Lifschitz fixed this.   Pincus will sketch out his way.

If we go to fundamentals, all EM is exchange of photos, creating blackbody radiation with an associated temp T.

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

$$\mathcal{H} = \sum_q \hbar \omega_q \left(n_q + \tfrac{1}{2} \right) \qquad \text{where } n_q = \frac{1}{e^{\hbar \omega_q / T} - 1}$$

$$\hookrightarrow \hbar c q$$

$$F = -T \ln Z$$

$$= T \sum_q \ln \left[2 sh\, \frac{\hbar \omega_q}{2T} \right]$$

Since $E = 0$ at each surface, we can think of plane waves in a waveguide. $\lambda < \frac{D}{2}$.

$$\Pi = -\frac{\partial F}{\partial D} \Rightarrow -\frac{\hbar c}{D^4}$$

Compare this to our simplistic result. We have c ~~Ξ~~ this time. (We also have $\hbar$, but that was actually hidden in there.) For $c \to \infty$ this would diverge too, which shows that our problem originated in ignoring retardation.

This is a <u>depletion interaction</u>! A certain kind of photon is excluded from the center.

Fluctuation Forces

First, recall Flory-Huggins from Rubenstein's talk.

$$\chi \propto \left[U_{AB} - \frac{U_{AA} + U_{BB}}{2} \right]$$

Suppose that these U variables come from $U = -\frac{\epsilon \alpha_1 \alpha_2}{r^6}$.

$$\chi \propto \frac{\epsilon}{r^6} \left[-\alpha_A \alpha_B + \frac{\alpha_A \alpha_A + \alpha_B \alpha_B}{2} \right] = \frac{\epsilon}{2 r^6} (\alpha_A - \alpha_B)^2 > 0$$

Using $U \propto r^{-6}$ as an additive pairwise interaction is wrong, but for insulators it mostly works.

HW: Change half-space ~~conductors~~ insulators to ~~conductors of~~ insulators with t. $\Pi = -\frac{A}{D^3} g(t/D)$

Thinking back to <u>conducting</u> walls...

Free Energy of blackbody radiation
$$F = T \sum_q \ln \left[2 \sinh \frac{\hbar \omega(q)}{T} \right] \qquad \omega(q) = cq$$

$$\Pi \propto -\frac{\hbar c}{D^4}$$

If we consider a more realistic imperfect conductor, we need $\varepsilon(q, \omega)$, modifying $\omega(q) = cq$.

We can imagine that as we dial between a perfect conductor $(\Pi \propto -D^{-4})$ and an insulator $(\Pi \propto -D^{-3})$ there is some transition parameter $\zeta = \frac{AD}{\hbar c}$. OK.

Another way to understand this whole setup: kinetic theory.

$$\Delta p = 2 \hbar q \cos \theta$$
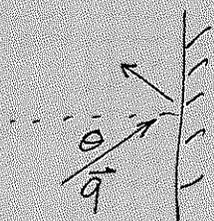
$$\Pi = \frac{1}{(2\pi)^3} \int dq \, du \, (2 \hbar q u) \, c \, n(q) \, q^2 dq \, du$$

where $u = \cos \theta$
and $n(q) = \left[e^{\hbar \omega(q)/T} - 1 \right]^{-1}$

Integrate over excluded modes that are
unbalanced in the interior.

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

If the gap D is large enough that $T > \frac{\hbar c}{D}$, expand exp
and get $\Pi = -\frac{1}{(2\pi)^3} T \int_0^{\pi/D} q^2 dq \approx -\frac{T}{D^3}$ which is
equipartition —
$T \times \#$ modes!

So: Things always attract at high T
in the presence of a medium.

But we are usually not in this limit. $T > \frac{\hbar c}{D} \Rightarrow D \sim 10^{-3} cm.$

Take the other limit. If $T \to 0$ we have to remember
zero point energy: $n = \frac{1}{2} + \dots$

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

HW: What about thin conductors?

We have QM fluctuations, thermal fluctuations, and
BCs. It's messy.

Back to that interpolation idea:

$$\Pi = -\frac{\hbar c}{D^4} \frac{1}{(1 + k\frac{\hbar c}{AD})} \quad \text{at } T = 0$$

$c \to \infty \Rightarrow \Pi \sim -\frac{A}{D^3}$

$c \to 0 \Rightarrow \Pi \sim -\frac{\hbar c}{D^4}$

Electrostatics

The Coulomb interaction, when things are charged (ionized, like salt in water), dominates in soft matter.

Water

It dilectric constant at Troom is $\epsilon = 80$, which is high. ϵ varies with T, but it usually enters as $\frac{e^2}{\epsilon T}$ and ϵT is roughly constant, from freezing to boiling.

Consider salt dissolving.

$$NaCl \leftrightharpoons Na^+ + Cl^-$$
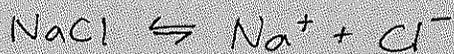
In a vacuum, $V(r) = -\frac{e^2}{a} \sim 10\ eV$

In water, $V(r) \sim \frac{1}{10}\ eV$, close to the level where entropy can ionize it ($\frac{1}{40}\ eV$). But there is more!
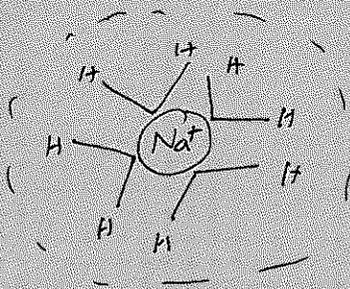
HYDRATION:
Water would love to do this. They become rigidly attached.

This is mysterious. You lose some water entropy; you break H-bonds. It's not understood in detail.

The Na^+ has a much larger effective size, so the charge separation a is enlarged and $V(r)$ is further reduced.

At low T, of course, Coulomb wins over entropy.

DNA is almost the most highly charged molecule known to man. $\sigma \sim 1 \ nm^{-2}$ ← ⟨e/nm²⟩ ~~e/nm²~~

↑ Charge number density

Debye-Hückel theory

What happens when I have ~~some~~ low concentrations of small ions in solution. I have basically a plasma.

All salt is ionized.

Temperate T
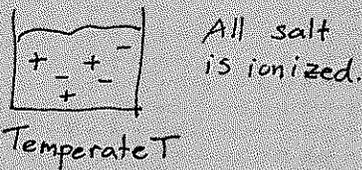
Treat water like a dielectric continuum. It's like a vacuum with a dielectric constant. (Ignore hydration.) Call up Maxwell.

$$\nabla \cdot \vec{D} = 4\pi\rho$$

$$-\epsilon \nabla^2 \phi = 4\pi\rho(\vec{r})$$

But we don't know where the charges are! Take them to be Maxwell-distributed in the potential of ~~the~~ all the other charges. (*Mean Field*)

$$\rho(r) = \frac{c}{z_+} e^{-e\phi/T}$$

$$\rho(r) = ec_+ e^{-e\phi/T} - ec_- e^{e\phi/T} \quad \longleftarrow \quad \text{a mean field approx}$$

c_+ and c_- are, if you like, Lagrange multipliers.

$$-\epsilon \nabla^2 \phi = -8\pi c_0 e \sinh\left(\frac{e\phi}{T}\right)$$

$$\boxed{\nabla^2 \varphi = \kappa^2 \sinh \varphi} \quad \text{where } \varphi = \frac{e\phi}{T} \text{ and } \kappa^2 = 8\pi c_0 \ell$$

Bjerrum length $\ell \equiv \frac{e^2}{\epsilon T} \sim \frac{1}{2} \ nm$

Second-Order Nonlinear D.Eq.

~~Linearized I.~~

To solve this scary D.E, linearize! This assumes $\varphi \rightarrow 0$, which is tantamount to $c_0 \rightarrow 0$.

Debye length $K^{-1} \sim 10 \, nm$ at $1 mM$ salt

$\nabla^2 \varphi = K^2 \varphi$ for small φ. (I used $\sinh x \approx x$.)

$$\varphi = \frac{1}{r} e^{-Kr}$$

Interpretation: A positive charge at the origin pulls $(-)$ closer, pushes $(+)$ away, such that at $r > K^{-1}$, it looks essentially neutral.

From freshman E.M: $U = \frac{1}{2} e \phi$ ← energy per unit volume

$$= \frac{1}{2} e \phi_+ c - \frac{1}{2} e \phi_- c$$

(Recall $\varphi = \frac{e\phi}{T} \Rightarrow \phi = \frac{T\varphi}{er} e^{-Kr}$.)

It diverges at the origin. Damn. ~~Sol~~ Get around this.

$$\varphi \approx \frac{1}{r}(1 - Kr + \dots)$$

$$U \approx -K \ell c = -\frac{TK^3}{8\pi} \propto -c^{3/2}$$

Linearized M.F. theory with a "one loop correction". It's not a virial expansion. The first correction goes at $c^{3/2}$, and it's negative. Fluctuations always lower energy, so it makes sense that it's negative.

Notice that U decreases as c increases. "All neutral systems tend to condense." Only entropy works against this.