Soft Matter Problem set 4 – Interfaces and surfactants

Problem 13

Use the molecular view of interfacial tension ($\gamma \approx u/2a^2$) to explain which of the following interfaces have a higher interfacial tension.

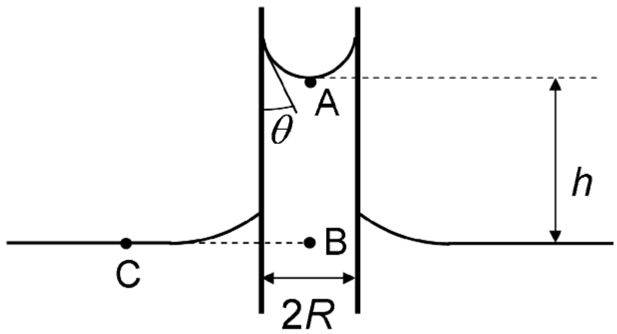
a) Water-air and water-ice.

b) Water-air and water-toluene.

c) A colloidal liquid-colloidal gas interface with particles of radius $a = 200$ nm and $a = 1$ μm.

Problem 14

We will derive the equation for capillary rise $h = 2\gamma \cos\theta/\rho g h$.



a) What is the Laplace pressure ($\Delta p = p_A - p_0$) according to the Young-Laplace equation?

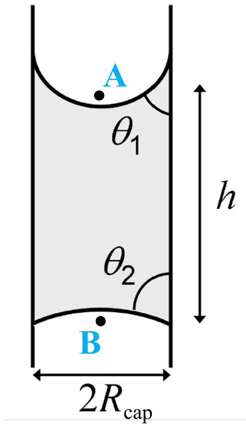
b) What is the pressure at points B and C? The interface at B is flat, and C is at the same height as B.

c) The pressure difference between points A and B is purely hydrostatic, i.e., the weight of the water column. Give an expression for the force per unit area ($f/A = \delta p_{AB} = p_B - p_A$) due to the weight of the water column above B.

d) Use your answer to a, b and c to derive the capillary rise equation. What size of capillary is required to rise a liquid by 100 m (the height of the tallest trees)?

Problem 15

Contact angle hysteresis makes it possible to capture a liquid column of height h suspended in a vertical capillary of radius R_{cap}, as shown in the figure below.



a) What is the microscopic origin of the contact angle hysteresis?

The Laplace pressure at a curved interface is given by: $\Delta p = \dfrac{2\gamma \cos\theta}{R}$, with R the radius of curvature.

b) What is the pressure difference between points A and B in the drawing? Use this pressure difference to derive an expression for the maximum height h of the capillary plug that can remain inside the capillary without falling down due to gravity.

Problem 16

The formation of micelles starts quite abruptly at a threshold concentration, known as the critical micelle concentration (CMC). Above the CMC, the number of micelles increases approximately linearly with increasing surfactant concentration. To explain the abrupt formation and linear dependence of micelle concentration on surfactant concentration, we will consider the formation of micelles as a reversible reaction between n surfactants:

$$n\,\mathrm{A} \rightleftharpoons \mathrm{A}_n$$

See also the lecture notes.

a) At what total mole fraction of surfactant is the amount of free surfactant x_1 equal to the amount of surfactant in micelles x_n?

b) Make a sketch of x_n as a function of x_1. How could you estimate the aggregation number n (the average number of surfactants per micelle) and the difference in standard chemical potentials, $\mu_1^0 - \mu_n^0$, from a plot of x_n versus x_1?

c) Another way to estimate the aggregation number, is to look at the shape of the surfactant molecules. A typical surfactant, sodium dodecyl sulfate or SDS ($C_{12}H_{25}SO_3^-$ Na^+), forms spherical micelles. The length ℓ of an SDS molecule is about 12×1.3 $\mathring{A}$ (per C-C bond) plus 1.5 $\mathring{A} = 17,1\mathring{A}$, which is the radius of the spherical SDS micelle. The effective area of the polar sulfate head group $a_0 = 60$ $\mathring{A}^2$. The molecular volume v of a single SDS molecule is about 360 $\mathring{A}^3$. Estimate the maximum number of SDS molecules per spherical micelle.

d) What would happen to the CMC and the aggregation number n of SDS when salt is added to the solution? Explain your answer.