Suspensions and polymer solutions

Solution of Exercise 3

1. The free energy of interaction, per unit area, between membranes separated by distance D is

$$\frac{F_{\rm DLVO}}{S} = \frac{F_{\rm el}}{S} + \frac{F_{\rm vdW}}{S} \simeq \frac{8\pi\sigma^2}{\epsilon\kappa} e^{-\kappa D} - \frac{H}{12\pi D^2}. \tag{1}$$

Differentiating with respect to D and setting the result to zero, we get the equation,

$$\frac{48\pi^2 D^3 \sigma^2}{\epsilon H} e^{-\kappa D} = 1.$$

Defining the dimensionless parameters $x \equiv \kappa D$ and $\alpha \equiv \epsilon H \kappa^3/(48\pi^2\sigma^2)$, we obtain the following equation for the extrema of $F_{\rm DLVO}$:

$$x^3 e^{-x} = \alpha. \tag{2}$$

(a) The left-hand side of Eq. (2) is bounded between 0 and $\alpha_{\rm c} = 3^3 e^{-3} \simeq 1.34$. Hence, the equation has either no solution (for $\alpha > \alpha_{\rm c}$) or two solutions (for $\alpha < \alpha_{\rm c}$) corresponding to a maximum and a minimum of $F_{\rm DLVO}$. A necessary condition for the stack not to collapse is that $F_{\rm DLVO}$ should have a maximum, i.e., an energy barrier, which will prevent the system from reaching the global minimum at $D = 0$. Thus, a necessary condition is

$$\frac{\epsilon H \kappa^3}{48\pi^2\sigma^2} < 27e^{-3} \simeq 1.34 \sim 1.$$

This can be ensured by either strengthening the electrostatic repulsion (increasing the charge density σ, decreasing the dielectric constant ϵ, increasing the screening length κ^{-1}), or weakening the van der Waals attraction (decreasing the Hamaker constant H).

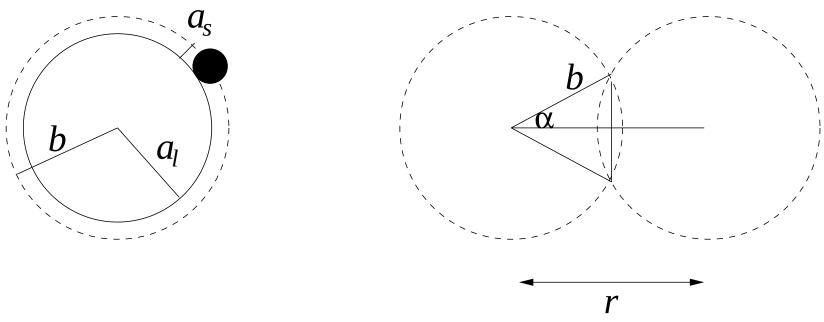
(b) The inverse screening length is

$$\kappa = \left(\frac{8\pi e^2 c_s}{\epsilon k_{\rm B} T}\right)^{1/2} \simeq \left[\frac{8\pi \cdot (4.8\times 10^{-10})^2 \cdot (0.1 \cdot 6.0 \times 10^{23} \cdot 10^{-3})}{80 \cdot 1.4 \times 10^{-16} \cdot 300}\right]^{1/2} \simeq 1.0 \times 10^7 \ {\rm cm}^{-1},$$

i.e., a screening length of 1 nm. For water we get

$$\alpha = \frac{\epsilon H \kappa^3}{48\pi^2\sigma^2} \simeq \frac{80 \cdot 1.5 \times 10^{-12} \cdot (1.0 \times 10^7)^3}{48\pi^2 \cdot (4.8 \times 10^{-10} \cdot 10^{14})^2} \simeq 0.11.$$

We now substitute this value of α in Eq. (2) and solve it numerically. There are two solutions, $x_1 \simeq 0.58$ and $x_2 \simeq 8.7$, the first corresponding to the maximum of $F_{\rm DLVO}$ (the barrier), and the second to the minimum. Since $\kappa^{-1} \simeq 1.0$ nm, we conclude that the equilibrium separation between membranes is $D \simeq 8.7$ nm. Note that the separation is significantly larger than the screening length; this is a manifestation of the weakness of the van der Waals interaction compared to the electrostatic one for such highly charged surfaces.



2. As we showed in class, the free energy of the depletion interaction is given by

$$F_{\text{dep}} = p_s \Delta V_{\text{ex}}, \tag{3}$$

where p_s is the osmotic pressure of the small particles, and ΔV_{ex} is the change in the volume excluded for the centers of small particles compared to the case of the two large particles being far apart.

We define $b \equiv a_l + a_s$ as the radius of the exclusion sphere. (See figure.) Obviously, if the distance r between the centers of the two large spheres is larger than $2b$, there is no change in the excluded volume, and $F_{\text{dep}} = 0$. If $r < 2b$, the two exclusion spheres overlap, and ΔV_{ex} is equal to minus the volume of the resulting overlap "lens" (figure). We therefore need to calculate the volume of the lens.

We first calculate the volume of the sphere section spanned by the angle 2α:

$$\text{section volume} = \int_0^b dRR^2 \int_0^\alpha d\theta \sin\theta \int_0^{2\pi} d\varphi = \frac{2\pi}{3} b^3 (1 - \cos\alpha) = \frac{2\pi}{3} b^3 \left(1 - \frac{r}{2b}\right).$$

Next we calculate the volume of the cone spanned by the angle 2α:

$$\text{cone volume} = \frac{1}{3}\pi (b \sin\alpha)^2 \frac{r}{2} = \frac{\pi}{6} b^2 r \left(1 - \frac{r^2}{4b^2}\right).$$

The lens volume is just twice the difference between the section volume and the cone volume, leading to

$$\text{lens volume} = \frac{4\pi}{3} b^3 \left(1 - \frac{3}{4}\frac{r}{b} + \frac{1}{16}\frac{r^3}{b^3}\right).$$

Substituting $r = 2b$ we confirm that this overlap volume vanishes as required.

Using the result in Eq. (3), we finally have

$$F_{\text{dep}}(r) = \begin{cases} -p_s \frac{4\pi}{3}(a_l + a_s)^3 \left[1 - \frac{3}{4}\frac{r}{a_l + a_s} + \frac{1}{16}\frac{r^3}{(a_l + a_s)^3}\right], & 2a_l < r < 2(a_l + a_s) \\ 0, & r \geq 2(a_l + a_s). \end{cases} \tag{4}$$