Entropy

- is max^m for isolated system in thermal eq.

- $S = k \ln W$

- N sites, N_p particles. $\Rightarrow$ concentration : $C = \frac{N_p}{N}$

  $\Rightarrow$ # microstates : $W = \frac{N!}{N_p!\,(N-N_p)!}$

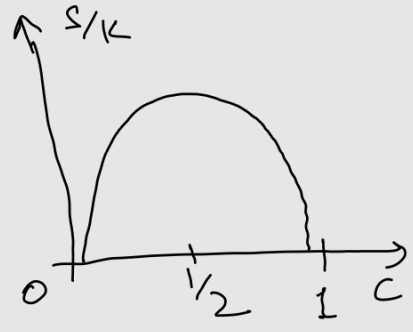
$\therefore \quad S = k \ln \frac{N!}{N_p!\,(N-N_p)!}$

using Stirling approximation :

$$\ln N! \approx N \ln N - N + \ldots\ldots$$

$\therefore \quad S = kN\left[c \ln c + (1-c)\ln(1-c)\right]$

- entropy as a fn of concentration



* entropy is extensive
↳ doubling the system size doubles the entropy

* conc^n is intensive

→ another way to look at this:

in limit $N_p << N$,

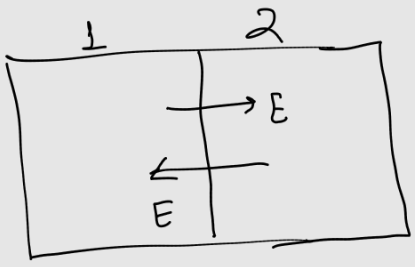
then $\frac{N!}{(N-N_p)!} \approx \frac{N!}{N} \approx N^N$

$\therefore W = \frac{N!}{N_p!(N-N_p)!} \approx \frac{N^N}{N_p!} = \frac{V^N}{N!}$

have to have this $N!$ to make entropy extensive.

Conditions for thermo. eqbm

1)



V & N same

* temperature must be same for thermal eqbm

$$T_1 = T_2$$

1st law:

$TdS = dE + PdV - \mu dN$

- $$\frac{1}{T} = \frac{\partial S}{\partial E}$$

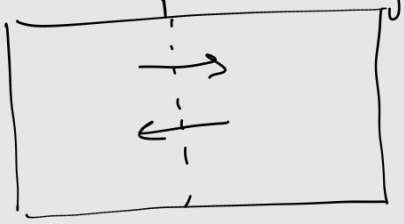
2)

* pressure must be same for thermal eqbm

$$P_1 = P_2$$

- $$\frac{P}{T} = \frac{\partial S}{\partial V}$$

3) particles can go through partition.



$$\mu_1 = \mu_2$$

- $$\frac{\mu}{T} = \frac{-\partial S}{\partial N}$$

- For N_p particles in N boxes:

$$\mu = -kT[\ln c + \ln(1-c)]$$

. for systems in contact with reservoir ⇒ minimum of the free energy determines the thermodynamic eqb'

⇒ fixed T: E can change

Helmholtz: $F(T,V,N) = E - TS$

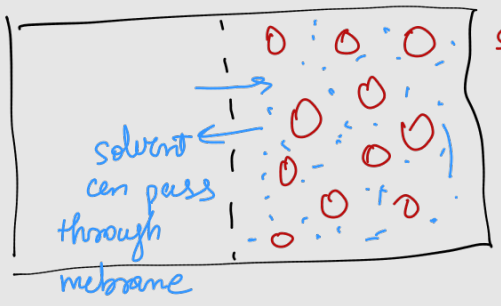
$S \equiv S(E,V,N)$ in $S = k \ln W$

So we need to perform a Legendre transformation to go from variables (E,V,N) of S to (T,V,N) of free energy $(F(T,V,N))$

V is allowed to change: P fixed, T fixed

Gibbs: $G(T, P, N) = E + PV - TS$

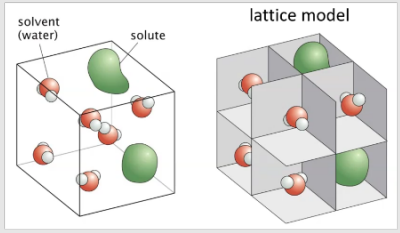
— x —



solvent (colloid) can't pass through the semi-permeable membrane.

- fixed T ⇒ Gibbs free energy

Thermodynamics of Solutions



- gibbs free energy must be extensive
- the only extensive quantity in G is the num. of particles N. (T & P are intensive)

⇒ If we just have water, we must expect:

gibbs free energy : $G_{tot} = N_w \mu_w^0$

- now adding solute, $N_s \varepsilon_s - TS_{mix}$

for same reason as water.

energy cost of introducing solute to the system.

$$\therefore \boxed{G_{total} = N_w \mu_w^0 + N_s \varepsilon_s - TS_{mix}}$$

entropy of mixing:

$$\boxed{S_{mix} = -K\left(N_w \ln\left(1 - \frac{N_s}{N_w}\right) + N_s \ln\left(\frac{N_s}{N_w}\right)\right)}$$

$$\therefore \quad \mu_{solute} = \left(\frac{\partial G_{total}}{\partial N_s}\right)_{T,P}$$

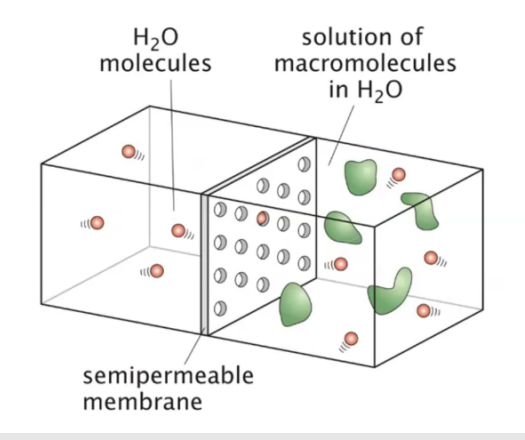
$$\Rightarrow \boxed{\mu_{solute} = \varepsilon_s + kT \ln C/C_0} \qquad C = \frac{N_s}{V_{box}}, \; C_0 = \frac{N_w}{V_{box}}$$

$$\& \quad \mu_w(T,P) = \left(\frac{\partial G_{total}}{\partial N_w}\right)_{T,P}$$

$$\Rightarrow \boxed{\mu_w(T,P) = \mu_w^0(T,P) - \frac{N_s}{N_w} kT}$$

Osmotic Pressure

$$\mu_w(T,P) = \mu_w^0(T,P) - \frac{N_s}{N_w} kT$$



* in this case, the condition for thermodynamic eqbm is μ is same on both sides

→ so how can L.H.S ≠ R.H.S of the above eqn be the same?

the only way this equation holds, that is...

.. the only way the system reaches eqbm is that pressure is different on both sides.

i.e.

$$\mu_w^0(T, P_1) = \mu_w^0(T, P_2) - \frac{N}{N_w} kT$$

* → P_1 & P_2 are pretty close, not a lot of deviation.

expand: $\mu_w^0(T, P_2) \approx \mu_w^0(T, P_1) + \left(\frac{\partial \mu_w^0}{\partial P}\right)_T (P_2 - P_1)$

working P_1 instead of P_2 as $P_1 \approx P_2$

$\left(\frac{\partial \mu_w^0}{\partial P}\right)_T$ → V (volume per molecule)

comparing with eqn above, this term is equal to $+\frac{N_s}{N_w} kT$

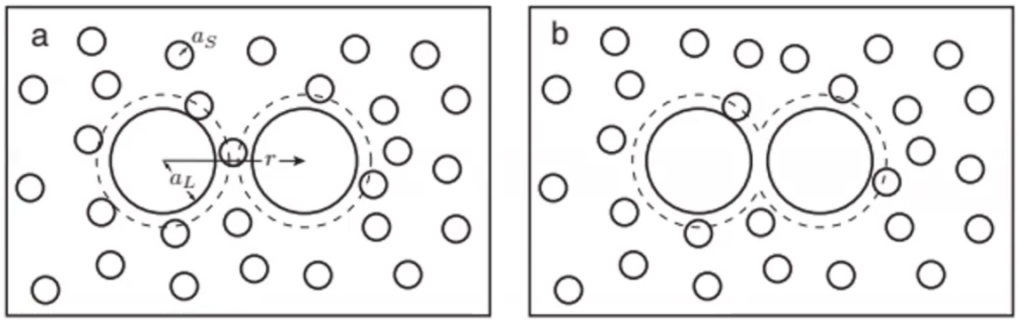
$$\Rightarrow \boxed{P_2 - P_1 = \frac{N_s}{V} kT}$$

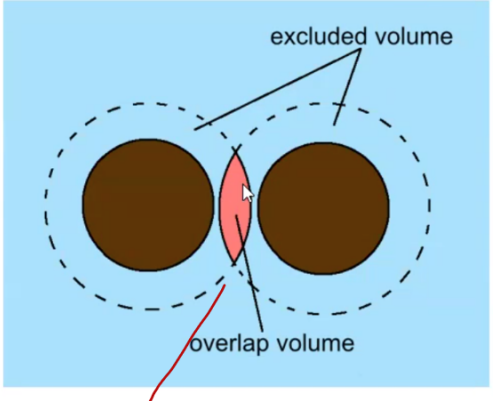
Van't Hoff formula.

- $V \approx N_w v$

For cells, osmotic pressure difference across plasma membrane can be several atm 10 atm ~ 1 pN/nm^2

Depletion Force / Asakura - Osawa





Osmotic pressure of "depletant" of concentration c

$$\Pi = c\,kT$$

$$dG(r) = \Pi\, dV_{excl}(r)$$

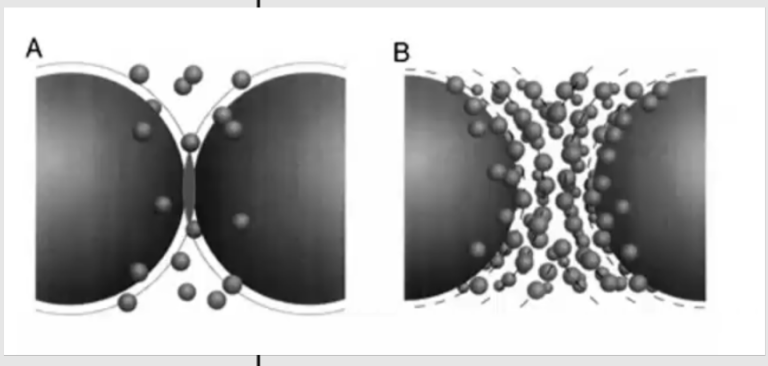
Attraction force $$F(r) = -\frac{dG}{dr} = -\Pi\frac{dV_{ex}(r)}{dr}$$

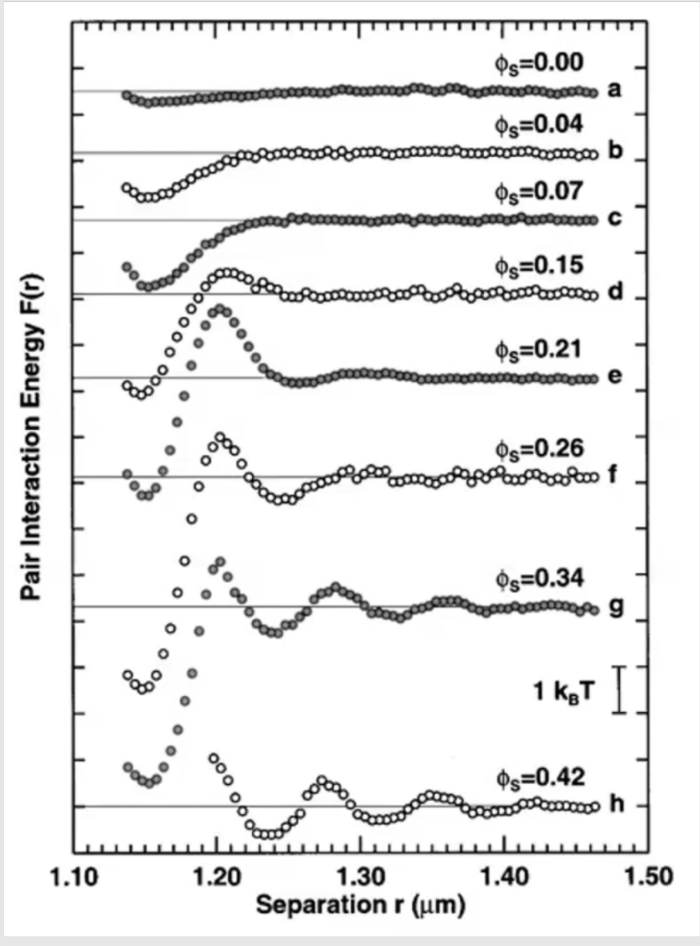
this overlap volume region & the excluded volume region two seperate compartments (similar to semi-permeable membrane example on the previous page)

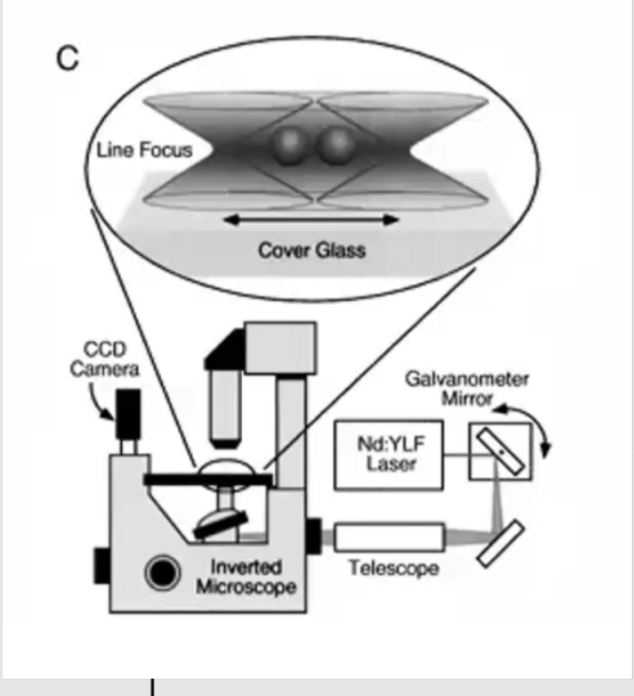
work required to change gibbs free energy ($P dV$)

(so is Gibbs free energy here equal to work???)

Example of depletion force measurements in binary colloid systems

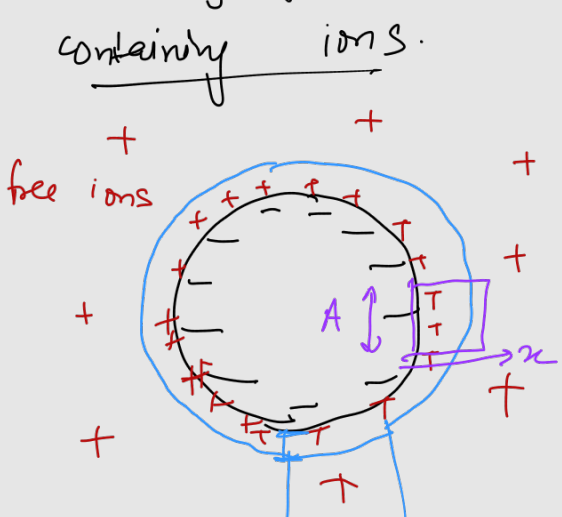


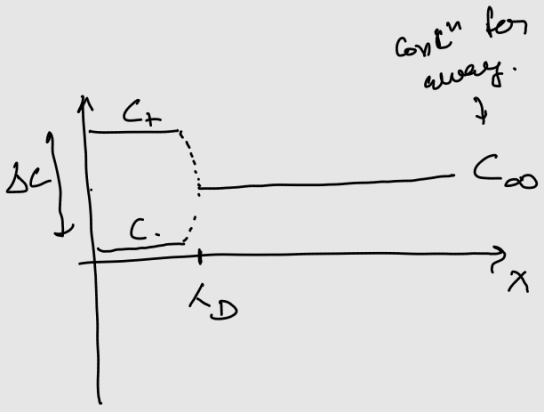




Polarization & charge interaction in water

Screening of e-stetic interactions in a sol^n containing ions.





enhanced con^n of + ions near the negatively charged particle surface

λ_D the width is called Debye - Huckel length or the screening length

- ions can come in & out of this shell
  - inside the cloud, the chemical potential would be:

$$\mu = \mu_0 + kT \ln \frac{C_\infty + \frac{\Delta C}{2}}{C_0} + e V_{cloud}$$

entropy

potential energy

energy

Net charge over A $\quad Q = e \Delta C A \lambda_D$

$$E_{cloud} = \frac{Q}{\varepsilon_0 D A}$$

↑ dielectric constant of water ($D \approx 80$)

$$\Rightarrow V_{cloud} \approx -\frac{1}{2} E_{cloud} \lambda_D \qquad (V \approx E d)$$

⋮

solve for λ_D

$$\lambda_D = \sqrt{\frac{1}{4\pi C_\infty l_B}}$$

where $\quad l_B = \frac{e^2}{4\pi \varepsilon_0 D k T}$

$$\frac{e^2}{4\pi \varepsilon_0 D l_B} = k_B T$$