soft matter - problem set 1

1. a) Buoyant mass: $m^* = V(\rho_c - \rho_s)$,

sort of 'effective' mass of a colloidal particle of mass density ρ_c in a solvent of mass density ρ_s

$$F_g = m^* g = V(\rho_c - \rho_s) g = V \Delta\rho\, g.$$

b). $F_{up} = -\frac{1}{n(h)} \frac{d\Pi}{dh}$ $\quad [\Pi] \to$ pressure $\to \frac{N}{m^2}$

$[h] \to$ length $\to m$

$[n(h)] \to$ number density $\to \frac{1}{m^3}$

$$\therefore [F_{up}] = \frac{1}{\left(\frac{1}{m^3}\right)} \cdot \frac{\left(\frac{N}{m^2}\right)}{m} = \frac{m^3}{m}\left(\frac{N}{m^2}\right) = N \quad \to \text{force} \checkmark$$

c). $\Pi(h) = n(h) k_B T$ $\quad$ Force balance: $F_{up} + F_{down} = 0$

$$\left.\begin{aligned} \therefore\ F_{up} &= F_{down} \\ \frac{1}{n(h)}\frac{d\Pi}{dh} &= -V\Delta\rho g \\ \frac{d\Pi}{dh} = \frac{d}{dh}(n(h)kT) &= kT\frac{dn(h)}{dh} \end{aligned}\right\} \quad \frac{kT}{n(h)}\frac{dn(h)}{dh} = -V\Delta\rho g$$

as $\frac{1}{x}dx = d\ln x$

$$\int_{n(h=0)}^{n(h)} \frac{1}{n(h)}\, dn(h) = -\frac{V\Delta\rho g}{kT}\int_{h=0}^{h} dh$$

$$\Rightarrow \ln\frac{n(h)}{n(0)} = \frac{-V\Delta\rho g h}{kT} \to n(h) = n(0)\exp\left[-\frac{\Delta\rho V g h}{kT}\right].$$

$h = l_g$: gravitational length.

d). $\frac{n(h)}{n(0)} = \frac{1}{e} = \exp\left(-\frac{\Delta\rho V g}{kT} l_g\right)$

$\Rightarrow \frac{\Delta\rho V g\, l_g}{kT} = 1 \rightarrow l_g = \frac{k_B T}{\Delta\rho V g}$

$V = \frac{\pi}{6} d^3$ (d = diameter) $\rightarrow l_g = \frac{6 kT}{\Delta\rho \pi d^3 \cdot g}$

$\rho_c = 1.05\ g\,cm^{-3}$
$\rho_s = 1.00\ g\,cm^{-3}$ } $\Delta\rho = 0.05\ g\,cm^{-3} = 0.05 \cdot 10^3 \frac{kg}{m^3} = 50 \frac{kg}{m^3}$.
$g = 9.81\ m\,s^{-2}$
$T = 300\ K$

	d (m)	l_g	
50 :	$0.1 \cdot 10^{-6}$	$0.016\ m = 16\ mm$	→ hardly any sediment
	$1 \cdot 10^{-6}$	$16\ \mu m$	→ sediment
	$10 \cdot 10^{-6}$	$16\ nm$	→ dense sediment

note: $l_g \sim \frac{1}{d^3}$: hence steps of 10^3 in l_g above.

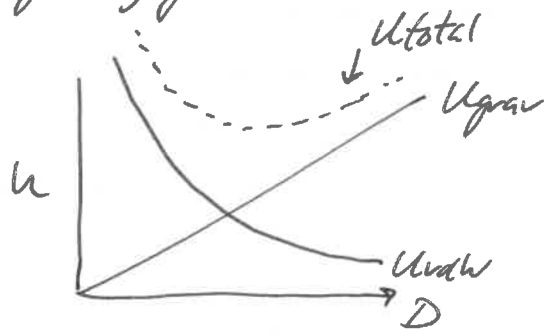
Oxygen: no buoyant mass! $F_g = m \cdot g$.

$l_g = \frac{k_B T}{m g}$
$m_{O_2} \simeq 16 \cdot 1.66 \cdot 10^{-27}\ kg$ } $l_g = \frac{4 \cdot 10^{-21}}{16 \cdot 1.66 \cdot 10^{-27} \cdot 9.81} \simeq 15\ km$.

(so much much larger than colloids & on order of Mount Everest, that's why you can't breathe well up there).

② $U_{vdw} = \dfrac{-A}{12\pi D^2}$ $A = -7\cdot10^{-21}\,J$

$U_{grav} = \rho g h D$

a). 

$U_{total} = U_{vdw} + U_{grav}$

$= -\dfrac{A}{12\pi D^2} + \rho g h D.$

b). equil. thickness → U_{tot} = minimal : $\dfrac{dU}{dD} = 0$

$U_{tot} = \dfrac{-A}{12\pi D^2} + \rho g h D \rightarrow \dfrac{dU}{dD} = \dfrac{A}{6\pi D^3} + \rho g h = 0$

$D_{eq.}(h = 0.01\,m) = \left(\dfrac{-A}{6\pi\rho g h}\right)^{1/3} = \left(\dfrac{7\cdot10^{-21}}{6\pi\cdot703\cdot9.81\cdot0.01}\right)^{1/3}$

$= 1.75\cdot10^{-8}\,m = 17.5\,nm$

c). w | vac | o → so: (w) (o) in vacuum

from lectures: $A_{wo} \simeq \sqrt{A_{ww}A_{oo}} = \sqrt{3.7\cdot10^{-20}\cdot5.1\cdot10^{-20}}$

$A_{wo} = 4.3\cdot10^{-20}\,J.$

d). $A_{132} = A_{12} + A_{33} - A_{13} - A_{23}$

air (2)
oil (3)
water (1)

$A_{woa} = A_{wa} + A_{oo} - A_{wo} - A_{oa}$

$A_{oo} = 5.1\cdot10^{-20}\,J$ & $A_{wo} = 4.3\cdot10^{-20}\,J$ (from c)

now: A_{wa} & A_{oa} are both ≈ 0 as $A = C\rho_1\rho_2\pi^2$

and because $\rho_{air} \ll \rho_w, \rho_o$ & $\rho_{air} \rightarrow 0$

so: $A_{woa} = A_{oo} - A_{wo} = 5.1\cdot10^{-20} - 4.3\cdot10^{-20} = 0.8\cdot10^{-20}\,J > 0$

e). $U = -\dfrac{A}{12\pi D^2}$ A > 0 (see d), so water-air across oil have attractive interaction, hence oil will be "pushed" out: dewetting

∴ oil will not spread on water

(3) $k^{-1} = \sqrt{\dfrac{\varepsilon \varepsilon_0 k_B T}{2 e^2 n_0 z^2}}$

$T = 298\,K$

a). 1.00 mM KNO_3, $\varepsilon = 78$, $\varepsilon_0 = 8.85 \cdot 10^{-12} \frac{C^2}{Nm^2}$, $e = 1.6 \cdot 10^{-19}\,C$, $z = 1$

n_0 = number density! $n_0 = \frac{N_+}{V} = \frac{N_-}{V} = \frac{N}{V}$

conc: $C = \frac{mol}{V}$

$C \cdot N_{AV} = n_0$

$C = 1 \cdot 10^{-3} \frac{mol}{dm^3} = 1 \frac{mol}{m^3}$

$$k^{-1} = \sqrt{\frac{8.85 \cdot 10^{-12} \cdot 78 \cdot 1.38 \cdot 10^{-23} \cdot 298}{2 \cdot (1.6 \cdot 10^{-19})^2 \cdot \underset{\uparrow n_0}{1} \cdot \underset{\uparrow N_{AV}}{6 \cdot 10^{23}}}} = 9.6 \cdot 10^{-9}\,nm \quad (\simeq 10\,nm).$$

b). i). $C = 1.75 \cdot 10^{-3}\,M$ KNO_3 — this is larger than c in a), and $k^{-1} \sim \frac{1}{\sqrt{c}}$ so Debye length will decrease

(ii). 1.00 mM K_2SO_4 $\rightarrow$ KNO_3 is a 1:1 electrolyte $z=1$, but K_2SO_4 is a 2:1 electrolyte, so dissolving the same amount in water will result in a higher salt concentration (ionic strength) Debye length decreases.

c). $$\Phi(x) = 2 \ln \left[\frac{1 + \tanh(\Phi_0/4) \cdot e^{-kx}}{1 - \tanh(\Phi_0/4) \cdot e^{-kx}} \right].$$

$\tanh(x) \simeq x$: $$\Phi(x) = 2 \ln \left[\frac{1 + \Phi_0/4 \cdot e^{-kx}}{1 - \Phi_0/4 \cdot e^{-kx}} \right]$$

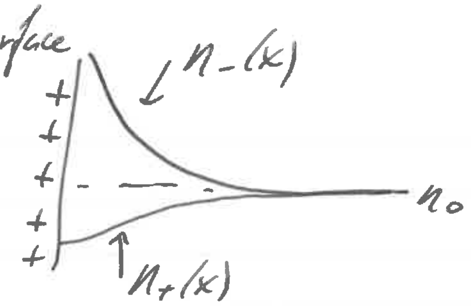
$$\Phi(x) = 2 \left\{ \ln\left(1 + \frac{\Phi_0}{4} e^{-kx}\right) - \ln\left(1 - \frac{\Phi_0}{4} e^{-kx}\right) \right\}$$

$\ln(1+x) \simeq x$: $$\Phi(x) = 2 \cdot \left\{ \frac{\Phi_0}{4} e^{-kx} - \frac{-\Phi_0}{4} e^{-kx} \right\} =$$

$$= 2 \cdot \left(\frac{2\Phi_0}{4} e^{-kx} \right) \Rightarrow \Phi(x) = \Phi_0 e^{-kx}$$

(solution to lin. Poisson-Boltzmann eq.).

d). see lectures:



close to charged wall: excess of counter-ions and depletion of co-ions compared to bulk concentration n_0.

→ this region is called the <u>electric double layer</u> and its thickness is characterised by the <u>Debye length</u> → $\Phi(x) = \Phi_0 e^{-\kappa x}$

also seen as typical decay length for $\Phi(x)$.

e). $\sigma = -\int_0^\infty \rho(x)\,dx \qquad \rho(x) = -2ze n_0 \Phi(x)$ (note linearised version of full $\rho(x)$)

$\Phi_0 = ze\beta\phi_0 \qquad \beta = \frac{1}{kT}$

$$\sigma = \int_0^\infty + 2zen_0 \cdot \Phi(x)\,dx = \int_0^\infty 2zen_0 \Phi_0 e^{-\kappa x} dx$$

$$= 2zen_0 \cdot ze\beta\phi_0 \int_0^\infty e^{-\kappa x} dx = \frac{2z^2e^2n_0}{kT}\phi_0 \left[\frac{-1}{\kappa}e^{-\kappa x}\right]_0^\infty$$

$$= \frac{2z^2e^2n_0}{kT}\phi_0\left[-\frac{1}{\kappa}\cancel{e^{-\infty}} + \frac{1}{\kappa}e^0\right] = \boxed{\frac{2z^2e^2n_0}{kT}}\frac{\phi_0}{\kappa}$$

$$\kappa^2 = \frac{2e^2z^2n_0}{\varepsilon\varepsilon_0 kT} \longrightarrow = \varepsilon_0\varepsilon\kappa^2$$

$$\therefore \sigma = \varepsilon\varepsilon_0\kappa\phi_0$$

f). $\sigma = 1e/nm^2 = \frac{1.6\cdot10^{-19}}{(10^{-9})^2} = 0.16\ C/m^2$, $\underbrace{C = 0.1M\ NaCl}$

$\varepsilon = 78 \quad \varepsilon_0 = 8.85\cdot10^{-12}\ C/Vm^2$

either fully calculate κ^{-1} or use that $\kappa^{-1} \sim \frac{1}{\sqrt{c}}$

$\kappa^{-1} \simeq 1nm$ as $C = 100mM = 100\times$ larger than $1mM$ in part a so $\kappa^{-1} \sim \frac{1}{\sqrt{c}} \to \kappa^{-1}$ $10\times$ smaller than $10nm$.

$$\phi_0 = \frac{\sigma}{\varepsilon\varepsilon_0\kappa} = \frac{\sigma\cdot\kappa^{-1}}{\varepsilon\varepsilon_0} = \frac{0.16\cdot1\cdot10^{-9}}{78\cdot8.85\cdot10^{-12}} \simeq 0.22V \simeq 220mV$$

~~so~~ $\phi_0 \gg 26mV$, so Lin. PB is typically not applicable for colloids, (yet very insightfull!)

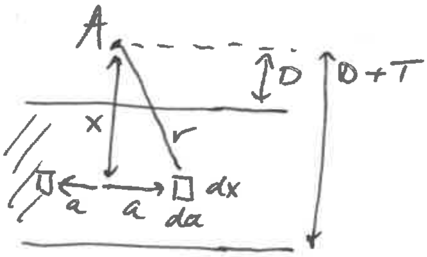
4 a). $U = -\frac{AR}{12D}$

i). $U = \frac{-6\cdot10^{-20}\cdot 0.5\cdot10^{-6}}{12\cdot100\cdot10^{-9}} = -2.5\cdot10^{-20}\,J. \quad \gg kT$

ii). $U = \frac{-0.8\cdot10^{-20}\cdot0.5\cdot10^{-6}}{12\cdot100\cdot10^{-9}} = -3.3\cdot10^{-21}\,J \qquad \approx kT$

iii). $k_BT \simeq 4\cdot10^{-21}\,J$, so in vacuum attr. is much stronger than kT
→ particles will stick.
in water $U \approx kT$ → so much less sticking, prob. even stable colloidal system.

b). follow derivation in lecture, but diff. boundary conditions.
• interaction atom A with mlc in ~~ring~~ ring of radius a



- number of particles in ring: $\rho\, 2\pi a\, da\, dx$
- interaction: $-\frac{C}{r^6} = \frac{-C}{(x^2+a^2)^3}$

$$\Rightarrow U = -C\cdot 2\pi\rho \int_D^{D+T} dx \int_0^\infty da \frac{a}{(x^2+a^2)^3}$$

to integrate $\int da$ → realise $\frac{1}{\ldots+a^2}$ → so rewrite to get $da \to da^2$

$\frac{da^2}{da} = 2a \to da^2 = 2a\,da \Rightarrow$ hence $a\,da = \frac{1}{2}da^2$

$$\Rightarrow U = -2\pi\rho C \int_D^{D+T} dx\, \underbrace{\frac{1}{2}\int_0^\infty \frac{da^2}{(x^2+a^2)^3}}_{y=a^2}$$

$$\frac{1}{2}\int_0^\infty \frac{dy}{(x^2+y)^3} = \frac{1}{2}\int_0^\infty (x^2+y)^{-3}dy$$

$$= \frac{1}{2}\left[-\frac{1}{2}(x^2+y)^{-2}\right]_0^\infty = \frac{1}{4x^4}$$

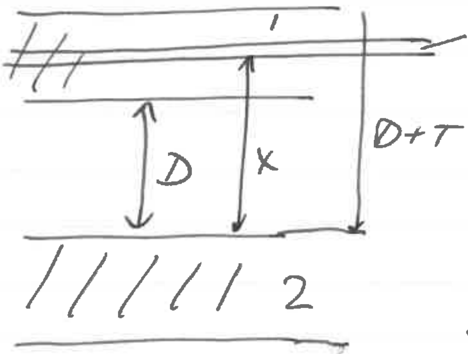
$$\text{So: } U = -2\pi\rho C\int_D^{D+T} dx \frac{1}{4x^4} =$$

$$= \frac{-2\pi\rho C}{4}\left[-\frac{1}{3}x^{-3}\right]_D^{D+T} = \frac{\pi\rho C}{6}\left[\frac{1}{(D+T)^3} - \frac{1}{D^3}\right]$$

$$\Rightarrow U = -\frac{\pi C\rho}{6}\left(\frac{1}{D^3} - \frac{1}{(D+T)^3}\right)$$

interaction between atom and plate of thickness T.

c). now interaction with other plate:



slab 1 with plate 2, thickness dx

number of atoms in slab 1 ~~per area~~ ~~[illegible]~~ $\rho\, dx$ [per unit area].

so interaction: slab-plate 2

$$-\frac{\pi C \rho}{6}\left(\frac{1}{x^3} - \frac{1}{(x+T)^3}\right) \cdot \rho\, dx$$

→ now $\int_D^{D+T} dx$:

$$U = -\frac{\pi C \rho^2}{6}\int_D^{D+T}\left(\frac{1}{x^3} - \frac{1}{(x+T)^3}\right) dx = \frac{-\pi\rho^2 C}{6}\left[-\frac{1}{2x^2} + \frac{1}{2(x+T)^2}\right]_D^{D+T}$$

$$= \frac{-\pi\rho^2 C}{12}\left[-\frac{1}{(D+T)^2} + \frac{1}{(D+2T)^2} + \frac{1}{D^2} - \frac{1}{(D+T)^2}\right] =$$

$$= \frac{-\pi\rho^2 C}{12}\left[\frac{1}{D^2} - \frac{2}{(D+T)^2} + \frac{1}{(D+2T)^2}\right] =$$

$$= \frac{-A}{12\pi}\left[\frac{1}{D^2} - \frac{2}{(D+T)^2} + \frac{1}{(D+2T)^2}\right] \qquad A = \pi^2\rho^2 C$$

$\ast\ T \to \infty$ $\quad U = -\frac{A}{12\pi}\left[\frac{1}{D^2} - \frac{2}{\infty} + \frac{1}{\infty}\right]$

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

✓. interaction between two half-spaces.

4.