Question 1

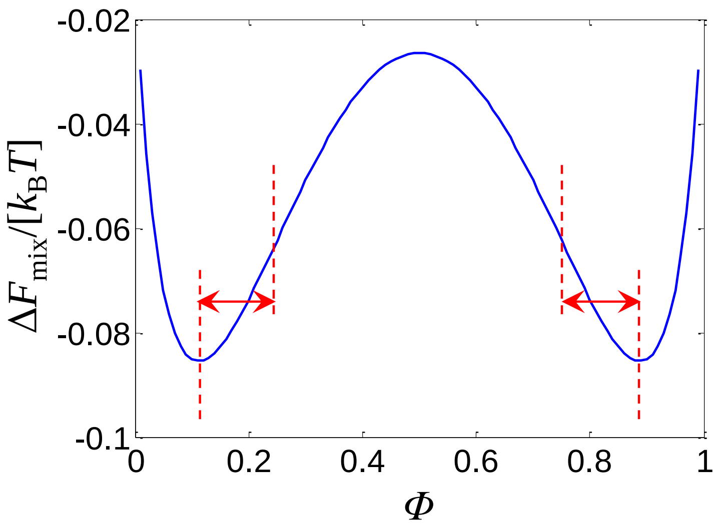
(10p)

The regular solution model for a binary liquid mixture is:

$$\Delta F_{\mathrm{mix}} = k_{\mathrm{B}}T\left[\Phi_{\mathrm{A}}\log(\Phi_{\mathrm{A}}) + \Phi_{\mathrm{B}}\log(\Phi_{\mathrm{B}}) + \Phi_{\mathrm{A}}\Phi_{\mathrm{B}}\chi\right]$$

Estimate the metastable regions when $\chi = 8/3$ and illustrate them in a sketch of the curve of the free energy of mixing.

Regular solution model with $\chi > 2$ means that metastable regions are between minima and inflection points in ΔF_{mix} curve. Set $\Phi = \Phi_{\mathrm{A}} = 1 - \Phi_{\mathrm{B}}$. Derive ΔF_{mix} with respect to Φ: $k_{\mathrm{B}}T[\log(\Phi) - \log(1 - \Phi) + [1 - 2\Phi]\times 8/3]$ Solve for minima numerically by testing values, which gives $\Phi \approx 0.11$. By symmetry the other minima is then at $\Phi \approx 0.89$. Derive ΔF_{mix} a second time: $k_{\mathrm{B}}T[1/\Phi + 1/[1 - \Phi] - 16/3]$ Solve second degree equation for inflection points $\Phi = 1/4$ and $\Phi = 3/4$. The curve must then look like this:



Question 2

(10p)

A colloidal suspension is formed by adding spherical silica particles (density 2.5 g/cm^3) of radius r = 10 nm to water. Estimate if this will be a stable suspension or if you expect to have sedimentation! In the estimation take into account the influence of Brownian motion and carefully motivate any assumptions.

Some useful relations:

Stokes-Einstein relation:

$$Df = k_B T$$

Stokes friction:

$$F_f = fv = 6\pi\eta r v$$

The suggested solution is to solve for the steady-state sedimentation velocity by setting the sum of forces equal to zero. The forces are gravity, buoyancy and liquid friction. This should give $v = 2r^2 g[\rho_p - \rho_l]/[9\eta]$ where the density and viscosity of the water need to be inserted (1000 kgm^{-3} and 10^{-3} Pas). Inserting the radius and density of the colloids gives $v = 3\times10^{-10}$ m/s. A nanoparticle has almost no inertia so it can be assumed that this velocity is reached instantly. However, the velocity is anyway too low to be significant compared with diffusion. The diffusion constant is $D = 2\times10^{-11}$ m^2/s at room temperature which means that the Brownian motion during one second is several micrometers. Hence there is no sedimentation.

Question 3

A (3p)

In what form is fat present in milk? Why does not the fat content in milk phase separate even after one week? (Possible hint: Why is milk white?)

Microemulsions, stabilized by amphiphilic proteins.

B (4p)

How do the values of plateau modulus and terminal time for a polymer melt change with temperature? Explain if you expect each parameter to increase, decrease or remain the same and motivate why. (It is not necessary to refer to any math formula.)

The plateau modulus is estimated by assuming the entanglement points act as cross-links in a rubber. Stretching polymers means countering an entropic force, which will be more significant at higher temperatures. Thus the modulus increases with temperature. (This also follows from the formula.) The terminal time is determined by the time it takes for the chains to diffuse out of entanglement. Diffusion is faster at higher temperatures so the terminal time should be shortened. (Again this can be seen in the formula.)

C (3p)

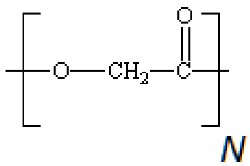
A gel based on a hydrophilic polymer such as poly(acrylamide) can take up a lot of water. There is a free energy reduction when water is added to the polymer, but the swelling does not continue indefinitely. Which free energy cost is countering further swelling when the equilibrium size has been reached?

The gel consists of cross-linked hydrophilic polymer chains. Adding water is like stretching a rubber. Eventually the force needed to expand the gel network becomes too high.

Question 4

A (3p)

Polyglycolide is a biodegradable polymer and the simplest type of polyester. It has the structure:



Assume the monomer is 5 Å long. Polyglycolide can only be dissolved well in certain fluorinated solvents. In such a solvent the Kuhn length is 3.0 nm. Calculate the end to end distance of the coil if the molecular weight is 20 kg/mol!

The monomer weight is m = 58 gmol^{-1} so there are N = 345 monomers. The rescaled Flory radius is $b[aN/b]^{3/5}$ with $a = 5\times10^{-10}$ m and $b = 5\times10^{-9}$ m, which gives R_F = 34 nm.

B (3p)

One usually refers to the "critical concentration" of a polymer solution as the concentration where there is exactly one coil in a volume of R_F^3. What is the critical concentration in terms of mass per volume for the polyglycolide in part A?

The mass of one coil, for instance in grams, is $20\times10^3/N_A$ (Avogadro's number). The volume, for instance in liters, is $[34\times10^{-8}]^3$. This gives a critical concentration of 0.8 g/L.

C (4p)

Assume the solvent evaporates. Estimate a new end to end distance for the polyglycolide molecules by assuming the same monomer size and Kuhn length! What could be a major source of error in this estimate?

In the resulting melt the end to end distance is $[abN]$1/2 = 23 nm. The problem with this model is that one cannot know if the polymer has the same atomic configuration and flexibility in the absence of the solvent. Both a and b may be different, which is what the χ parameter is all about. (The scaling relation should always be $N^{1/2}$ though.)