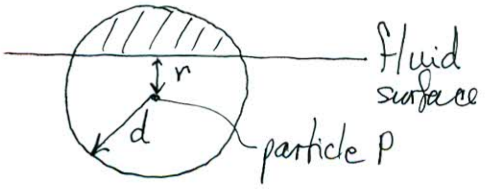
Internal energy of a liquid [Rowlinson & Widom, Dupré (1869), Massieu]

- suppose there is a simple pairwise interaction energy $u(r)$ with range d
  - let $f(r) = -\frac{du}{dr}$ be the force between 2 molecules at separation r

$$\text{if } r>d, \; u(r)=0 \;\&\; f(r)=0$$



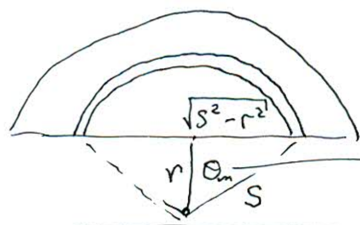
if $r>d \Rightarrow$ no net force on P by symmetry

for $r<d$ the net force is the negative of the outwards force due to shaded region

$$\therefore \text{inwards force } F(r) = \underbrace{-2\pi}_{\text{angular integration}} \underset{\uparrow}{\rho} \underbrace{\int_r^d ds\, s^2 f(s) \int_0^{\cos^{-1}(r/s)} d\theta \sin\theta \underbrace{\cos\theta}_{\text{projection along vertical}}}_{\text{from integrating over shells}}$$

density of particles

$$\int_0^{\cos^{-1}(r/s)} d\theta \sin\theta\cos\theta = \frac{1}{2}\underbrace{\sin^2\left(\cos^{-1}(r/s)\right)}_{\frac{s^2-r^2}{s^2}}$$



θ runs from 0 (vertical) to $\cos^{-1}(r/s)$

$$\therefore F(r) = -2\pi\rho\cdot\frac{1}{2}\int_r^d ds\, s^2 f(s)\frac{(s^2-r^2)}{s^2} = \boxed{-\pi\rho\int_r^d ds\,(s^2-r^2)f(s)}$$

given $F(r)$, we obtain the energy to remove a particle by:

$$\int_{-d}^{d} F(r)dr = \pi\rho\int_{-d}^{d} dr \underbrace{\int_r^d du(s)\,(s^2-r^2)}_{\cancel{(d^2-r^2)u(d)} - \cancel{(r^2-r^2)u(r)} - \int 2s\,u(s)ds}$$

using $f(s)ds = -\frac{du}{ds}ds = -du(s)$

$\downarrow$

internal energy

$$\Rightarrow -2\pi\rho\int_{-d}^{d}dr\int_{r}^{d}s\,ds\,u(s)$$

let $dV = dr \quad V = r$

$\mathcal{U} = \int_{r}^{d}s\,ds\,u(s) \quad d\mathcal{U} = -r\,dr\,u(r)$

$$\parallel$$

$$-2\pi\rho\left[r\int_{r}^{d}s\,ds\,u(s)\Big|_{r=-d}^{d} - \int_{-d}^{d}dr\,(-r)\,r\,u(r)\right]$$

$$d\cancel{\int_{d}^{d}s\,ds\,u(s)} - \underbrace{(-d)\int_{-d}^{d}s\,ds\,u(s)}_{\Rightarrow 0 \text{ since } u(s) \text{ is even}}$$

$$= -2\pi\rho\int_{-d}^{d}dr\,r^2u(r) = -\rho\int_{0}^{d}d^3r\,u(r)$$

and work $= -2\times$(energy to dissociate liquid)

$\Rightarrow$ internal energy $\frac{U}{N} = -\frac{1}{2}\left\{-\rho\int d^3r\,u(r)\right\}$

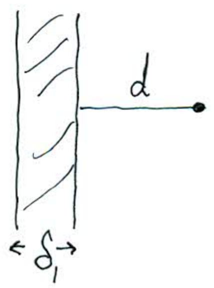
$$\Downarrow$$

$$\frac{U}{N} = \boxed{\frac{1}{2}\rho\int d^3r\,u(r)}$$

Van der Waals interactions

Two slabs

interaction of 1 slab and a single atom a distance d away



$$V_{1S}(d) = -\int_d^{d+\delta_1} dz \int_0^{2\pi} d\phi \int_0^{\infty} r\,dr\,\rho \frac{C}{(z^2+r^2)^3}$$

$$= -2\pi C\rho \int_d^{d+\delta_1} dz \left(-\frac{1}{4}\right) \underbrace{\frac{1}{(z^2+r^2)^2}\Bigg|_0^{\infty}}_{\frac{1}{4z^4}} = -2\pi C\rho \cdot \frac{1}{4}\left(-\frac{1}{3}\right) \cdot \left\{\frac{1}{(d+\delta_1)^3} - \frac{1}{d^3}\right\}$$

$$\therefore \boxed{V_{1S}(d) = -\frac{\pi C\rho}{6}\left\{\frac{1}{d^3} - \frac{1}{(d+\delta_1)^3}\right\}}$$

integrate over slab 2 to get energy/area

$$\frac{E}{A} = -\frac{\pi C\rho^2}{6} \underbrace{\int_d^{d+\delta_2} d\zeta \left\{\frac{1}{\zeta^3} - \frac{1}{(\zeta+\delta_1)^3}\right\}}_{-\frac{1}{2\zeta^2}\Big|_d^{d+\delta_2} + \frac{1}{2(\zeta+\delta_1)^2}\Big|_d^{d+\delta_2}}$$

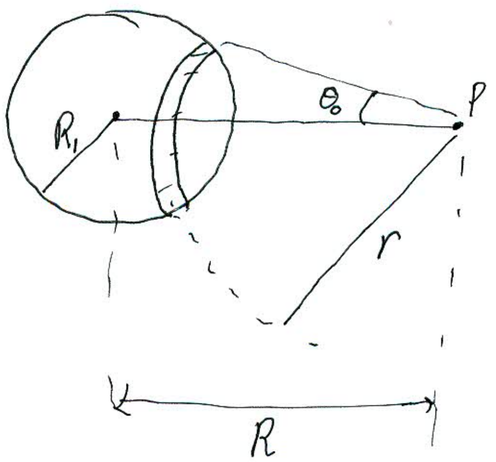
$$\boxed{-\frac{\pi C\rho^2}{12}\left\{\frac{1}{d^2} - \frac{1}{(d+\delta_1)^2} - \frac{1}{(d+\delta_2)^2} + \frac{1}{(d+\delta_1+\delta_2)^2}\right\}}$$

Taylor expanding one finds $\{\ \} \simeq \frac{6\delta_1\delta_2}{d^2} + \cdots$ for $d \gg \delta_{1,2}$

$$\boxed{\frac{E}{A} \simeq -\frac{\pi C\rho^2}{2} \cdot \frac{\delta_1\delta_2}{d^4}}$$

symmetric $1 \leftrightarrow 2$ as expected

Hamaker's calculation



surface area of shaded slice:

$$\int_0^{2\pi} d\phi \int_0^{\theta_0} d\theta\, r^2 \sin\theta$$

where $R_1^2 = R^2 + r^2 - 2rR\cos\theta_0$

$$2\pi r^2(-\cos\theta)\Big|_0^{\theta_0} = 2\pi r^2(1-\cos\theta_0)$$

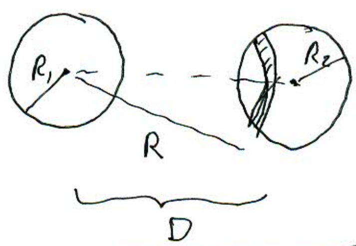
but $\cos\theta_0 = \dfrac{R^2+r^2-R_1^2}{2rR}$

$$\cancel{2}\pi r^{\cancel{2}}\left\{\frac{2Rr-(R^2+r^2-R_1^2)}{\cancel{2}\cancel{r}R}\right\} = \frac{\pi r}{R}\left\{2Rr-(R^2+r^2-R_1^2)\right\} = \frac{\pi r}{R}\left\{R_1^2-(R-r)^2\right\}$$

so, volume of shaded area is $dr \times$

and potential energy of an atom at P $\equiv E_p = -\displaystyle\int_{R-R_1}^{R+R_1} \frac{C\rho}{r^6}\,\pi\frac{r}{R}\left\{R_1^2-(R-r)^2\right\}dr$

if we now integrate over a second sphere whose centre is D from that of #1



total energy is $E = \displaystyle\int_{D-R_2}^{D+R_2} E_p\,\rho\pi\frac{R}{D}\left\{R_2^2-(D-R)^2\right\}dR$

$$= \boxed{-\frac{\pi^2\rho^2 C}{D}\int_{D-R_2}^{D+R_2} dR\,\left\{R_2^2-(D-R)^2\right\}\int_{R-R_1}^{R+R_1} dr\,\frac{\left\{R_1^2-(R-r)^2\right\}}{r^5}} \quad \text{exact}$$

2nd integration $\displaystyle\int_{R-R_1}^{R+R_1} dr\left\{\frac{R_1^2-R^2}{r^5}+\frac{2R}{r^4}-\frac{1}{r^3}\right\} = -\frac{(R_1^2-R^2)}{4}\left\{\frac{1}{(R+R_1)^4}-\frac{1}{(R-R_1)^4}\right\}$

$$-\frac{2R}{3}\left\{\frac{1}{(R+R_1)^3}-\frac{1}{(R-R_1)^3}\right\}+\frac{1}{2}\left\{\frac{1}{(R+R_1)^2}-\frac{1}{(R-R_1)^2}\right\}$$

integration $= -\frac{1}{4}\left\{\frac{R_1-R}{(R+R_1)^3}+\frac{R+R_1}{(R-R_1)^3}\right\}-\frac{2R}{3}\left\{\frac{1}{(R+R_1)^3}-\frac{1}{(R-R_1)^3}\right\}+\frac{1}{2}\left\{\frac{1}{(R+R_1)^2}-\frac{1}{(R-R_1)^2}\right\}$

look at terms:

$$\frac{1}{12}\frac{1}{(R+R_1)^3}\Big[\underbrace{-3R_1-5R}_{2R_1-5(R+R_1)}\Big] \quad +\frac{1}{12}\frac{1}{(R-R_1)^3}\Big[\underbrace{-3R_1+5R}_{2R_1+5(R-R_1)}\Big]$$

$$\frac{1}{12}\left\{\frac{2R_1}{(R+R_1)^3}-\frac{5(R+R_1)}{(R+R_1)^3}+\frac{2R_1}{(R-R_1)^3}+\frac{5(R-R_1)}{(R-R_1)^3}+\frac{6}{(R+R_1)^2}-\frac{6}{(R-R_1)^2}\right\}$$

$$=\frac{1}{12}\left\{\frac{2R_1}{(R+R_1)^3}+\frac{2R_1}{(R-R_1)^3}+\frac{1}{(R+R_1)^2}-\frac{1}{(R-R_1)^2}\right\}$$

$$\therefore\quad E=-\frac{\pi^2\rho^2 C}{12D}\int_{D-R_2}^{D+R_2} dR\left\{R_2^2-(D-R)^2\right\}\left\{\frac{2R_1}{(R+R_1)^3}+\frac{2R_1}{(R-R_1)^3}+\frac{1}{(R+R_1)^2}-\frac{1}{(R-R_1)^2}\right\}$$

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let's quote Hamaker on the final integral:

$$E=-\frac{\pi^2\rho^2 C}{6}\left\{\frac{2R_1R_2}{D^2-(R_1+R_2)^2}+\frac{2R_1R_2}{D^2-(R_1-R_2)^2}+\ln\frac{D^2-(R_1+R_2)^2}{D^2-(R_1-R_2)^2}\right\}$$

let $x=\frac{d}{2R_1}$ $\quad y=\frac{R_2}{R_1}$ $\quad\Rightarrow E(x)=-\pi^2\rho^2 C\,E_y(x)$

$D=R_1+R_2+d$

at $y=1$ $\quad E_1(x)=\frac{1}{12}\left\{\frac{1}{x^2+2x}+\frac{1}{x^2+2x+1}+2\ln\frac{x^2+2x}{x^2+2x+1}\right\}$

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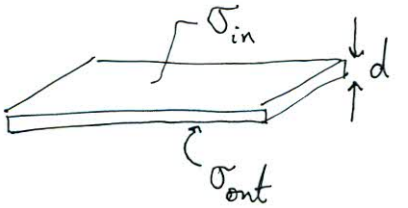
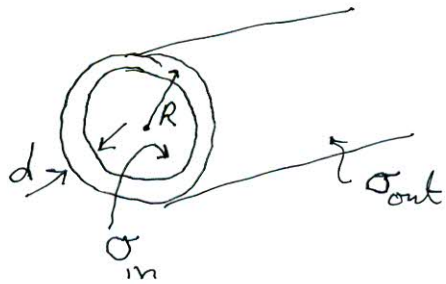
when $x\ll 1$ $\quad E_1(x)\simeq\frac{1}{24x}$

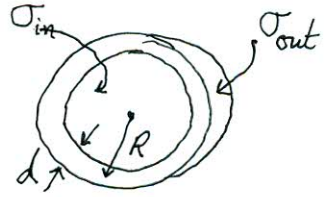
$$\boxed{E\simeq-\frac{\pi^2\rho^2 C\,R}{12d}}$$

Electrostatic contributions to elastic energy of surfaces

The easiest way to do the calculation is to follow Winterhalter + Helfrich, J. Phys. Chem. 92, 6865 (1988) – but take care with units...







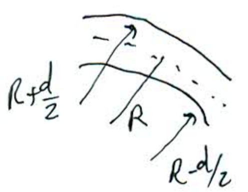
since the plane, cylinder, and sphere have uniform charge densities on both sides we need only focus on the electrostatic energies per unit area $\int ds \frac{1}{2}\sigma\phi$

let's call these factors g_{plane}, g_{cyl}, g_{sp}

notation (W+H): assume that charge densities remain unchanged on bending, letting

$$\boxed{\begin{aligned}\sigma_{in} &= \sigma(1-\delta)\\ \sigma_{out} &= \sigma(1+\delta)\end{aligned}}$$ (defines σ)

by geometry, for the cylinder, the area of the inner surface $A^{(in)}_{cyl}$ relative to the area of a cylinder of radius R, A_{cyl}, is $\frac{A^{(in)}}{A_{cyl}} \simeq 1-\frac{d}{2R}$ & $\frac{A^{(out)}}{A_{cyl}} \simeq 1+\frac{d}{2R}$



Likewise, $\frac{A^{(in)}}{A_{sp}} \simeq 1-d/R$ $\quad \frac{A^{(out)}}{A_{sp}} \simeq 1+d/R$ to the order we need ($1/R^2$)

$$\therefore \quad \boxed{g_{plane} = g^{(in)}_{plane} + g^{(out)}_{plane}}$$

$$\boxed{g_{cyl}} = g^{(in)}_{cyl}\frac{A^{(in)}}{A_{cyl}} + g^{(out)}_{cyl}\frac{A^{(out)}}{A_{cyl}} \simeq \boxed{g^{(in)}_{cyl}\left(1-\frac{d}{2R}\right) + g^{(out)}_{cyl}\left(1+\frac{d}{2R}\right)}$$

$$\boxed{g_{sp}} \simeq g^{(in)}_{sp}\frac{A^{(in)}}{A_{sp}} + g^{(out)}_{sp}\frac{A^{(out)}}{A_{sp}} \simeq \boxed{g^{(in)}_{sp}\left(1-\frac{d}{R}\right) + g^{(out)}_{sp}\left(1+\frac{d}{R}\right)}$$

for a plane:

$$g = \frac{2\pi\lambda\sigma_0^2}{\epsilon} \text{ (one-sided)} \Rightarrow g_{pl}^{(in)} = \frac{2\pi\lambda\sigma_{in}^2}{\epsilon} = 2\pi\frac{\lambda\sigma^2(1-\delta)^2}{\epsilon}$$

$$g_p^{(out)} = \frac{2\pi\lambda\sigma^2(1+\delta)^2}{\epsilon}$$

$$\Rightarrow \boxed{g_{pl}} = \frac{2\pi\lambda\sigma^2}{\epsilon}\left[(1-\delta)^2+(1+\delta)^2\right] = \boxed{\frac{4\pi\lambda}{\epsilon}\sigma^2(1+\delta^2)}$$

cylinder:

inner/outer problems: $(\nabla^2-\kappa^2)\phi = 0$ $\quad \left[r^2\frac{d^2}{dr^2} + r\frac{d}{dr} - (\kappa r)^2\right]\phi = 0$

$\kappa = 1/\lambda$

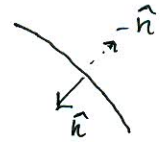
$\phi \sim K_0(\kappa r)$ outer $\quad (K_0 \to 0$ @ $\infty)$

$\sim I_0(\kappa r)$ inner $\quad (I_0$ well behaved as $r \to 0)$

outer: $\boxed{\phi = \frac{4\pi\lambda\sigma_{out}}{\epsilon}\frac{K_0(\kappa r)}{K_1(\kappa R^+)}}$

note: $K_0' = -K_1$

so $-\left.\frac{\partial\phi}{\partial r}\right|_{R^+} = \frac{4\pi\sigma_{out}}{\epsilon}$



$R^+ = R + d/2$

$R^- = R - d/2$

inner $\boxed{\phi = \frac{4\pi\lambda\sigma_{in}}{\epsilon}\frac{I_0(\kappa r)}{I_1(\kappa R^-)}}$

where $I_0' = I_1$

so $\left.\frac{\partial\phi}{\partial r}\right|_{R^-} = \frac{4\pi\sigma_{in}}{\epsilon}$

$$\therefore g_{cyl}^{(in)} = \frac{2\pi\lambda\sigma^2(1-\delta)^2}{\epsilon}\frac{I_0(\kappa R^-)}{I_1(\kappa R^-)}$$

$$g_{cyl}^{(out)} = \frac{2\pi\lambda\sigma^2(1+\delta)^2}{\epsilon}\frac{K_0(\kappa R^+)}{K_1(\kappa R^+)}$$

$$\Rightarrow \boxed{g_{cyl} = \frac{2\pi\lambda\sigma^2}{\epsilon}\left\{(1-\delta)^2(1-d/2R)\frac{I_0(\kappa R^-)}{I_1(\kappa R^-)} + (1+\delta)^2(1+d/2R)\frac{K_0(\kappa R^+)}{K_1(\kappa R^+)}\right\}}$$

finally, the sphere: basic solutions of DH eqn are $\frac{e^{\pm\kappa r}}{r}$

κ

outer
$$\boxed{\phi(r) = \frac{4\pi\sigma_{out}}{\epsilon} \frac{\lambda R^+}{\lambda + R^+} \frac{R^+}{r} e^{-(r-R^+)/\lambda}}$$

inner
$$\boxed{\phi(r) = \frac{4\pi\sigma_{in}}{\epsilon} \frac{\lambda R^-}{[R^- \cosh \kappa R^- - \lambda \sinh \kappa R^-]} \frac{R^-}{r} \sinh(\kappa r)}$$

OK, now we expand everything, starting with the Helfrich energy density

$$g_H = \frac{1}{2} k\left(\frac{1}{R_1} + \frac{1}{R_2} - H_0\right)^2 + \frac{1}{2} k_G \cdot \frac{1}{R_1 R_2}$$

plane: $R_1 = R_2 = \infty$ $\qquad g_H^{pl} = \frac{1}{2} k H_0^2$

cylinder: $R_1 = R$, $R_2 = \infty$ $\qquad g_H^{cyl} = \frac{1}{2} k\left(\frac{1}{R} - H_0\right)^2 = \frac{1}{2} k\left(\frac{1}{R^2} - \frac{2H_0}{R} + H_0^2\right)$

sphere: $R_1 = R_2 = R$ $\qquad g_H^{sp} = \frac{1}{2} k\left(\frac{2}{R} - H_0\right)^2 + \frac{1}{2} k_G \cdot \frac{1}{R^2}$

$$= \frac{1}{2} k\left(\frac{4}{R^2} - \frac{4H_0}{R} + H_0^2\right) + \frac{1}{2} \frac{k_G}{R^2}$$

so, if

$$g_{cyl} = \alpha_{cyl} + \frac{\beta_{cyl}}{R} + \frac{\gamma_{cyl}}{R^2}$$

$$g_{sp} = \alpha_{sp} + \frac{\beta_{sp}}{R} + \frac{\gamma_{sp}}{R^2}$$

then comparing we have

$$\boxed{\begin{aligned} -kH_0 &= \beta_{cyl} \\ -2kH_0 &= \beta_{sp} \end{aligned}}$$

$$\frac{1}{2} k = \gamma_{cyl}$$

$$2k + \frac{1}{2} k_G = \gamma_{sp}$$

$$\Downarrow$$

$$2k = 4\gamma_{cyl} \quad \text{or} \quad \boxed{\frac{1}{2} k_G = \gamma_{sp} - 4\gamma_{cyl}}$$

$$\boxed{k = 2\gamma_{cyl}}$$

$$\boxed{H_0 = -\frac{\beta_{cyl}}{k} = -\frac{\beta_{cyl}}{2\gamma_{cyl}}}$$

$$K_0(z) = \sqrt{\frac{\pi}{2z}}\, e^{-z}\left\{1 - \frac{1}{8z} + \frac{9}{128z^2} + \cdots\right\}$$

$$K_1(z) = \sqrt{\frac{\pi}{2z}}\, e^{-z}\left\{1 + \frac{3}{8z} - \frac{15}{128z^2} + \cdots\right\}$$

$$I_0(z) = \frac{e^z}{\sqrt{2\pi z}}\left\{1 + \frac{1}{8z} + \frac{9}{128z^2} + \cdots\right\}$$

$$I_1(z) = \frac{e^z}{\sqrt{2\pi z}}\left\{1 - \frac{3}{8z} - \frac{15}{128z^2} + \cdots\right\}$$

$$\boxed{\frac{K_0}{K_1}} \sim \frac{\left(1 - \frac{1}{8z} + \frac{9}{128z^2} + \cdots\right)}{\left(1 + \frac{3}{8z} - \frac{15}{128z^2} + \cdots\right)} \simeq \left(1 - \frac{1}{8z} + \frac{9}{128z^2} + \cdots\right)\left(1 - \frac{3}{8z} + \frac{15}{128z^2} + \frac{9}{64z^2} + \cdots\right)$$

$$1 - \frac{3}{8z} + \frac{33}{128z^2} + \cdots$$

$$\simeq \left(1 - \frac{3}{8z} + \frac{33}{128z^2} + \cdots - \frac{1}{8z} + \frac{3}{64z^2} + \frac{9}{128z^2} + \cdots\right) \qquad \frac{33+6+9}{128} = \frac{48}{128} = \frac{3}{8}$$

$$\simeq \boxed{\left(1 - \frac{1}{2z} + \frac{3}{8z^2} + \cdots\right)}$$

$$\boxed{\frac{I_0}{I_1}} \sim \frac{\left(1 + \frac{1}{8z} + \frac{9}{128z^2} + \cdots\right)}{\left(1 - \frac{3}{8z} - \frac{15}{128z^2} + \cdots\right)}$$ as above w/ $z \to -z$

$$\simeq \boxed{\left(1 + \frac{1}{2z} + \frac{3}{8z^2} + \cdots\right)}$$

$$\therefore\ g_{cyl} = \frac{2\pi\lambda\sigma^2}{\epsilon}\left\{(1-\delta)^2(1-d/2R)\left(1 + \frac{\lambda}{2R^-} + \frac{3\lambda^2}{8R^{-2}} + \cdots\right) + (1+\delta)^2(1+d/2R)\left(1 - \frac{\lambda}{2R^+} + \frac{3\lambda^2}{8R^{+2}} + \cdots\right)\right\}$$

note that, apart from leading terms in $1 + \frac{\lambda}{2R} + \frac{3}{8}\frac{\lambda^2}{R^2}$, the $1-d/2R$ factors cancel to the order of interest

so

$$g_{cyl} \simeq \frac{2\pi\lambda\sigma^2}{\epsilon}\left\{\left[(1-\delta)^2 + (1+\delta)^2\right] + \left[(1+\delta)^2 - (1-\delta)^2\right]\cdot\frac{d}{2R} + \left[(1-\delta)^2 - (1+\delta)^2\right]\frac{\lambda}{2R} + \left[(1-\delta)^2 + (1+\delta)^2\right]\cdot\frac{3\lambda^2}{8R^2} + \cdots\right\}$$

and $(1-\delta)^2 + (1+\delta)^2 = 2(1+\delta^2)$ $\qquad (1+\delta)^2 - (1-\delta)^2 = 4\delta$

so $$\boxed{g_{cyl} = \frac{4\pi\lambda\sigma^2}{\epsilon}\left\{(1+\delta^2)\left[1+\frac{3}{8}\frac{\lambda^2}{R^2}\right] + \frac{\delta(d-\lambda)}{R} + \cdots\right\}}$$

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finally, for the sphere

$$g_{sp}^{(out)} = \frac{2\pi\sigma^2(1+\delta)^2}{\epsilon}\,\frac{\lambda R^+}{\lambda+R^+} \simeq \frac{2\pi\sigma^2(1+\delta)^2}{\epsilon}\lambda\left(1-\frac{\lambda}{R^+}+\frac{\lambda^2}{R^{+2}}+\cdots\right)$$

for the inner problem,

$$\phi(R^-) = \frac{4\pi\sigma_{in}}{\epsilon}\,\frac{\lambda R^-}{[R^-\cosh(\kappa R^-)-\lambda\sinh(\kappa R^-)]}\sinh(\kappa R^-) = \frac{4\pi\sigma_{in}}{\epsilon}\,\frac{\lambda}{\coth(\kappa R^-)-\lambda/R^-}$$

but, we are interested in $\kappa R^- \gg 1$ and $\coth \to 1$ exponentially,

$$\therefore\ g_{sp}^{(in)} \simeq 2\pi\frac{\lambda\sigma^2(1-\delta)^2}{\epsilon}\,\frac{1}{1-\lambda/R^-} \simeq \frac{2\pi\lambda\sigma^2}{\epsilon}(1-\delta)^2\left(1+\frac{\lambda}{R^-}+\frac{\lambda^2}{R^{-2}}+\cdots\right)$$

and $$g_{sp} = \frac{2\pi\lambda\sigma^2}{\epsilon}\left\{(1-\delta)^2\left(1-\frac{d}{R}\right)\left(1+\frac{\lambda}{R^-}+\frac{\lambda^2}{R^{-2}}+\cdots\right) + (1+\delta)^2\left(1+\frac{d}{R}\right)\left(1-\frac{\lambda}{R^+}+\frac{\lambda^2}{R^{+2}}+\cdots\right)\right\}$$

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here we have to be careful at order $1/R^2$ since $R^\pm = R \pm d/2R$ whereas we have factors $(1\pm d/R)$

when the dust settles,

$$\boxed{g_{sp} = \frac{4\pi\lambda\sigma^2}{\epsilon}\left\{(1+\delta^2)\left[1+\frac{1}{R^2}\left(\lambda^2-\frac{\lambda d}{2}\right)\right] + \delta\cdot\frac{2}{R}(d-\lambda)\right\}}$$

!!

Thus, referring back to p.3,

$$\boxed{k = \frac{4\pi\lambda\sigma^2}{\epsilon}(1+\delta^2)\cdot\frac{3}{4}\lambda^2} \sim \frac{\sigma^2\lambda^3}{\epsilon}$$

$$\boxed{\frac{1}{2}k_a = -\frac{4\pi\lambda\sigma^2(1+\delta^2)}{\epsilon}\cdot\frac{1}{2}(\lambda^2+\lambda d)}$$

$$\boxed{H_0 = \delta\cdot\frac{4}{3\lambda}\frac{(1-d/\lambda)}{(1+\delta^2)}} \sim \frac{\text{charge density difference}}{\text{mean charge density}}\cdot\frac{1}{\lambda}$$

dimensionally sensible

so $H_0^{-1} \sim$ nanometers

$$k, k_a \sim 4\pi\frac{\sigma^2\lambda^3}{\epsilon} \sim 10^{-11}\,\text{erg} \quad \text{when } \sigma \sim \frac{1e}{10^2 Å^2}$$

Interaction of charged surfaces

$+d/2$ ———————— $\sigma = \alpha \cos kx$

$-d/2$ ———————— $\sigma = \alpha \cos(kx + \theta) = \alpha \cos kx \cos\theta - \alpha \sin kx \sin\theta$

use $-\hat{n} \cdot \nabla \phi \Big|_{\text{surface}} = \dfrac{4\pi\sigma}{\epsilon}$ $\quad \mathcal{F} = \frac{1}{2} \int ds\, \sigma \phi$ is energy

$\uparrow$ outward

top surface: $-\hat{n} = -(-)\dfrac{\partial}{\partial z} = \dfrac{\partial}{\partial z}$

bottom surface: $-\hat{n} = -\dfrac{\partial}{\partial z}$

$$\boxed{\begin{aligned} \left.\frac{\partial \phi}{\partial z}\right|_{d/2} &= \frac{4\pi\alpha \cos kx}{\epsilon} \\ \left.\frac{\partial \phi}{\partial z}\right|_{-d/2} &= -\frac{4\pi\alpha}{\epsilon}\{\cos kx \cos\theta - \sin kx \sin\theta\} \end{aligned}}$$

key point: general form of ϕ:

$$\phi = \cos kx\left[A \cosh \kappa_k y + B \sinh \kappa_k y\right] + \sin kx\left[D \cosh \kappa_k y + E \sinh \kappa_k y\right]$$

where $\kappa_k^2 \equiv \kappa^2 + k^2$

Debye-Huckel $(\nabla^2 - \kappa^2)\phi = 0 \quad \kappa = 1/\lambda$

$\therefore$ (comparing terms) top

$$\frac{4\pi\alpha}{\epsilon} = \kappa_k\left[A \sinh \kappa_k d/2 + B \cosh \kappa_k d/2\right] \quad (a)$$

$$0 = \kappa_k\left[D \sinh \kappa_k d/2 + E \cosh \kappa_k d/2\right] \quad (b)$$

let $\xi = \kappa_k d/2$

$$\Rightarrow E = -D \tanh \kappa_k d/2 = -D \tanh \xi$$

bottom

$$\kappa_k\left[-A \sinh\xi + B \cosh\xi\right] = -\frac{4\pi\alpha}{\epsilon}\cos\theta \quad (c)$$

$$\kappa_k\left[-D \sinh\xi + E \cosh\xi\right] = \frac{4\pi\alpha}{\epsilon}\sin\theta \quad (d)$$

combining (a) & (c) (add)

$$2\kappa_k B \cosh\xi = \frac{4\pi\alpha}{\epsilon}(1 - \cos\theta) \Rightarrow \boxed{B = \frac{2\pi\alpha}{\epsilon}\frac{(1-\cos\theta)}{\kappa_k \cosh\xi}}$$

subtract $\rightarrow$ $2AK_k \sinh\xi = \frac{4\pi\alpha}{\epsilon}(1+\cos\theta) \Rightarrow \boxed{A = \frac{2\pi\alpha}{\epsilon}\frac{(1+\cos\theta)}{K_k \sinh\xi}}$

so,

$$\boxed{\begin{aligned}\phi = &\frac{2\pi\alpha}{\epsilon K_k}\left\{\frac{(1+\cos\theta)}{\sinh\xi}\cosh K_k y + \frac{(1-\cos\theta)}{\cosh\xi}\sinh K_k y\right\}\cos kx \\ &+ \frac{2\pi\alpha}{\epsilon K_k}\left\{-\frac{\sin\theta}{\sinh\xi}\cosh K_k y + \frac{\sin\theta}{\cosh\xi}\sinh K_k y\right\}\sin kx\end{aligned}}$$

energy $\frac{1}{2}\sigma\phi$ at top $= \frac{1}{2}\alpha\cos kx \cdot \frac{2\pi\alpha}{\epsilon K_k}\left\{[\ ]\cos kx + [\ ]\sin kx\right\}$

integrates out

$$= \frac{\pi\alpha^2}{\epsilon K_k}\left\{(1+\cos\theta)\coth\xi + (1-\cos\theta)\tanh\xi\right\}\cos^2 kx \quad + \text{irrelevant}$$

bottom $\frac{1}{2}\alpha \cdot \frac{2\pi\alpha}{\epsilon K_k}\left\{\cos kx\cos\theta - \sin kx \sin\theta\right\}\left\{[\ ]\cos kx + [\ ]\sin kx\right\}$

$$[\ ]\cos\theta\cos^2 kx + \text{cross terms} - \sin\theta[\ ]\sin^2 kx$$

$$= \frac{\pi\alpha^2}{\epsilon K_k}\Big\{\cos\theta\left[(1+\cos\theta)\coth\xi - (1-\cos\theta)\tanh\xi\right]\cos^2 kx$$
$$-\sin\theta\left[-\sin\theta\coth\xi - \sin\theta\tanh\xi\right]\sin^2 kx\Big\}$$

averaging over 1 period $\langle\cos^2 kx\rangle = \langle\sin^2 kx\rangle = \frac{1}{2}$

$$\tilde{\gamma} = \frac{\pi\alpha^2}{2\epsilon K_k}\Big\{(1+\cos\theta)\coth\xi + (1-\cos\theta)\tanh\xi + \cos\theta(1+\cos\theta)\coth\xi$$
$$-\cos\theta(1-\cos\theta)\tanh\xi + \sin^2\theta\coth\xi + \sin^2\theta\tanh\xi\Big\}$$

$$= \frac{\pi\alpha^2}{2\epsilon K_k}\Big\{\coth\xi + 2\cos\theta\coth\xi + \tanh\xi - 2\cos\theta\tanh\xi + \coth\xi + \tanh\xi\Big\}$$

so, $$\boxed{\tilde{f} = \frac{\pi\alpha^2}{\epsilon K_h}\left\{ \mathrm{COTH}\,\xi + \mathrm{TANH}\,\xi + \left[\underbrace{\mathrm{COTH}\,\xi - \mathrm{TANH}\,\xi}_{>0}\right] \cos\theta \right\}}$$

$\therefore$ energy is minimized for $\theta = \pi$

OUT OF PHASE! as expected

(like charges repel)

+++ — — — +++ — — —

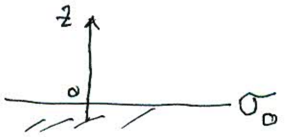
— — — +++ — — — +++

Poisson-Boltzmann in $d=1$

$$\boxed{\frac{d^2\phi}{dz^2} - \frac{8\pi c e}{\epsilon}\sinh(\beta e\phi) = 0}$$

let $\psi = \beta e \phi$ $\quad \xi = \frac{z}{\lambda}$ $\quad \frac{1}{\lambda^2} = \frac{8\pi c e^2}{\epsilon k_B T}$

$$(*) \quad \Rightarrow \boxed{\frac{d^2\psi}{d\xi^2} = \sinh\psi}$$



boundary condition : $-\hat{n}\cdot\underset{\sim}{\nabla}\phi\Big|_0 = \frac{4\pi\sigma}{\epsilon}$

$\hat{n} = \hat{e}_z \quad \longrightarrow \quad \frac{\partial\phi}{\partial z}\Big|_0 = -\frac{4\pi\sigma}{\epsilon}$

or

$\frac{1}{\beta e}\frac{\partial\psi}{\partial\lambda\xi} = -\frac{4\pi\sigma_0}{\epsilon}$

$$\boxed{\frac{\partial\psi}{\partial\xi}\Big|_{\xi=0} = -4\pi\tilde{\sigma}_0}$$

where $\tilde{\sigma}_0 = \frac{e\lambda}{\epsilon k_B T}\sigma_0$

$*$ has a 1^{st} integral : (multiply by $\frac{d\psi}{d\xi}$) $\quad \frac{d\psi}{d\xi}\frac{d^2\psi}{d\xi^2} = \sinh\psi\,\frac{d\psi}{d\xi}$

integrate

$\frac{1}{2}\left(\frac{d\psi}{d\xi}\right)^2 = \cosh\psi + \text{const}$ $\quad\Big|\quad$ as $\xi\to\infty$ $\frac{d\psi}{d\xi}\to 0$, $\psi\to 0$

so const $= -1$

$$\frac{d\psi}{d\xi} = -\sqrt{2(\cosh\psi - 1)} = -2\sinh(\psi/2)$$

choose this sign
so ψ decreases
as $\xi\to\infty$

$$\Rightarrow \boxed{\frac{d\psi}{d\xi} = -\left(e^{\psi/2} - e^{-\psi/2}\right)}$$

let $\alpha = e^{\psi/2}$ $\quad 2\ln\alpha = \psi$ $\quad d\psi = \frac{2}{\alpha}d\alpha$

$$\frac{d\psi}{\alpha - \frac{1}{\alpha}} = -d\xi = \frac{2}{\alpha}\frac{d\alpha}{\alpha - \frac{1}{\alpha}} = \frac{2d\alpha}{\alpha^2 - 1} = d\alpha\left\{\frac{1}{\alpha-1} - \frac{1}{\alpha+1}\right\}$$

$$d\ln(\alpha-1) - d\ln(\alpha+1) = -d\xi \quad \Rightarrow \quad \ln\frac{\alpha-1}{\alpha+1} = -\xi + \text{const}$$

or $$\frac{\alpha-1}{\alpha+1} = Ae^{-\xi} = \frac{\cancel{e^{\psi/4}}\left(e^{\psi/4} - e^{-\psi/4}\right)}{\cancel{e^{\psi/4}}\left(e^{\psi/4} + e^{-\psi/4}\right)} = \tanh(\psi/4)$$

$$\Rightarrow \boxed{\psi = 4\tanh^{-1}\left(Ae^{-\xi}\right)}$$

PB in $d=1$

now we invoke the bdy condition $\left.\frac{d\psi}{d\xi}\right|_0 = -4\pi\tilde{\sigma}_0$

$$\frac{d\,\mathrm{TANH}^{-1}x}{dx} = \frac{1}{1-x^2} = \mathrm{COSH}^2$$

$$\left.\frac{d\psi}{d\xi} = 4\underbrace{(-Ae^{-\xi})}_{\mathrm{TANH}\,\psi/4}\cdot \mathrm{COSH}^2\,\psi/4\right|_0 = -4\pi\tilde{\sigma}_0$$

or $\underbrace{\mathrm{TANH}\,\psi_0/4\ \mathrm{COSH}^2\psi_0/4}_{\frac{1}{2}\mathrm{SINH}(\psi_0/2)} = \pi\tilde{\sigma}_0$ $\Rightarrow$ $\mathrm{SINH}(\psi_0/2) = 2\pi\tilde{\sigma}_0$

$$\boxed{\psi_0 = 2\,\mathrm{SINH}^{-1}(2\pi\tilde{\sigma}_0)}$$

weak-field limit $\psi_0 \sim 4\pi\tilde{\sigma}_0$

$\left[\phi_0 = \frac{4\pi\lambda\sigma_0}{\epsilon}\ \checkmark\right]$

the free energy per unit area is

$$\int^{\sigma_0}\phi(\sigma')\,d\sigma' \qquad \phi = \frac{\psi}{\beta e} \qquad \sigma = \frac{\epsilon k_B T}{e\lambda}\tilde{\sigma}$$

$$\Downarrow$$

$$\frac{\epsilon(k_BT)^2}{e^2\lambda}\int_0^{\tilde{\sigma}_0}\psi(\tilde{\sigma}')\,d\tilde{\sigma}'$$

and

$$2\int_0^{\tilde{\sigma}_0}\mathrm{SINH}^{-1}(2\pi\sigma)\,d\sigma = 2\cdot\frac{1}{2\pi}\int_0^{2\pi\tilde{\sigma}_0}\mathrm{SINH}^{-1}(y)\,dy = \frac{1}{\pi}\left\{y\,\mathrm{SINH}^{-1}y - \sqrt{1+y^2}\right\}\Big|_0^{2\pi\tilde{\sigma}_0}$$

$$= \boxed{\frac{1}{\pi}\left\{2\pi\tilde{\sigma}_0\,\mathrm{SINH}^{-1}(2\pi\tilde{\sigma}_0) + 1 - \sqrt{1+(2\pi\tilde{\sigma}_0)^2}\right\}}$$

when the charge density is low, we Taylor expand and obtain

$$\int\phi\,d\sigma \sim \frac{\epsilon(k_BT)^2}{e^2\lambda}\cdot\frac{1}{\pi}\cdot\frac{1}{2}(2\pi\tilde{\sigma}_0)^2 = \frac{\epsilon(k_BT)^2}{e^2\lambda}\cdot 2\pi\tilde{\sigma}_0^2$$

$\tilde{\sigma}_0 = \frac{e\lambda}{\epsilon k_B T}\sigma_0$ so $\frac{\text{free energy}}{\text{area}} \to \frac{\epsilon (k_B T)^2}{e^2 \lambda} \cdot 2\pi \cdot \frac{e^2\lambda^2}{\epsilon^2 (k_B T)^2}\sigma_0^2$

$$= \frac{2\pi\lambda\sigma_0^2}{\epsilon}, \text{ which is correct.}$$

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putting this together with the vdW interaction between 2 membranes (using weak-field limit of electrostatics derived in class)

$$\frac{\text{free energy}}{\text{area}} = \frac{2\pi\sigma_0^2\lambda}{\epsilon}\left\{\coth\left(\frac{d}{2\lambda}\right)-1\right\} - \frac{A}{12\pi}\left\{\frac{1}{d^2}+\frac{1}{(d+2\delta)^2}-\frac{2}{(d+\delta)^2}\right\}$$

scale distances by δ : $d = \delta\zeta$ ζ dimensionless

scale $\frac{\text{energy}}{\text{area}}$ by $\frac{A/\delta^2}{12\pi}$

$$\boxed{\hat{f} = \frac{12\pi(\text{energy/area})}{A/\delta^2} = \Sigma_0\left\{\coth(\zeta l)-1\right\} - \left\{\frac{1}{\zeta^2}+\frac{1}{(\zeta+2)^2}-\frac{2}{(\zeta+1)^2}\right\}}$$

where $l = \frac{\delta}{2\lambda}$ and $\Sigma_0 = \frac{24\pi^2\sigma_0^2\delta^2\lambda}{\epsilon A}$

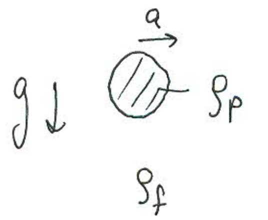
see Matlab program dlvo.m for plotted examples.

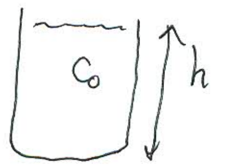
note: $\delta \sim$ a few nm $\quad l \sim 0.1$ or so

$\lambda \sim 10$ nm

Σ_0 can vary from <1 to $\gg 1$ depending on charge density, etc.

Sedimentation





$$j = -D\frac{\partial c}{\partial z} - \frac{\Delta\rho \cdot v \cdot g}{\zeta} c$$

v = particle volume $= \frac{4}{3}\pi a^3$

ζ = drag coeficient $= 6\pi \eta a$

η: viscosity

note Stokes–Einstein relation $D = \frac{k_B T}{\zeta}$

$$\therefore\ j = D\left(-\frac{\partial c}{\partial z} - \frac{\Delta m g c}{k_B T}\right)$$

$\Delta m = v(\rho_p - \rho_f)$

define $l = k_B T/\Delta m g$, a length

equilibrium: $j = 0 \Rightarrow c(z) = A e^{-z/l}$

normalization $c_0 = \frac{1}{h}\int_0^h c(z)dz = \frac{A}{h}(-l)(e^{-h/l} - 1) = +\frac{Al}{h}(1 - e^{-h/l})$

$\therefore A = \frac{c_0 h}{l}\frac{1}{1-e^{-h/l}}$

$$\boxed{c(z) = c_0 \cdot \frac{h}{l}\frac{e^{-z/l}}{1-e^{-h/l}}}$$

$$\boxed{\frac{c(h)}{c(0)} = e^{-h/l}}$$

here, with $\rho_p - \rho_f < 0$, $l < 0$ $\qquad \frac{c(h)}{c(0)} = e^{h/|l|}$

$0.91 - 1$

$\simeq -0.1\, g/cm^3$

$$|l| = \frac{k_B T}{\frac{4}{3}\pi a^3 (0.1 \frac{g}{cm^3}) \cdot 10^3 \frac{cm}{s^2}} \sim \frac{4\times 10^{-14}\, erg}{4\cdot 10^{-12} cm^3 \cdot 10^2 \frac{g\, cm}{s^2}} \simeq \boxed{10^{-4}\, cm}$$

$a \sim 1\,\mu m = 10^{-4}\, cm$

so $\frac{h}{|l|} \gg 1$ all particles @ surface

milk is an <u>emulsion</u>, not really a colloidal suspension