Master φCS

2020–2021

Statistical Physics of Simple and Complex Fluids
Soft Condensed Matter Theory
HOMEWORK #2
Interfaces and membranes: self-organization, mechanical energy

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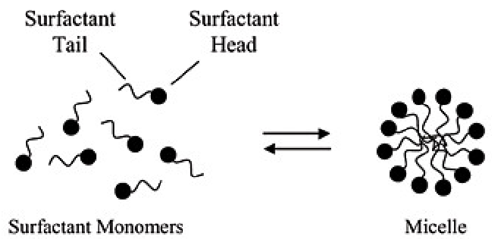
1 Self-organization of amphiphilic molecules: Critical Micelle Concentration

Amphiphilic (or surfactant) molecules are made of a polar hydrophilic head and one (or two) hydrophobic tail(s). They can self-organize intro supramolecular structures, called *micelles*, when their concentration in the solvent reaches a given value, called *Critical Micelle Concentration* (CMC). In this exercise we want to study the equilibrium between free molecules and micelles, and determine the CMC value.



Schematic illustration of the reversible monomer-micelle thermodynamic equilibrium (Based on Liu et al., 1996). The black circles represent the surfactant heads (hydrophilic moieties) and the black curved lines represent the surfactant tails (hydrophobic moieties). When micelles form in aqueous solution above the CMC, the surfactant monomers aggregate (self-assemble) with the tails inside the micelle shielded from water and the heads at the micelle surface in contact with water.

1. In a micelle, hydrophobic tails are prevented from contact with solvent molecules (see Fig. 1). Between q free molecules or assembled into one micelle, which configuration is energetically favorized ? And entropically ?

2. One considers a system of N_{tot} surfactant molecules in a volume V of solvent, at temperature T. One notes N the number of free molecules, and n the number of micelles. To simplifiy, one considers that all micelles are composed of q molecules. Give the relation between N_{tot}, N, n et q.

3. N and n are fluctuating variables and we want to determine their most probable values. Suppose for a moment that N and n are fixed; $F_{mol}(N, V, T)$ and $F_{mic}(n, V, T)$ are the free energy of the N free molecules and n micelles, respectively. Justify that the most probable value of N is the one that minimizes $F_{mol}(N, V, T) + F_{mic}(n, V, T)$ and that it coincides with its average value in the thermodynamic limit.

4. Which relation between the chemical potentials of a free molecule μ and of a micelle μ_{mic} this equilibrium condition implies ?

5. We modelize free molecules on one hand, and micelles on the other hand, as two ideal gases in uniform potentials caused by the interactions with the solvent. We note ϵ the potential energy of a free molecule, and $\epsilon - \Delta\epsilon$ the potential energy of a molecule within a micelle. We give the chemical potential of an ideal gas in a uniform potential u:

$$\mu = u + k_B T \ln(C\lambda_M^3),$$

with $\lambda_M = \sqrt{2\pi\hbar^2/Mk_\mathrm{B}T}$, where M is the mass of a "particle" of the gas, and C is their volumetric concentration. Express μ_{mic} as a function of q and the mass m of a single molecule.

6. Show that the concentration of free molecules is implicitly given by the two equations:

$$\phi' = \left(e^{\delta}\phi\right)^q \tag{1}$$

$$\phi + \phi' = \phi_{tot} \tag{2}$$

where $\phi = \lambda_m N/V$, $\phi' = \lambda_m N'/V$, $\phi_{tot} = \lambda_m N_{tot}/V$, and $\delta = \frac{\Delta\epsilon}{k_B T} + \frac{5}{2}\frac{\ln q}{q}$.

7. The Critical Micelle Concentration is defined as the value at which the number of free molecules is equal to the number of molecules assembled into micelles: $\phi_c = \phi = \phi'$. Experimentally, $q \sim 50 - -100$. Justify that, as long as $\phi < \phi_c$, one has $\phi' \simeq 0$, while as soon as $\phi = \phi_c$ every added molecule contributes to the creation of new micelles.

8. Show that the CMC $C_c = \phi_c/\lambda_m^3$ is given by:

$$C_c = \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2} e^{-\Delta\epsilon/k_B T} \tag{3}$$

and discuss about the dependence of C_c with temperature and the association energetic gain $\Delta\epsilon$.

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2 Formation of a vesicle: competition between bending energy and boundary energy

The aim of this exercise is to determine under which conditions a lipid bilayer will adopt the topoly of a sphere and form a vesicle.

1. We first consider a flat bilayer with the shape of a disc with radius R. Lipids at the edge of the bilayer are in contact with the solvent so there is an energetic cost associated with the existence of a boundary. We note λ the energetic cost per unit length of the boundary. Express the energy of the membrane in terms of λ and R.

2. We now consider the same bilayer when adopted the shape of a sphere with same surface. What is the radius of the sphere ? Express its bending energy in terms of the two bending moduli κ_b and κ_G.

3. At zero temperature, the bilayer adopts the conformation with minimal energy. Discuss of which configuration is adopted as a function of R.