot 10^{10} \cdot 3 \text{ (nm)}^2 = 15.7 \mu\text{m}$
 $\phi \sim 8 \cdot 10^9 \left(\frac{3 \cdot 2}{15700}\right)^3 \approx 0.45$

Eukaryote theory: $\phi_{\min} \approx 0.25$, $2R_{\min} \approx 20 \mu\text{m}$

Simple idea $nv \sim 10^{10} \cdot 4 \cdot (4 \cdot 10^{-9})^3 = 4^4 \cdot 10^{-17} = 2$

packed radius $\phi = 1$
 $R = n^{1/3} r = 2 \cdot 10^3 \cdot r = 8 \mu\text{m}$

Thus, necessary conclusion.

24.09.2019

Teil: analyse an Brownische Bew.

Drift treibtes ilike fra.

$$\begin{aligned} \sigma^2 &= \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle \\ &= \langle x^2 \rangle - 2\langle x \rangle \langle x \rangle + \langle x \rangle^2 \\ &= \langle x^2 \rangle - \langle x \rangle^2 \end{aligned}$$

$$\langle x(t) \rangle = \frac{\sum_{i=1}^N x_i(t)}{N} \quad \langle x^2(t) \rangle = \frac{\sum_{i=1}^N x_i^2(t)}{N}$$

$$\begin{aligned} \sigma^2(t) &= \frac{1}{N} \sum x_i(t)^2 - \left(\frac{1}{N} \sum x_i(t) \right)^2 \\ &= \frac{1}{N} \sum \left(x_i(t)^2 - \frac{1}{N} \sum x_i(t)^2 \right) \end{aligned}$$

- Cut movie in pieces if too few tracks

- Remove drift !!

- We should have mean of many shorter tracks.

= Small msd => k too small because beads too close to glass wall

(Probably because too thin capillary)
0,2 x 4 mm better!

- Difference in wagn. 40x I got 0,1837

$$- k_B = 1,38 \cdot 10^{-23} \text{ J/K}$$

$$\text{I got } \left. \begin{aligned} \langle \sigma^2 \rangle / dt &= 18,85 \\ &15,45 \\ &20,00 \end{aligned} \right\} = 18,1 \frac{\text{m}^2}{\text{s}} \cdot \frac{\text{m}^2}{\text{s}} = 4 \cdot 10^{-14} \frac{\text{m}^2}{\text{s}}$$

$$D = 10^{-14} \frac{\text{m}^2}{\text{s}}$$

$$k_B = \frac{6\pi\eta R \cdot D}{T}$$

$$= \frac{18 \cdot 10^{-3} \cdot 10^{-14} \cdot R}{T} \cdot 10^{-6}$$

$$= 6 \cdot 10^{-19} \cdot 10^{-6} = 6 \cdot 10^{-25}$$

Exercise 10

$$1 \quad E_s = \frac{q^2}{8\pi\epsilon_r R}$$

$$r = \frac{e^2}{4\pi\epsilon_0} = 2,3 \cdot 10^{-28} \text{ Jm}$$

$$E_s = \frac{k}{2\epsilon_r R}$$

$$\Delta E_s = \frac{2,3 \cdot 10^{-28} \text{ Jm}}{2 \cdot \Delta \epsilon_r \cdot 1,33 \cdot 10^{-10} \text{ m}} = 1,1 \cdot 10^{-20} \text{ J}$$

$$= 11 \text{ pNm} \approx 3 \text{ kT}$$

$$b \quad \frac{c_1}{c_2} = e^{-\Delta E_s / kT} = e^{-3} = 6\%$$

$$2 \quad \partial_x V = -\frac{e c_0}{\epsilon_w} e^{-eV/kT}$$

$$\bar{V} \equiv \frac{eV}{kT} \quad \partial_x \bar{V} \cdot \frac{kT}{e} = \frac{e c_0}{\epsilon_w} e^{-\bar{V}}$$

$$\partial_x \bar{V} = \frac{-e^2 c_0}{kT \epsilon_w} e^{-\bar{V}}$$

$$l_B = \frac{e^2}{4\pi\epsilon_w kT}$$

$$\equiv 4\pi\epsilon_0 l_B e^{-\bar{V}}$$

28.09.2019

$$Q^2 = 1,6 \cdot 10^{-19} \text{ C}$$

$$= 40 \text{ kT}$$

$$\epsilon_0 = 8,9 \cdot 10^{-12} \frac{\text{C}^2}{\text{Nm}^2}$$

$$kT = 4,1 \text{ pNm}$$

$$10^{-12} \cdot 10^9$$

$$b) \quad \bar{V}(x) = B \ln(1 +$$

$$3) \quad 3,5 \text{ bonds} \quad \rightarrow 9 \text{ kT}$$

$$\Rightarrow 3,5 \cdot 9 \text{ kT}$$

molekule

$$\Rightarrow \Delta E = \frac{3,5 \cdot 9 \text{ RT}}{18 \cdot 10^{-3} \text{ kg}} = \frac{3,5 \cdot 9 \cdot 8,3 \cdot 373,1 \text{ J}}{18 \cdot 10^{-3} \text{ kg}}$$

$$18 \text{ g/mol} = 18 \cdot 10^{-3} \text{ kg/mol}$$

$$= 5,4 \cdot 10^6 \text{ J/kg}$$