

Phil Pincus

Fundamental Interactions I

- overview:
- Ubiquitous forces
 - Electrostatics
 - Hydrogen bonds, hydrophobicity
-

Soft Matter

"squishy"
→ elastic modulus

$$G \sim \frac{T_c}{L^3}$$

T_c ~ characteristic temperature

ex: $T_c \sim 0.1 \text{ eV} \sim 10 \frac{\text{room temp.}}{T} (k_B = 1)$

Hard $L \sim 10^{-8} \text{ cm}$

Soft $L \sim 10 \text{ \AA}$

$$G_{\text{soft}} \sim 10^{-3} G_{\text{hard}}$$

$$E_1 \sim \text{atomic} \sim \text{eV}$$

$$E_2 \sim \text{interaction} \sim 0.1 \text{ eV}$$

$$E_3 \sim \text{entropy} \sim 0.01 \text{ eV}$$

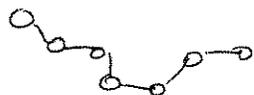
} Soft matter

Colloids - solid particles: $100 \text{ \AA} - 1 \mu\text{m}$
in solvent

Emulsions - liquid droplets

foams - gas in solvent

polymers - connected "beads"



Dilute Solution Thermodynamics

concentration $c \equiv \frac{N}{V}$ #/vol.

dilute: c is small

assume short-range forces

free energy

free energy density

$$\frac{F}{\text{volume}} = \frac{F_0}{T} + B_1 c + \frac{1}{2} B_2 c^2 + \frac{1}{6} B_3 c^3 + \dots + \underbrace{c(\ln c - 1)}_{\text{entropy of mixing}}$$

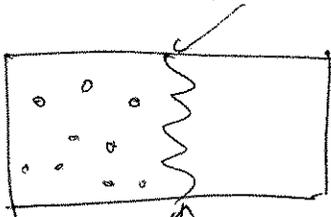
Virial expansion

$(T \approx k_B T)$
room temp.

chemical potential (of solute)

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{V, T} = T(B_1 + B_2 + \ln c + \dots)$$

Osmotic pressure: $\Pi = c \frac{\partial F}{\partial c} - F$

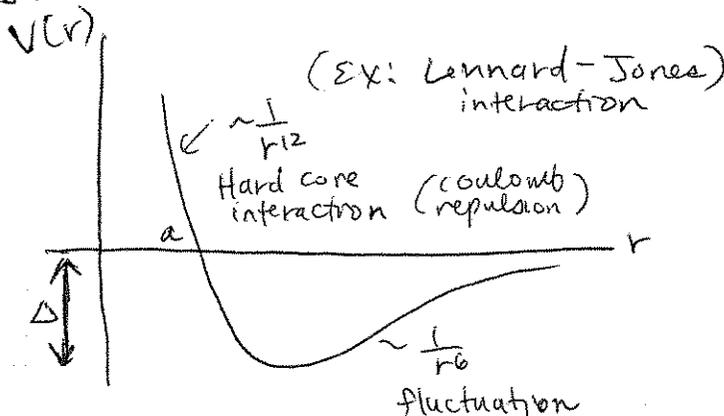


membrane permeable to solvent, not solute

$$= T \left[c + \frac{B_2}{2} c^2 + \frac{1}{3} B_3 c^3 + \dots \right]$$

(B_1 does not affect Π)

typical interaction between molecules (in solvent)



2nd virial coefficient:

$$B_2 = \int [1 - e^{-V(r)/T}] d^3r$$

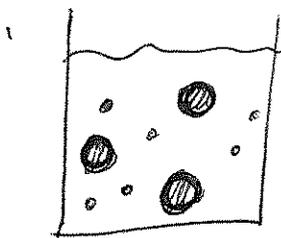
if $T \gg \Delta$:

$$B_2 \sim a^3 > 0 \quad (\text{note: dimension of volume})$$

if $T < \Delta$:

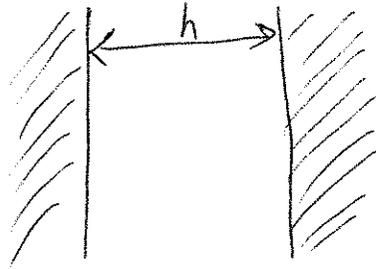
$$B_2 \sim -a^3 e^{\Delta/T}$$

if $B_2 > 0 \Rightarrow$ repulsive interaction of solutes. (good solvent)



Depletion Interactions (Oosawa)

Zoom in on 2 ~~big~~ ^{big} particles
(approx. flat)



radius of small particles $r = b$

if $h < b$:

- small particles can't fit \rightarrow depletion zone between big particles
 - pressure on big particles from the outside: $\pi \sim cT$
- \Rightarrow attraction between big spheres

$$\pi = -cT$$

range $\sim b$

Hydrogen atom (cgs)

$$E = \frac{p^2}{2m} - \frac{e^2}{r}$$

Bohr quantization $\oint \vec{p} \cdot d\vec{r} = n \cdot h$ Planck's const. $1, 2, 3$

$$2\pi r p = n h$$

(remember)
1 eV = k_BT / 40

$$E_1 = 13.6 \text{ eV} \leftarrow E_n = -\frac{1}{2} \frac{m e^4}{n^2 \hbar^2}, \quad m = \text{electron mass}$$

$$r_1 = 0.5 \text{ \AA} \leftarrow r_n = \frac{n^2 \hbar^2}{m e^2}$$

1s state: $\psi \sim e^{-r/a}$ spherically symmetric
dipole $\langle \mu \rangle = 0$

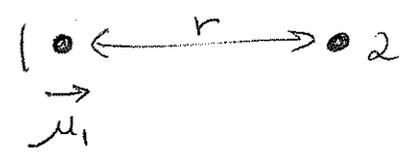
Atom in electric field:

$$\vec{\mu} = \alpha \vec{E}, \quad \alpha \equiv \text{polarizability}$$

$$\sim \frac{e l}{e} l^2 \sim l^3 \quad \left. \begin{array}{l} \text{dimensions [L]} \\ \text{volume} \end{array} \right\}$$

$$\sim r_1^3 \quad (\text{the only length scale is } r_1)$$

2 hydrogen atoms



$$E_{21} \sim \frac{\mu_1}{r^3} \Rightarrow \mu_2 = E_{21} \alpha \Rightarrow U \sim \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} = -\alpha \frac{\mu_1^2}{r^6} \sim -\frac{e^2 a^5}{r^6}$$

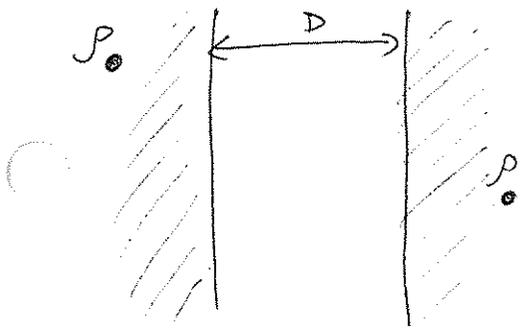
dipole-dipole interaction

$$\langle \mu_1^2 \rangle = (ea)^2$$

short range interaction, weak, arises from quantum fluctuations (not pairwise additive)

this was derived neglecting retardation.

references: Parsegian, Nisnam-Mohantany, Abrikosov et al



interaction energy (per area) \leftarrow atomic energy $\frac{e^2}{a}$

$$U_{\text{area}} = \frac{-\rho^2 a^2 \epsilon}{D^2}$$

dimensional analysis \rightarrow

$$= -\frac{A}{12\pi} \frac{1}{D^2}$$

approx. breaks down for 2 infinite conductors (w/ ∞ polarizability) \sim size

$A \equiv$ Hamaker Constant
(\sim eV in vacuum)

Lifshitz - immerse in blackbody radiation

$$Z = \text{Tr } e^{-\beta H}$$

$$H = \sum_{\ell} \hbar \omega_{\ell} \left(n_{\ell} + \frac{1}{2} \right)$$

\downarrow Bose-Einstein distribution

$$n_{\ell} = \frac{1}{e^{\hbar \omega_{\ell} / T} - 1}$$

$$F = -T \ln Z$$

$$= T \sum_{\ell} \ln \left[2 \text{sh} \frac{\hbar \omega_{\ell}}{2T} \right]$$

$$\Pi = \frac{-\partial F}{\partial D} \rightarrow \left(-\frac{\hbar c}{D^4} \right)$$

(need to subtract out modes of ~~lengths~~ ^{wavelengths} not internal multiples of $D/2$)