ETH (1)

Deutsch
Srednicki

$$|\psi(t)\rangle = \sum_n c_n e^{-iE_n t} |E_n\rangle$$

$$\langle \psi(t)|\hat{A}|\psi(t)\rangle = \sum_{n,n'} c_{n'}^* c_n e^{-i(E_n - E_{n'})t} \langle E_{n'}|\hat{A}|E_n\rangle$$

$$= \sum_n |c_n|^2 \langle E_n|\hat{A}|E_n\rangle + \sum_{n\neq n'} c_{n'}^* c_n e^{-i(E_n - E_{n'})t} \langle E_{n'}|\hat{A}|E_n\rangle$$

$\langle E_{n'}|\hat{A}|E_n\rangle$ small $\rightarrow$ fluctuations.

c_n: off-diag. elements add up.

$$\langle \psi(t)|\hat{A}|\psi(t)\rangle\Big|_{t \gg t_{th}} \simeq \sum_n |c_n|^2 \langle E_n|\hat{A}|E_n\rangle$$

$$\langle E_n|\hat{A}|E_n\rangle = A(E_n)$$

$c_n \sim 1/\sqrt{\Omega}$ ← # of states

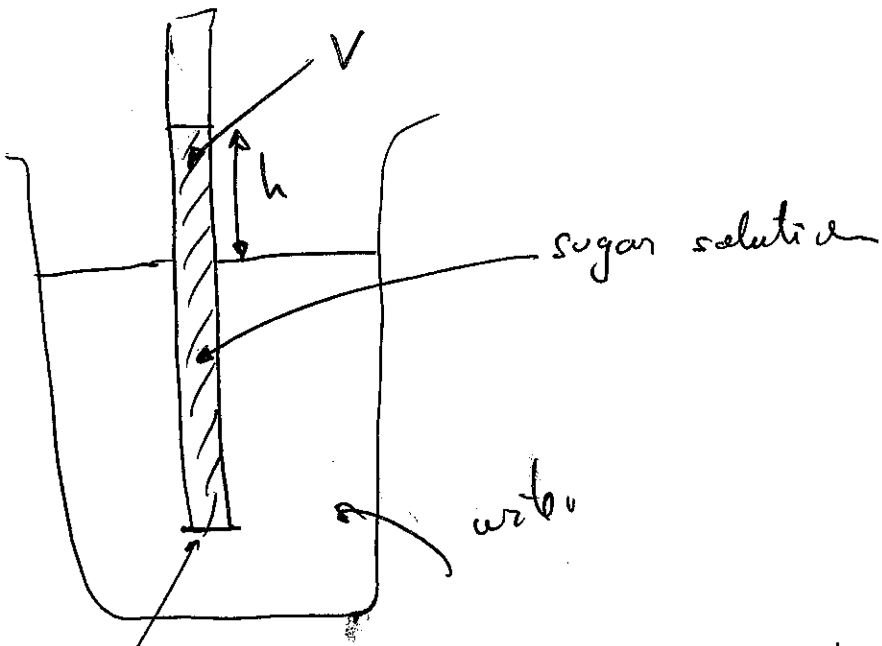
$$\sum_{n,n'} \underbrace{c_{n'}^* c_n}_{1/\Omega} \sim 1$$

$\Omega\ \Omega$ $\rightarrow \Omega$

$\langle E_{n'}|\hat{A}|E_n\rangle \sim 1/\sqrt{\Omega}$ eqs.

random phases ~ random walk $\sqrt{\Omega}$

Osmotic pressure



membrane, lets water go through but not sugar.

$$p = \rho g h = \frac{n_1 R T}{V} = \frac{N_1 k_B T}{V}$$

n_1 : moles of solute

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thermodynamics of weak solutions.

$$c = \frac{n}{N} \quad \begin{matrix} n \leftarrow \text{solute} \\ N \leftarrow \text{solvent} \end{matrix} \qquad c \ll 1.$$

$\Phi_0 (P, T, N)$ Gibbs potential

$$\Phi = E - TS + pV = \mu N$$

$$E = TS - PV + \mu N$$

$$d\Phi = -S\,dT + V\,dp + \mu\,dN$$

$$\Phi_0 = N\mu_0(P,T)$$

add one molecule of solute.

$$\Delta\Phi = \alpha(P,T,N)$$

non-interacting $\Rightarrow$ add n $\rightarrow$ $\Delta\Phi = n\,\alpha(P,T,N)$

However we have to divide by $n!$ (identical particles).

$$-\beta A \rightarrow -\ln n! = -n\ln n + n$$

$$A \rightarrow A + k_B T(n\ln n - n)$$

$$\Phi \rightarrow \Phi + n\alpha + k_B T(n\ln n - n)$$

$$\Phi = N\mu_0(P,T) + n\,\alpha(P,T,N) + k_B T\, n \ln(n/e)$$

$$= N\mu_0(P,T) + n k_B T \ln\left(\frac{n}{e} e^{\alpha/k_B T}\right)$$

homogeneous in n, N

$$e^{\alpha/T} = \frac{f(P,T)}{N}$$

$$\Rightarrow \quad \Phi = N\mu_0(P,T) + n k_B T \ln\left(\frac{n}{eN} f(P,T)\right)$$

$$= N\mu_0(P,T) + n k_B T \ln\left(\frac{n}{eN}\right) +$$

$$+ \underbrace{n k_B T \ln f(P,T)}_{\psi(P,T)}$$

$$\Phi = N\mu_0(P,T) + n\,\psi(P,T) + n k_B T \ln\left(\frac{n}{eN}\right) + \mathcal{O}(n^2/N)$$

$$\mu = \frac{\partial \Phi}{\partial N} = \mu_0(P,T) - \frac{n}{N} k_B T \quad ; \ \mu \text{ of solvent.}$$

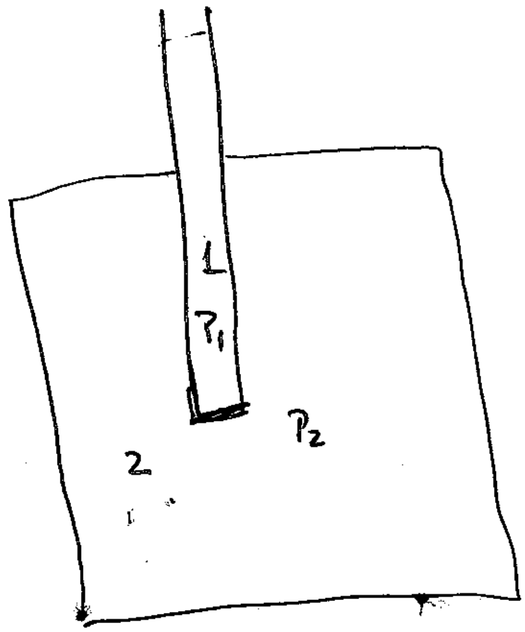
$$\mu' = \frac{\partial \Phi}{\partial n} = \psi(P,T) + k_B T \ln\left(\frac{n}{eN}\right) - k_B T$$

$$= k_B T \ln\left(\frac{n}{N}\right) + \psi(P,T)$$

Osmotic pressure :

$\mu_1 = \mu_2$

only for water



$T_1 = T_2$

$$\mu_0(P_1, T) - \overset{n/N}{\overset{\downarrow}{c}}\, K_B T = \mu_0(P_2, T)$$

$P_1 \approx P_2 \Rightarrow P_1 = P_2 + \delta p$

$$\frac{\partial \mu_0}{\partial p} \cdot \delta p = c K_B T$$

$$\delta p = \frac{c K_B T}{\partial \mu_0 / \partial p}$$

$$= \frac{n}{N} \frac{K_B T}{V/N} = \frac{n}{V} K_B T \Rightarrow$$

$$N \frac{\partial \mu}{\partial p} = V$$

$$\frac{\partial \mu}{\partial p} = V/N$$

$$\boxed{\delta p_{osmotic} = \frac{n}{V} K_B T} \checkmark$$

From Einstein paper.

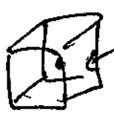
Should be same for a suspension of small particle?

$$-\beta A = \ln \int d^{3N}x\, d^{3N}p\, d^{3N}x'\, d^{3N}p' \; e^{-\frac{1}{k_B T}E}$$

$E-TS$

$$S = \frac{E}{k_B T} + k_B \ln \int d^3 \text{---} \; e^{-\beta E}$$

V^* : volume of solution + solvent.

 position of particle 1.

$$Z = \int d^3x_1 \ldots d^3x_n \; \underbrace{\int d \ldots e^{-\beta E}}_{\text{indep. of } V^*}$$

because the water does not see the wall

also indep. of $\vec{x}_1 \ldots \vec{x}_n$

because of translation symmetry

$$Z = (V^*)^n \cdot Z_0$$

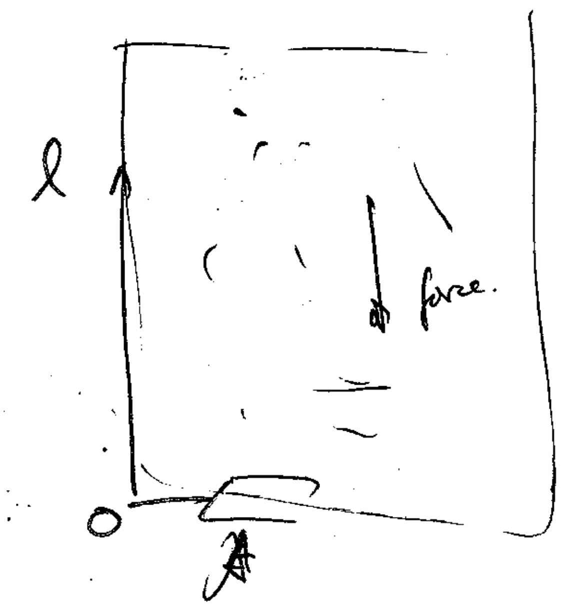
$$-\beta A = n \ln V^{\alpha} + \ln Z_0$$

$$A = -n k_B T \ln V^{\alpha} - k_B T \ln Z_0$$

$$dA = -S\,dT - p\,dV + \mu\,dN$$

$$p = -\frac{\partial A}{\partial V^{\alpha}} = \frac{n k_B T}{V^{\alpha}} \quad \checkmark .$$

necessary to move wall.



Suspended particles. $\nu = n/V$

$$\delta A = \delta E - T\delta S = 0 \quad \text{equilibrium.}$$

$\nu(x)$: density of particles

$$E = A \int_0^{l} dx\, \nu(x)\, \underbrace{mgx}_{\text{gravity}}.$$

$$S = ?$$

From dilute solution

$$\Phi = N\mu_0(P,T) + n\,\psi(P,T) + nk_BT \ln(n/eN)$$

$$S = -\frac{\partial \Phi}{\partial T} = -N\frac{\partial \mu_0}{\partial T} - n\frac{\partial \psi}{\partial T} - nk_B \ln(n/eN)$$

For a small portion of solution $\underset{A}{I\,dx}$

$$\Delta S = \underset{\uparrow}{\cancel{N} s_0} = \underbrace{\rho \cdot A \cdot dx}_{\text{solvent}}\, s_0 + A \cdot dx\, \nu(x) \underset{\text{of solute}}{s} +$$

$$- A \cdot dx\, k_B\, \nu(x) \ln\left(\frac{\nu(x)}{e\rho_{\text{of solvent}}}\right)$$

$$S = \underset{\text{solvent}}{S_0} + n \underset{\substack{\text{of solute} \\ \text{indep. of } \nu(x)}}{s} - A k_B \int \nu(x) \ln\left(\frac{\nu(x)}{e\rho}\right) dx$$

Free energy:

$$A = \mathcal{A}\left\{ \int_0^\ell dx\, \nu(x)\, mg\, dx + K_BT \int_0^\ell \nu(x) \ln\left(\frac{\nu(x)}{e\rho}\right) dx + cst \right\}$$

Lagrange multiplier

$$A = \mathcal{A}\left\{ \int_0^\ell dx\, \nu(x)\, mgx\, dx + K_BT \int_0^\ell \nu(x) \ln\left(\frac{\nu(x)}{e\rho}\right) dx + \lambda\left(\int_0^\ell \nu(x)\, dx - \frac{n}{\mathcal{A}}\right) \right\}$$

$$\frac{\delta A}{\delta \nu(x)} = 0$$

$$mgx + K_BT \ln \frac{\nu(x)}{e\rho} + K_BT + \lambda = 0$$

$$mgx + K_BT \ln \nu(x) + K_BT \ln(\cancel{e}\rho) \cancel{+K_BT} + \lambda = 0$$

$$\ln \nu(x) = -\frac{mgx}{K_BT} \cancel{+} \ln\rho + \frac{\lambda}{K_BT} \;\Big|\; \Rightarrow \nu(x) = C\, e^{-\frac{mgx}{K_BT}}$$

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$$A\int_0^\ell \nu(x)\,dx = CA\int_0^\ell e^{-\frac{mgx}{k_BT}}\,dx =$$

$$= CA\left.\frac{e^{-\frac{mgx}{k_BT}}}{-\frac{mg}{k_BT}}\right|_0^\ell = -\frac{CAk_BT}{mg}\Big(\underbrace{e^{-\frac{mg\ell}{k_BT}}}_{\approx 0}-1\Big)$$

$$= \frac{CAk_BT}{mg} = n \Rightarrow C = \frac{mgn}{Ak_BT}$$

$$\boxed{\nu(x) = \frac{mg}{Ak_BT}\,n\,e^{-\frac{mgx}{k_BT}}}$$

$$P_{osmotic} = \nu k_BT = \frac{mg}{A}\,n\,e^{-\frac{mgx}{k_BT}}$$

$$\frac{\partial P}{\partial x} = -\frac{mg}{k_BT}\,\frac{mg}{A}\,n\,e^{-\frac{mgx}{k_BT}} = -mg\,\nu(x)$$

pressure gradient

force.

o spherical particles
moving in fluid

terminal velocity $v = \frac{mg}{6\pi K R}$

radius

friction

$v\,\delta t$ 

$\nu(x)\, v\,\delta t\, A$

flux. $\frac{\nu m g}{6\pi K R}$

Diffusion $-D\frac{\partial \nu}{\partial x}$ flux created by gradient of concentration. ν

coeff. of diffusion

$c = \frac{n}{N} = \frac{\nu}{\rho}$

gradient of ν ↓ flux $-D\frac{\partial \nu}{\partial x} = \frac{\nu m g}{6\pi K R}$

$\frac{\partial \nu}{\partial x} = -\frac{mg}{k_B T}\nu$ $D\frac{\cancel{mg}}{k_B T}\cancel{\nu} = \frac{\cancel{\nu m g}}{6\pi K R}$

$$\boxed{D = \frac{k_B T}{6\pi k R}}$$

In Einstein's paper gas constant
$k_B = R/N_A$ Avogadro #

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

diffusion. friction

relation.