Soft Matter - Problem set 1
Solutions

Problem 1

a) Buoyant mass: $m^* = V(\rho_c - \rho_s)$
Sort of 'effective' mass of a colloidal particle of mass density ρ_c in solvent with mass density ρ_s

$$\begin{aligned} F_g &= m^* g \\ &= V(\rho_c - \rho_s)g \qquad \text{(Recognize: } \Delta\rho = \rho_c - \rho_s) \\ &= V\Delta\rho g \end{aligned}$$

b) Recall that:

$$\begin{aligned} [\Pi] &= \text{Pa} = \frac{\text{N}}{\text{m}^2} \\ [h] &= \text{m} \\ [n(h)] &= \frac{1}{\text{m}^3} \end{aligned}$$

Inserting into formula for F_{up}:

$$\begin{aligned} F_{up} &= -\frac{1}{n(h)}\frac{d\Pi}{dh} \\ [F_{up}] &= \frac{1}{\frac{1}{\text{m}^3}}\frac{\frac{\text{N}}{\text{m}^2}}{\text{m}} = \text{m}^3\frac{\text{N}}{\text{m}^3} = \text{N} \end{aligned}$$

c) Force balance: $\sum F = 0$

$$\begin{aligned} F_{up} &= F_g \\ \frac{1}{n(h)}\frac{d\Pi}{dh} &= -V\Delta\rho g \qquad \left[\frac{d\Pi}{dh} = \frac{d}{dh}[n(h)k_\text{B}T] = k_\text{B}T\frac{dn(h)}{dh}\right] \\ \frac{k_\text{B}T}{n(h)}\frac{d\,n(h)}{dh} &= -V\Delta\rho g \\ \int_{n(0)}^{n(h)} \frac{d\,n(h)}{n(h)} &= -\frac{V\Delta\rho g}{k_\text{B}T}\int_0^h dh \\ \ln\frac{n(h)}{n(0)} &= -\frac{V\Delta\rho g h}{k_\text{B}T} \\ n(h) &= n(0)\exp\left[-\frac{V\Delta\rho g h}{k_\text{B}T}\right] \end{aligned}$$

d)

$$\frac{n(h)}{n(0)} = e^{-1}$$

$$\frac{V\Delta\rho g l_g}{k_b T} = -1 \qquad g = l_g (\text{gravitational length})$$

$$l_g = \frac{k_\text{B} T}{V\Delta\rho g} \qquad \text{Recall: } V = \frac{\pi}{6} d^3 \text{ with diameter d}$$

$$l_g = \frac{6 k_\text{B} T}{\Delta\rho g \pi d^3}$$

Now the calculations:

$$d = 0.1\ \mu\text{m} \qquad l_g = \frac{6 \cdot 1.38 \times 10^{-23} \cdot 300}{50 \cdot 9.81 \cdot (0.1 * 10^{-6})^{-3}} = 16\ \text{mm}$$

$$d = 1\ \mu\text{m} \qquad l_g = 16\ \mu\text{m}$$

$$d = 10\ \mu\text{m} \qquad l_g = 16\ \text{nm}$$

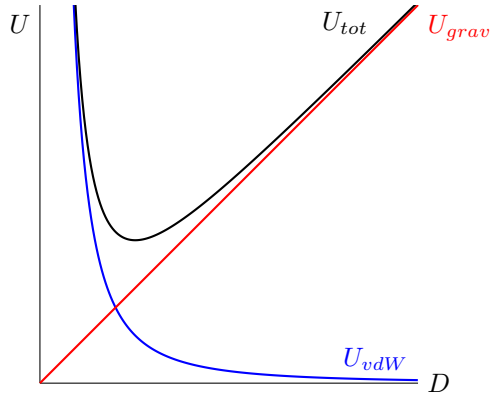
Checking for oxygen molecule: no buoyant mass!

$$l_g = \frac{k_\text{B} T}{mg} = \frac{k_\text{B} \cdot 300}{16 \cdot 1.66 * 10^{-27} \cdot 9.81} \approx 15\ \text{km}$$

Much larger than colloidal particles! Roughly the height of Mount Everest, that's why breathing up there is hard.

Problem 2

a) Use that: $U_{tot} = U_{vdW} + U_{grav}$

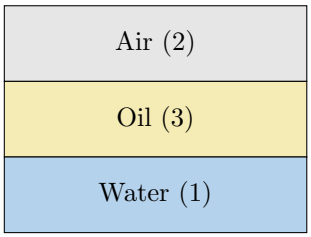


b) Equilibrium thickness → Minimum in U_{tot}.

$$\begin{aligned} U_{tot} &= U_{vdW} + U_{grav} \\ &= -\frac{A}{12\pi D^2} + \rho g h D \\ \frac{dU}{dD} &= -\frac{A}{6\pi D^3} + \rho g h = 0 \\ \frac{A}{6\pi D^3} &= \rho g h \\ D_{eq} &= \sqrt[3]{\frac{A}{6\pi \rho g h}} = \sqrt[3]{\frac{7 \cdot 10^{-21}}{6\pi \cdot 703 \cdot 9.81 \cdot 0.01}} = 1.75 \cdot 10^{-8} \text{ m} = 17.5 \text{ nm} \end{aligned}$$

c) $A_{wo} = \sqrt{A_{ww} A_{oo}} = \sqrt{3.7 \cdot 10^{-20} \cdot 5.1 \cdot 10^{-20}} = 4.3 \cdot 10^{-20}$ J

d) A small picture first:



$$\begin{aligned} A_{132} &= A_{12} + A_{33} - A_{13} - A_{23} \\ A_{woa} &= A_{wa} + A_{oo} - A_{wo} - A_{oa} \end{aligned}$$

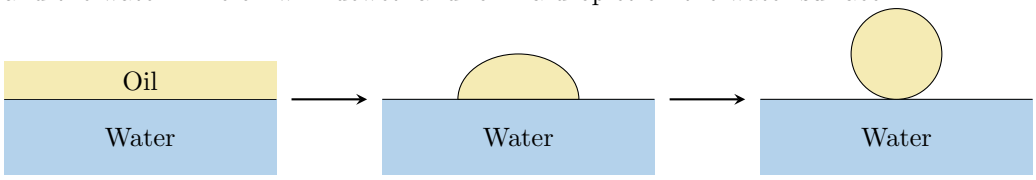
Notice: A_{wa} & A_{oa} are both pretty much 0 due to:
$A = C\rho_1\rho_2\pi^2$
$\rho_{air} << \rho_w, \rho_o$
$\rho_{air} \to 0$.

$$\begin{aligned} A_{woa} &= A_{oo} - A_{wo} \\ &= 5.1 \cdot 10^{-20} - 2.3 \cdot 10^{-20} = 0.8 \cdot 10^{-20} \text{J} \end{aligned}$$

e) Taking a closer look:

$$U = -\frac{A}{12\pi D^2} \quad \text{with} \quad A > 0$$

Which results in a negative sign for U, and thus an attractive interaction between the oil and the water. The oil will 'dewet' and form a droplet on the water surface.



Problem 3

a) Begin from the definition of the Debye length and the known parameters:
$C = 1.00$ mmol KNO_3
$\epsilon = 78$
$\epsilon_0 = 8.85 \cdot 10^{-12}$ $C^2\,N^{-1}\,m^{-2}$
$T = 298$ K
$Z = 1$

$$\begin{aligned}\kappa^{-1} &= \sqrt{\frac{\epsilon\epsilon_0 k_B T}{2e^2 n_0 z^2}} \xrightarrow{n_0=\frac{N}{V}=CN_A} \sqrt{\frac{\epsilon\epsilon_0 k_B T}{2e^2 C N_A z^2}} \\ &= \sqrt{\frac{78 \cdot 8.85 \times 10^{-12} \cdot 1.38 \times 10^{-23} \cdot 298}{2 \cdot (1.602 \times 10^{-19})^2 \cdot 1 \cdot 6.022 \times 10^{23}}} \\ &= 9.6 \times 10^{-9} \text{ m } (\approx 10 \text{ nm}).\end{aligned}$$

b) The Debye length decreases with increase of the ionic concentration in this way:

$$\kappa^{-1} \propto \frac{1}{\sqrt{C}}$$

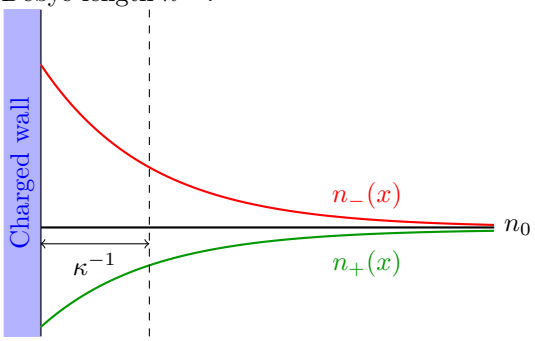
(i) $C = 1.75$ mmol KNO_3
This is higher than in question 3a and thus the Debye length decreases.

(ii) $C = 1.00$ mmol K_2SO_4
Which is the same molar concentration as in 3a, however here the ionic concentration is actually higher due to this being a $Z = 2$ electrolyte unlike KNO_3.

c)

$$\begin{aligned}\Phi(x) &= 2\ln\left[\frac{1+\tanh\left(\Phi_0/4\right)\cdot e^{-\kappa x}}{1-\tanh\left(\Phi_0/4\right)\cdot e^{-\kappa x}}\right] \qquad \text{Use first given hint: } \tanh(x) \approx x \\ &= 2\ln\left[\frac{1+\left(\Phi_0/4\right)\cdot e^{-\kappa x}}{1-\left(\Phi_0/4\right)\cdot e^{-\kappa x}}\right] \\ &= 2\left[\ln\left(1+\Phi_0/4\cdot e^{-\kappa x}\right)-\ln\left(1+\Phi_0/4\cdot e^{-\kappa x}\right)\right] \qquad \text{Use second hint: } \ln(1+x) \approx x \\ &= 2\left[\Phi_0/4\cdot e^{-\kappa x}+\Phi_0/4\cdot e^{-\kappa x}\right] \\ &= \Phi_0\cdot e^{-\kappa x} \qquad \text{(solution to linearised Poisson-Boltzmann equation)}\end{aligned}$$

d) Close to the charged wall an excess of counter-ions are present and thus a depletion of co-ions are here compared to the bulk concentration n_0
This region is called the *electric double layer* and it's thickness is characterised by the Debye length κ^{-1}.



e) Substitute in all dependant variables for easier integrating:

$$\begin{aligned}
\sigma &= -\int_0^\infty \rho(x)dx \qquad \text{Use: } \rho(x) = -2zen_0\Phi(x) \quad \& \quad \Phi(x) = \Phi_0 e^{-\kappa x} \\
&= \int_0^\infty 2zen_0\Phi_0 e^{-\kappa x} \qquad \text{Use: } \Phi_0 = ze\beta\phi_0 \\
&= 2z^2e^2n_0\beta\phi_0 \int_0^\infty e^{-\kappa x}dx \qquad \text{Use: } \beta = 1/k_\mathrm{B}T \\
&= \frac{2z^2e^2n_0}{k_\mathrm{B}T}\phi_0\left[-\frac{e^{-\infty}}{\kappa} + \frac{e^0}{\kappa}\right] = \underbrace{\frac{1}{\epsilon\epsilon_0}\frac{2z^2e^2n_0}{k_\mathrm{B}T}}_{\kappa^2}\phi_0\left[-\frac{e^{-\infty}}{\kappa} + \frac{e^0}{\kappa}\right] = \epsilon\epsilon_0\kappa\phi_0
\end{aligned}$$

f)

$$\text{Recognize: } [\sigma] = \frac{e}{\mathrm{nm}^2} = \frac{\mathrm{C}}{(10^{-9})^2\mathrm{m}}$$

$$\phi_0 = \frac{\sigma}{\epsilon\epsilon_0\kappa} = \frac{\sigma\kappa^{-1}}{\epsilon\epsilon_0} = \frac{0.16\times10^{-9}}{78\cdot8.85\times10^{-2}} = 0.022\ \mathrm{V} = 220\ \mathrm{mV}$$

As this result is much larger than 26 mV, the linearised Poisson-Boltzmann is typically not applicable for colloids (yet it is very insightful!!).

Problem 4

a) (i)

$$U = -\frac{AR}{12D} = -\frac{6\times10^{-20}\cdot0.5\times10^{-6}}{12\cdot100\times10^{-9}} = -2.5\times10^{-20}\ \mathrm{J}$$

(ii)

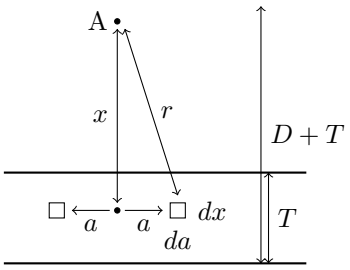
$$U = -\frac{AR}{12D} = -\frac{0.8\times10^{-20}\cdot0.5\times10^{-6}}{12\cdot100\times10^{-9}} = -3.3\times10^{-21}\ \mathrm{J}$$

(iii)

$$U = k_{\mathrm{B}} \cdot 298 \text{ K} = 1.38 \times 10^{-23} \cdot 298 = 4.11 \times 10^{-21} \text{ J}$$

So in vacuum the attractive van der Waals interaction is much larger than in water. In water, it is much less sticky and thus leads to a stable colloidal system.

b) Start by applying different boundary conditions to the derivation in the lecture.



The number of particles in this ring is:

$$2\pi\rho a \, da \, dx$$

$$\begin{aligned}
U(r) &= -\frac{C}{r^6} \\
&= -\frac{C}{(x^2+a^2)^3} \\
&= -2\pi C\rho \cdot \int_D^{D+T} dx \int_0^{\infty} \frac{a}{(x^2+a^2)^3} \, da \\
&\quad \text{Use: } a \, da = \frac{1}{2} da^2 \rightarrow da^2 = 2a \, da \\
&= -2\pi C\rho \cdot \int_D^{D+T} dx \, \underbrace{\frac{1}{2} \int_0^{\infty} \frac{da^2}{(x^2+a^2)^3}}_{y=a^2} \\
&= -2\pi C\rho \cdot \int_D^{D+T} dx \, \left[\int_0^{\infty} \frac{dy}{(x^2+y^2)^3} \right] \\
&= -2\pi C\rho \cdot \int_D^{D+T} dx \, \left[-\frac{1}{2(x^2+y)^2} \right]_0^{\infty} \\
&= \frac{\pi C\rho}{2} \cdot \int_D^{D+T} \frac{dx}{x^4} \\
U(D) &= \frac{\pi C\rho}{2} \cdot \left[-\frac{1}{3x^3} \right]_D^{D+T} = -\frac{\pi C\rho}{6} \left[\frac{1}{D^3} - \frac{1}{(D+T)^3} \right]
\end{aligned}$$

c) Continue with the obtained result in b) and integrate over the new plate. Now the particle density is given by:

$$\rho \, dx$$

$$
\begin{aligned}
U(D) &= -\frac{\pi C\rho^2}{6}\int_D^{D+T} \frac{1}{x^3} - \frac{1}{(x+T)^3}\, dx \\
&= -\frac{\pi C\rho^2}{6}\left[-\frac{1}{2x^2} + \frac{1}{2(x+T)^2}\right]_D^{D+T} \\
&= -\frac{\pi C\rho^2}{12}\left[-\frac{1}{(D+T)^2} + \frac{1}{(D+2T)^2} + \frac{1}{D^2} - \frac{1}{(D+T)^2}\right] \\
&= -\frac{\pi C\rho^2}{12}\left[\frac{1}{D^2} - \frac{2}{(D+T)^2} + \frac{1}{(D+2T)^2}\right] \qquad \text{recall: } A = \pi^2 C\rho^2 \\
&= -\frac{A}{12\pi}\left[\frac{1}{D^2} - \frac{2}{(D+T)^2} + \frac{1}{(D+2T)^2}\right]
\end{aligned}
$$

Now check if the half-space interaction is recovered using:

$$
\begin{aligned}
&\lim_{T\to\infty} U(D) \\
&= \lim_{T\to\infty} -\frac{A}{12\pi}\left[\frac{1}{D^2} - \frac{2}{(D+T)^2} + \frac{1}{(D+2T)^2}\right] \\
&= -\frac{A}{12\pi}\left[\frac{1}{D^2} - \frac{2}{\infty} + \frac{1}{\infty}\right] \\
&= -\frac{A}{12\pi}\left[\frac{1}{D^2}\right]
\end{aligned}
$$

Which indeed corresponds to the half space interaction.