ICFP M2 – SOFT MATTER PHYSICS
Tutorial 12. Stabilization of a microemulsion

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A microemulsion is a collection of small droplets of a given liquid into a continuous phase of another, immiscible, liquid. Due to surface tension, such an assembly is not stable and the droplets will eventually merge together and evolve towards the formation of two separated continuous phases – a phenomenon better known as Ostwald ripening. To fight against that process, several strategies are available, involving *e.g.* the addition of surfactants or species that are insoluble in the continuous phase (think about the *crucial* roles of Dijon mustard and salt in the French vinaigrette dressing for instance). Here, we would like to quantify further this statement. With this goal in mind, we first discuss the osmotic properties of emulsions, before addressing the phenomenon of Ostwald ripening, and the action of added species in the spirit of the work by Webster and Cates.

I Osmotic pressure

A U-shaped tube of 1 cm^2 cross-section is separated in two identical compartments by a membrane that is permeable to water molecules, but not to oil ones. A microemulsion is prepared at ambient pressure P_0 and room temperature T by mixing 1.5 mL of oil and 28.5 mL of water, the ensemble being poured in a first compartment of the tube. We neglect the volume of mixing, and we assume the emulsion to be monodisperse, with a large number n of identical spherical droplets of radius a, and thus volume $v = 4\pi a^3/3$. There is no elevation of temperature. The other compartment is filled with 30 mL of pure water. We observe a 5 mm difference between the heights of liquid in the two compartments.

1 What is the final volume V in the first compartment ?

2 What is the origin of the energy of mixing ? Provide the expression of the latter.

3 By describing the emulsion as an effective lattice containing $N = V/v$ sites (with $N >> n$) randomly occupied by the droplets (the rest being occupied by water), estimate the entropy of mixing and thus the free energy/enthalpy of mixing.

4 We note $\mu_{\text{w}}^0(T, P)$ the chemical potential of pure water at pressure P. Express the chemical potential of water in the (dilute) presence of the oil droplets, as a function of the molecular volume of water and the droplet concentration.

*This tutorial follows an original proposal by Annie Colin. We thank her for that.

5 At equilibrium, and invoking the Gibbs-Duhem relation, connect the height difference between the two compartments and the droplet concentration in the first compartment.

6 Estimate the number and size of the droplets.

II Ostwald ripening

We now consider a water droplet of radius a immersed in a continuous phase of oil. Moreover, at a large distance from the droplet, there is a flat oil-water interface.

1 What is the chemical potential of water in the droplet ?

2 There are in fact some water molecules also (dissolved) in oil and allowed to diffuse. Assuming an ideal solution, what is the chemical potential of the water molecules in oil as a function of their concentration ? One can *e.g.* introduce a reference chemical potential μ_{w}^* of water dissolved in oil at a reference concentration C^*.

3 Deduce the water concentration near the droplet.

4 What about the water concentration near the flat interface in the far field ? Comment on the droplet's longterm stability.

5 Assuming a quasi-static evolution, obtain the water concentration profile in the oil phase.

6 Write the first-order differential equation satisfied by the droplet radius, and solve it in the large-temperature limit.

7 Discuss the effects of temperature, viscosity, and the role of added surfactants.

III Stabilization by trapped species

We stay in the latter case of a water droplet in oil, but p molecules of a third species which are entirely immiscible with the continuous oil phase are now added to the droplet. We assume for simplicity this third species to be dilute within the droplet.

1 Explain qualitatively the role of such a trapped species. What is the scaling of the equilibrium droplet radius ?

2 How is the chemical potential of water in the droplet modified by the presence of the trapped species ?

3 In a quasi-static description, write the new first-order differential equation satisfied by the droplet radius in the large-temperature limit.

4 Provide the expression of the final droplet radius.