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Fundamental Forces I

Soft matter - compressible matter

elastic modulus $G \sim \frac{T_c}{l^3}$ $k_B = 1$

Hard matter

$\left.\begin{matrix} T_c \sim 0.1\,eV \sim \overset{10-100T}{10T} \\ L \sim 10^{-8}\,m \end{matrix}\right] \rightarrow G \sim$ T ≡ room temp

Soft matter

$L \sim 10\,Å$ $\rightarrow G \sim 10^{-3}\,G(\text{hard matter})$

Soft matter has larger ~~si~~ size scale

Energy scales

$\left.\begin{matrix} E_1 \sim \text{atomic} \sim eV \\ E_2 \sim \text{interactions} \sim 0.1\,eV \\ E_3 \sim \text{entropy} \sim 0.01\,eV \end{matrix}\right]$ relevant energy scales for us

Often we are dealing w/

- colloids ex Au nanoparticles in solution $\simeq 100\,Å - 1\,\mu m$
- Emulsions immiscible solvents → liquid droplets
- foams gas in solvent

- Polymers → larger than previous examples

Dilute solution thermodyn.

dilute $c \equiv \frac{N}{V} \ll 1$ $\Rightarrow$ short range forces

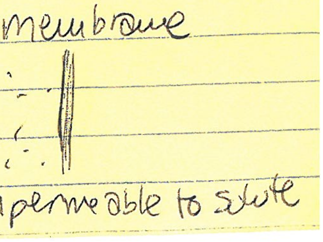
free energy $$\left.\frac{F}{T}\right|_{vol} = \underbrace{\frac{F_0}{T}}_{\text{pure solvent}} + \underbrace{B_1 c + \frac{B_2}{2}c^2 + \frac{1}{6}B_3 c^3}_{\text{virial expansion}} + \underbrace{c(\ln c - 1)}_{\text{entropy of mixing}}$$

$T \equiv k_B \overset{\uparrow}{T}$ ~room T

Chemical potential - work to do to add 1 particle (solute)

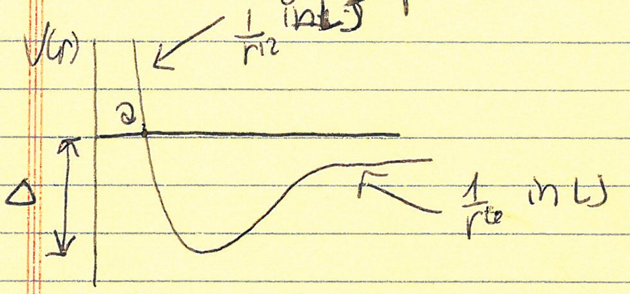
$$\mu = \left.\frac{\partial F}{\partial N}\right|_{V,T} = T\left(B_1 + B_2 c + \ln c + \ldots\right)$$

Osmotic pressure - pressure exerted on membrane



$$\Pi = c\frac{\partial F}{\partial c} - F = T\left[c + \frac{B_2}{2}c^2 + \frac{1}{3}B_3 c^3 + \ldots\right]$$

Intermoeecular potential



To 1st approx the only relevant force is EM interaction

→ interaction between objects in solvent.

All interactions between molecules roughly look like this

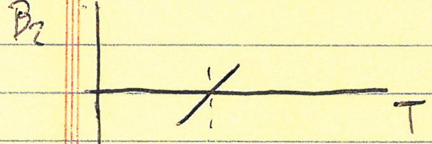
$$B_2 = \int \left[1 - e^{-\frac{V(r)}{T}}\right] d^3r$$

The V(r) depends on the solvent.

units of $B_2 = L^3$

$T \gg \Delta \quad B_2 \sim a^3 > 0$

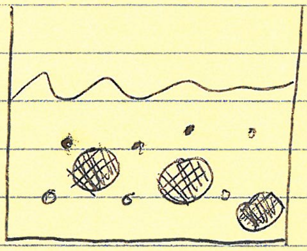
$T < \Delta \quad B_2 \sim -a^3 \exp(+\Delta/T)$



Flory T in polymer physics

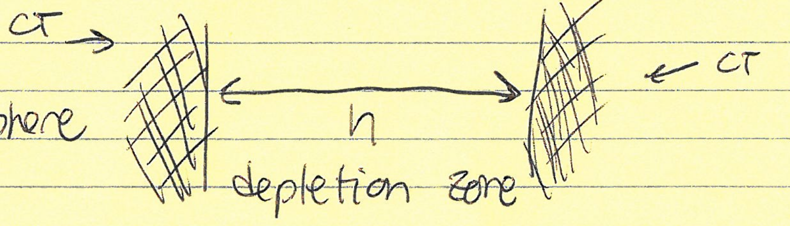
$B_2 < 0$ attractive interactions "poor" solvent

Depletion interaction



Depletion interaction - Oosawa

~~Approximately~~ Big spheres are so big that their interaction is ~ flat surface



b radius small sphere

if $h < b$ → won't fit

$\Pi = CT$ pressure from 2 sides not contrasted by anything (center is empty)

so attractive interaction

range ~ b $\Pi = -CT$

Force gets bigger if concentration of small spheres increases

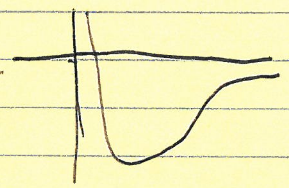
If we think of solvent + small particles as new solvent, Then we can incorporate this attraction in B_2.

Dispersion forces

(repulsive $1/r^6$ part)

Hydrogen atom $E = \frac{p^2}{2m} + \frac{e^2}{r}$ ⟵ CGS units $m_{prot} \to +\infty$

Bohr quantization $\oint \vec{p}\, d\vec{r} = n h$ ← integer



$2\pi r p = n h$

$E_n = \frac{1}{2} \frac{m e^4}{n^2 \hbar^2}$ $r_n = \frac{\hbar^2 n^2}{m e^2}$

$n=1$ $E_1 = 13.6\,eV$ $r_1 = 0.5\,Å = a$

wave function $\psi \sim e^{-r/a}$

1s is spherically symmetric → no dipole $\langle \mu \rangle = 0$

If we put the atom in $\vec{E}$ field $\overset{\text{dipole}}{\vec{\mu}} = \underset{\text{polarizability}}{\alpha} \vec{E}$

$\alpha \sim \frac{\overset{\mu}{e\ell}}{\underset{E\text{ field}}{e}}\ell^2 \sim \ell^3$ → dimension ~~of~~ V

Here only one length scale, a $\Rightarrow \alpha \sim a^3$

$\overset{1}{\oplus} \xleftrightarrow{r} \oplus_2$

E field at particle 2 due to dipole of 1

$E_{21} \sim \frac{\mu_1}{r^3}$ → 2 gets polarized

$\mu_2 = E_{21}\,\alpha$

dipole dipole interaction $U \sim \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} = -\alpha \frac{\mu_1^2}{r^6}$

$\langle \mu_1 \rangle = 0$

$\langle \mu_1^2 \rangle = (e a)^2$

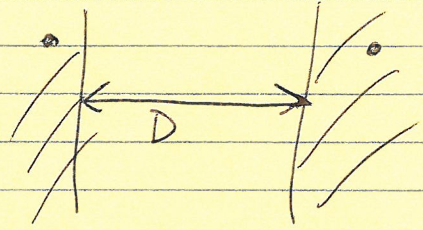
$\downarrow$

$= -\frac{e^2 a^5}{r^6}$

All neutral objects have attractive interaction like ↑. It is weak and short range but it is always there. This is due to quantum fluctuations (@ T = 0).

In a real case these forces are not pairwise additive and we have to worry about retardation effects.

Take 2 solids separated by D
Take 1 atom on each side,
assume they interact w/ dipole pot.
Assume it is additive and integrate.



$$U\Big|_{area} = -\frac{\rho^2\alpha^2\,\overset{\nearrow \text{energy scale } e^2/a}{\epsilon}}{D^2 \rightarrow \text{from dimentional analysis}}$$

Most of the time this gives a reasonable guess.

$$U\Big|_{area} = -\frac{A}{12\pi}\frac{1}{D^2}$$

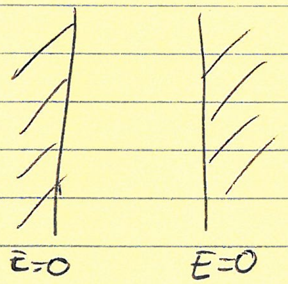
$A \equiv$ Hamaker constant
$A \simeq 0.01 - 0.1\ eV$ in solvent
$\simeq 1\ eV$ in vacuum

If we had 2 conducting plates $\alpha \sim V$, in this case $V \to \infty$ so $A \to \infty$.

To solve this for conductors (done by Lifshitz)
$Z = Tr\ e^{-\beta H}$

$$H = \sum_q \hbar\omega_q \underbrace{(n_q + 1/2)}_{\searrow \boxed{\hbar n_q}} \qquad n_q = \frac{1}{e^{\hbar\omega_q/T} - 1}$$

$$F = -T\ln Z = T\sum_q{}' \ln\left[2\,sh\frac{\hbar\omega_q}{2T}\right]$$



Solve wave eq w/ condition $E=0$ at surface

$$\Pi = -\frac{\partial F}{\partial D} \longrightarrow \frac{\hbar c}{D^4}$$ Kasimir force (?)

Fundamental Forces II

- Fluctuation forces

- Flory Huggins Michael $U = -\varepsilon \frac{\alpha_1 \alpha_2}{r^6}$

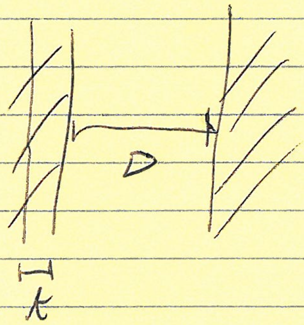
$$\chi \propto \left[U_{AB} - \frac{(U_{AA}+U_{BB})}{2}\right] = \frac{\varepsilon}{r^6}\left[\frac{\alpha_A^2+\alpha_B^2}{2} - \alpha_A\alpha_B\right]$$

$$= \frac{\varepsilon}{2r^6}(\alpha_A-\alpha_B)^2 > 0$$

This potential roughly works in insulators

- Exercise

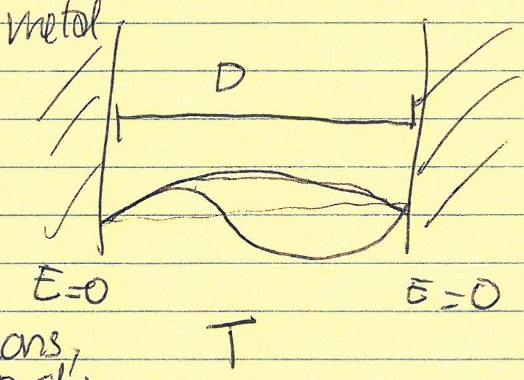
we did half ~~planes~~ spaces $\Pi = -\frac{A}{D^3}$



What if They become films of thickness t?

$$\Pi = -\frac{A}{D^3} f(t/D)$$

Metallic half space w/ black body radiation



$$F = T \sum_q \ln\left[2\,\mathrm{sh}\frac{\hbar\omega(q)}{T}\right]$$

$\omega(q) = cq$ in free space

Conductors come into play just to fix boundary conditions, or allowed values of wave vector.

Long wavelengths are excluded; longest is $\lambda = D/2$

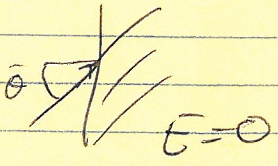
$$\Pi = -\text{const.}\ \frac{\hbar c}{D^4}$$

For real conductor, we have $\varepsilon_1(q,\omega)$ in metal and $\varepsilon_2(q,\omega)$ and this changes everything.

Another way of doing this is:
Take 1 conductor, in black body field.
A photon hitting the surface will be reflected, w/ a change in momentum

$p = \hbar\vec{q}$

$\Delta p = 2\hbar q \cos\theta$



We have distribution of photons

$$n(q) = \frac{1}{e^{\hbar c q/T} - 1}$$

$$\text{Pressure: } \Pi = \int \overbrace{\frac{dq\, q^2\, d\mu}{(2\pi)^3}}^{\int \text{over solid angle}} 2\hbar q\mu \; c\, n(q)$$

$\mu = \cos\theta$

check dimensions

$$\checkmark \; \frac{E}{L^3} = \frac{E\,t}{L^{\cancel{4}3}} \frac{L}{t}$$

In the center we have fewer modes pushing because some wavelengths are missing.

$$\Pi = -\frac{1}{(2\pi)^3} \int_0^{\pi/D} \frac{\hbar q^3 c\, dq}{e^{\hbar c q/T} - 1}$$

$2D = \lambda$

$1/\cancel{k}\lambda = 1/2D$

$k = 2\pi/\lambda = \pi/D$

At max. $q = \pi/D$ so ~~if~~ ~~[illegible]~~ $\frac{\hbar c q}{T}$ at max is $\frac{\hbar c \pi}{D T}$. If $T > \frac{\hbar c}{D}$ then we can expand denomin. in series:

$$\Pi \simeq \frac{1}{(2\pi)^3} T \int_0^{\pi/D} q^2 dq \sim -\frac{T}{D^3}$$

→ thermal fluctuations, no ħ so no quantum mechanics

$T > \frac{\hbar c}{D}$ → when is this valid? At room T this is only valid for $D \sim 10^{-3}$ cm

We are interested in smaller length ~~scales~~ scales

Other limit ~~k~~ $T \to 0$, exp $\neq +\infty$ for $n=0$

$$\Pi = -\frac{1}{(2\pi)^3}\int_0^{\pi/D} \hbar c\, q^3 dq \simeq -\frac{\hbar c}{D^4} \quad \to \text{QM fluctuations}$$

What if we change c, and take $c \to +\infty$

$$\Pi = -\frac{\hbar c}{D^4}\, \underbrace{\frac{1}{\left[1+\frac{k\hbar c}{AD}\right]}}_{\text{interpolation formula just to match the eq. for the} \neq \text{limits}}$$

A units of energy

$c \to +\infty$ $\quad \Pi \sim -A/D^3$

$A \sim \alpha^2 p^2 \epsilon$ atomic energy

These things are always there and always attractive. In soft matter only entropy leads to repulsion.

- Electrostatics

Strongest interaction we have in soft matter. So if things are charged, this will dominate over everything else.

Water ~~#~~ $\varepsilon \sim 80$
ε depends on T but it often comes in the combination $\frac{e^2}{\varepsilon T}$ and $\underline{\varepsilon T \sim \text{const}}$. (at least for liquid water)

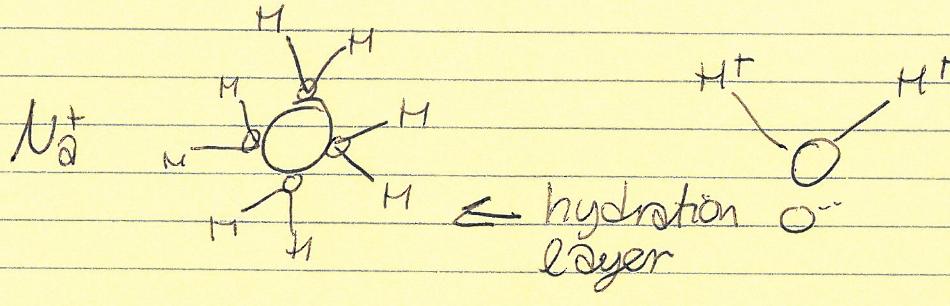
Potential (in CGS) $V(r) = \frac{q_1 q_2}{\varepsilon r}$

Any electrostatic interaction in H_2O is screened and decreased by about 100.
Ex. $NaCl \rightleftharpoons Na^+ + Cl^-$

No water: $-\frac{e^2}{a} \sim eV$ → $\gg kT$ so no dissociation; a → atomic size; in H_2O reduced by 100

atomic ~10 eV
in H_2O ~0.1 eV → close to dissociating

In addition H_2O is not just dielectric but it is also charged



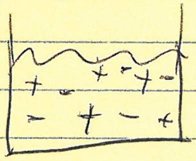
H_2O clusters around Na^+ which effectively becomes much larger. → a is no longer so small
↓
dissociation is possible

DNA - phosphates are charged so 1 charge almost every 1.7Å

If we take it as tube w/ $r \simeq 1nm$ we have charge / unit area → 1 charge / 1 nm^2 $\sigma = 1\,(nm)^{-2}$

- Salt water - the Debye-Huckel Theory

Treat ions at low concentrations as small objects



concentration $c \to 0$

Use Maxwell's eq $\nabla \cdot \vec{D} = 4\pi\rho$
Treat H_2O just as dielectric

$-\epsilon \nabla^2 \Phi = 4\pi \rho(\vec{r})$ but we don't know ρ or Φ.

So we do mean field theory each charge is distributed w/ Boltzmann distrib. around the mean field of all other particles.

$$\rho(r) = \overset{ec_+}{\cancel{q_+}}\, e^{-\frac{e\phi}{kT}} - ec_-\, e^{\frac{e\phi}{kT}}$$ c_+, c_- concentration

$$-\epsilon \nabla^2 \Phi = 4\pi \rho(r)$$

$$c_+ = c_- \Rightarrow \rho(r) = 8\pi c_0 e \sinh\left(\frac{e\phi}{T}\right)$$ $$\varphi = \frac{e\phi}{T}$$

$$\kappa^2 = 8\pi c_0 \ell$$

$$\nabla^2 \varphi = \overset{\kappa^2}{\cancel{\ell}} \sinh\varphi$$ $$\ell = \frac{e^2}{\epsilon T}$$

$$\boxed{\nabla^2 \varphi = \kappa^2 \sinh\varphi}$$

This is horrible so we linearize it for $\varphi \ll 1$
(a posteriori this corresponds to dilute systems)
↓

$$\nabla^2 \varphi = \kappa^2 \varphi$$ $$\kappa^2 = 8\pi c \ell$$

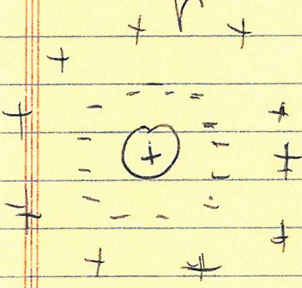
κ^{-1} Debye length

$\oplus$
at $r=0$

~~1 mMol salt~~
1 mM salt $\kappa^{-1} = 10$ nm
$\ell \simeq 0.5$ nm

$$\varphi = \frac{\ell}{r} e^{-\kappa r}$$

(spherical coord)
$$\nabla^2 \rightarrow \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)$$



screening

$$U = \frac{1}{2} e\phi(0)$$

$$U = \frac{1}{2} e\phi^+ c - \frac{1}{2} e\phi^- c$$ (energy/unit vol.)

at $r=0$ ϕ diverges so we do expansion for small r and subtract out the divergent part

$$\Phi(r \to 0) = \frac{\ell}{r}\Big(\underset{\downarrow}{1} - kr + \cdots\Big)$$

throw this out

$$\Phi(r \to 0) \simeq -k\ell$$

$$U = -k\ell c = \underset{\displaystyle \sim c^{3/2}}{\underset{\downarrow}{-\frac{Tk^3}{8\pi}}}$$

→ fluctuation on mean field energy

→ not like virial expansion, this comes from long range Coulomb interaction

we know it's fluctuation → lowers energy → − sign

↳ depends on T

energy density → depend on our only length scale

↓ $\underline{\underline{\text{has}}}$ to depend on k^3

$$F = U + \underbrace{Tc\log c}_{\text{entropy}}$$

Fundamental Forces III

- Debye Huckel salt solution

Boltzmann - Poisson

mean field, not very good $\nabla^2\phi = \kappa^2 \sinh\varphi$

$$F/T \overset{(-)}{=} 2c\ln c - \frac{1}{12\pi}\underset{\overset{\downarrow}{c^{3/2}}}{\kappa^3}\Big(+\kappa^3(\kappa b)\Big) \to \text{ionic radius}$$

To get here we did linearization

$\kappa^2 = 8\pi c l$ $\quad l \sim 1/T \quad l = e^2/\varepsilon T$

so linearization requires $cl^3 \ll 1$ to be valid

The 2 terms are antagonistic. At $T \to 0$, the 2nd one has to win.

Before that, could there be a phase transition?

osmotic compressibility $\propto \left[c^2\frac{\partial^2 F}{\partial c^2}\right]^{-1}$

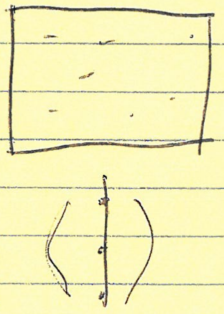
If this $= 0$ there is a phase transition. In this case it can happen, doing the math:

$c^* l^3 \sim 2/\pi$ $\quad \to c^* \sim 10-15\,M$ for salt in water

For too high a concentration the molecules don't disolve, system is unstable

- Suppose we have a plane and the ions can only live on the plane, fields do extend in 3D.

Screening, how does it work? And what is the free energy F?

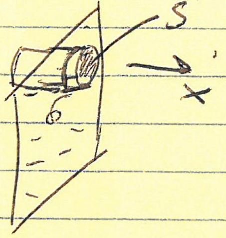


All this assumes point particles w/ just Coulomb interactions.

This is classical treatment, the measured critical exponents are ≠ from this and not understood.

- Highly charged surfaces ($\simeq 1$ charge/nm^2)

σ = # charges/area



Assume surface charged fixed in position on the surface.
Take water w/ no salt.
To get E field use Gauss' law

$2\epsilon E_x S = -4\pi e\sigma S$ $\qquad E(x) = -\frac{2\pi e\sigma}{\varepsilon} = -\frac{\partial\Phi}{\partial x}$

$\Phi(x) = \frac{2\pi e\sigma}{\varepsilon}x + \text{const}$

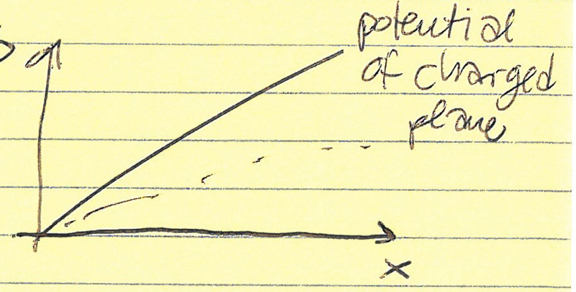
const = 0 → fix 0 of potential at $x=0$

$\varphi = \frac{e\Phi}{T} = 2\pi l\sigma x = \frac{x}{\lambda}$ $\qquad l = \frac{e^2}{\epsilon T}$

$\lambda = \frac{1}{2\pi l\sigma}$ Gouy Chapman length

In reality all our systems are neutral so start adding + charge to the system.

They "slide" down the potential curve and try to get to the surface. So some of the charge gets neutralized and slope gets smaller.



An ∞ surface can't ionize because ions will always make it to the surface to neutralize it.

Solve Boltzmann Poisson for this!

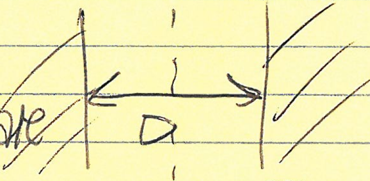
$$\frac{d^2\varphi}{dx^2} = \kappa^2 e^{-\varphi}$$

We assume that total system is neutral and that counter ions live at some distance from surface so close to it we have $E = \text{const}$ (charged plane)

$\varphi = 2\ln\left(1+\frac{x}{2\lambda}\right)$ This works fine for small σ but there it is useless.

$\rho \propto e^{-\varphi} \sim \frac{1}{\left(1+\frac{x}{2\lambda}\right)^2}$

If we have 2 of these surfaces, what is the force between them?



If we are in equilibrium stress is the same everywhere, I calculate it at center.
There $E = 0$ → stress from E field $= 0$

So $\frac{\Pi}{T} = c$ (midplane) > 0
$\downarrow$
conc. of ions.

Exercise: solve diff. eq in this system and calculate Π.

→ This is not possible so some problem w/ our theory so far.

- What is wrong?

- Ions are at distance $\lambda = \frac{1}{2\pi l\sigma}$ from surface, on surface charges are $1/\sqrt{\sigma}$ apart

$\lambda \sim 3\text{Å}$ $\qquad 1/\sqrt{\sigma} \sim 1\,\text{nm}$

So ions are much closer to surface than charges to each other.
Smearing the charge is not correct, charge is

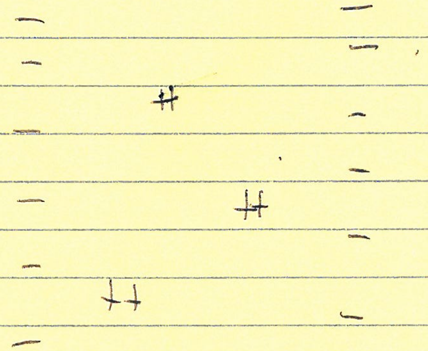
discrete.

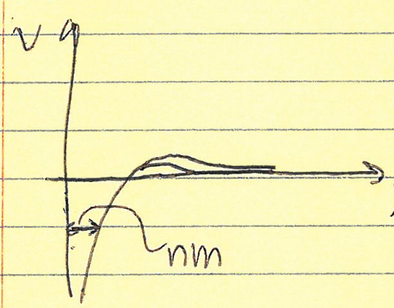
- Also $cl^3 << 1$ not true!

- Treating these as point charges is incorrect (distance of ions to surface ≃ 3Å)

To do something better:

- 1996 - Simulation of 2 charged lines w/ positive charges and cutoff to Coulomb potential at 1.6 nm.

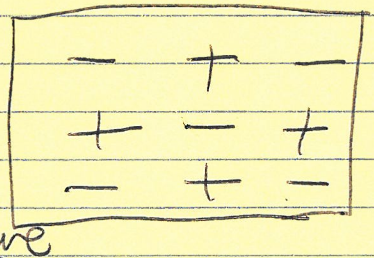




They got an attractive force (potential)

= Other simulation shows that DNA is mostly neutral, not charged and w/ + ions attached to it.

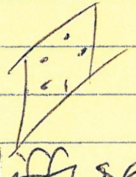
Ex. in mica, we could end up w/ something like this.



So the answer is that we have heterogeneously charged surfaces.

What we were doing w/ BP was using the wrong boundary cond.; we should take into account the counter ions at surface.

Exercise: Surface w/ discrete charges, n are neutralized w/ energy $-\ell/b$ per unit area, rest of charges in diffused

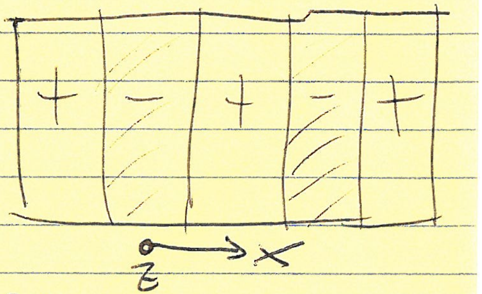


double layer

$$-\frac{\ell}{b} n + \sigma_{eff} \ln\left(\frac{\sigma_{eff}}{\lambda}\right) = \text{energy/area}$$ $\sigma_{eff} = \sigma - n$

find λ and n.

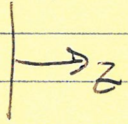
Toy problem: surface w/ stripes



$\sigma = \sigma_0 \cos qx$

$\varphi = \frac{\sigma_0 \ell}{q} \cos qx \, e^{-qz}$

So 2 surfaces like this w/ + over −, will attract.



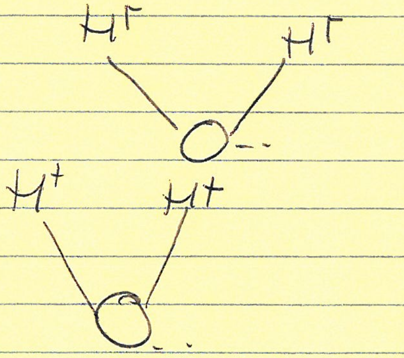
Highly charged surfaces: not much free charge.

Good review by Y. Levin, R. Adelman

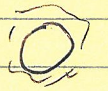
- H bonds

Cohesive energy in H_2O provided by H bond network.

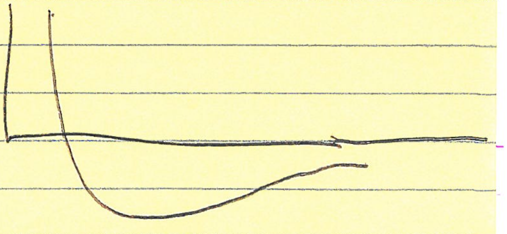
H ion very small, pointlike so it can get close.



$z=16$ $z+2$ electrons



The pot. a proton sees is like so it would like to sit on the charged surface.

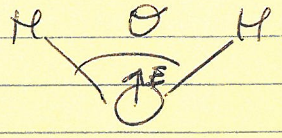


O^- is very polarizable so if H^+

doesn't sit on surface but a bit further, there is an E field so energy is:

$$U = -\frac{2e^2}{a} - \frac{1}{2}\alpha E^2 + \frac{e^2}{2a\sin\theta}$$

$$E = \frac{2e}{a}\cos\theta$$

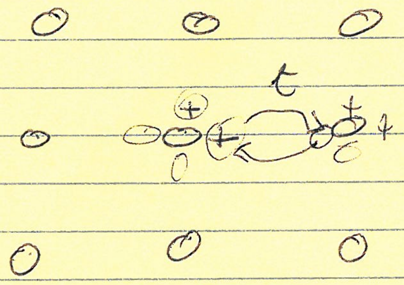


with this we ~~mini~~ minimize it and get $\theta = 109°$

Think of water as lattice, fix oxygen and start adding H^+.

What if I move a proton from one atom to the other?

It would cost energy $U \simeq 0.1 eV$



There is a probability t to do this hop.

So the energy of the state is lowered by $-\frac{t^2}{U}$

$t \sim 5T$

$\downarrow$

This is the way you can think about H bonds.

With this model you can do some calculations and also get hydrophobic interaction.