

Question 1

A (7p)

The free energy change upon freezing a spherical crystal in an undercooled liquid is:

$$\Delta G_{\text{nuc}}(r) = -\frac{4\pi r^3}{3} \frac{\Delta H_m \Delta T}{T_m} + 4\pi r^2 \gamma_{\text{SL}}$$

Determine the activation energy in $k_B T$ for homogeneous nucleation of water at -5°C ! Use the values $\gamma_{\text{SL}} = 0.03 \text{ J/m}^2$ and $\Delta H_m = 335 \text{ J/g}^{-1}$.

For ice the density is not so different from water (approximately 10^3 kgm^{-3}). This should be used to convert ΔH_m to enthalpy per volume. Further, T_m is around 273 K so the undercooling is $\Delta T = 5 \text{ K}$. Derive the expression with respect to r and find the maximum for r^* after which ΔG decreases with r . This should give $r^* = 2\gamma_{\text{SL}}T_m/[\Delta H_m\Delta T]$ and insertion into the original expression gives the activation energy $\Delta G^* = 16\pi\gamma_{\text{SL}}^3T_m^2/[3\Delta H_m^2\Delta T^2]$ Inserting all values gives $1.2 \dots \times 10^{-17} \text{ J}$ which means $\sim 3200k_B T$ at -5°C . (This shows that homogenous nucleation is unlikely.)

B (3p)

What does the Cahn-Hilliard equation describe, when is it applicable and what does its amplified wavevector represent?

The equation describes liquid-liquid unmixing by spinodal decomposition. It is applicable for unstable mixtures. The (inverse) amplified wavevector gives the characteristic lengthscale of the domain formation.

Question 2

A (6p)

The mole fraction of amphiphilic molecules in micelles, Φ_M , is related to the mole fraction of monomers, Φ_1 , by:

$$\Phi_M = M \left[\Phi_1 \exp\left(\frac{\varepsilon_1 - \varepsilon_M}{k_B T}\right) \right]^M$$

The energy difference between a molecule as a monomer in solution and as a molecule belonging to a micelle of aggregation number M is 21 kJmol^{-1} . Estimate the (dimensionless) critical micelle concentration!

From the text $\varepsilon_1 - \varepsilon_M = 21 \text{ kJmol}^{-1} \approx 8.43k_B T$, assuming room temperature ($T = 300 \text{ K}$). Micelles instead of monomers will start to form when the factor inside brackets approaches unity (it is taken to the power of M) since all concentrations must be lower than one. This means that $\Phi_1 = \exp(-8.43) = 2.19 \dots \times 10^{-4}$.

B (4p)

What is a (stabilized) microemulsion? What is a lipid vesicle? Draw simple pictures with amphiphilic molecules and indicate polar/unpolar solvents!

Microemulsion means colloids of one liquid inside another liquid (the continuous phase). The complete phase separation does not occur because of amphiphilic molecules at the interfaces. One example is fat content in milk. Lipid vesicles have a spherical bilayer shell of amphiphilic molecules. The same solvent is normally present on both inside and outside. (Schematics in lecture slides.)

Question 3

A (4p)

What is the Peclet number and how can it be used to predict shear-thinning in a suspension? (The formula for Pe is not so important, you should explain the physical meaning of the number.)

The dimensionless number is the characteristic time of diffusion, which is the time required for an object to diffuse a distance corresponding to its own size, divided by the characteristic time of convection (flow), i.e. the strain rate (velocity gradient). For high Pe shear-thinning occurs and saturates around $Pe = 1$.

B (4p)

Describe briefly how a colloidal suspension can form a glass!

At a high enough volume fraction of hard spheres ($\Phi \approx 0.58$) the viscosity becomes so high that the colloids are trapped in a metastable configuration and do not reach a crystalline arrangement.

C (2p)

What do the real and imaginary parts of a complex stress relaxation modulus represent physically?

The complex stress relaxation modulus is used to describe viscoelastic behavior. The real part is the “solid elastic” part (energy storage) and the imaginary part is the “liquid viscous” part (energy dissipation).

Question 4

A (4p)

Common nylon has the following chemical structure:



Assume the monomer is 2 nm long, the Kuhn length is 8 nm and the molecular weight is 30 kgmol^{-1} . Determine the end to end distance by treating the polymer chain as a random walk.

The monomer has 12 C, 2 O, 2 N and 22 H which gives a mass of $m = 226 \text{ gmol}^{-1}$. The number of monomers is then $N = M/m = 30 \times 10^3 / 226 \approx 133$. The random walk gives $R = [abN]^{1/2}$ after rescaling. With $a = 2 \text{ nm}$ and $b = 8 \text{ nm}$ this gives 46.1 nm.

B (4p)

The worm-like chain model gives the end to end distance as:

$$R_{\text{WLC}} = \left[2l_p r_{\text{max}} \left[1 - \frac{l_p}{r_{\text{max}}} \left[1 - \exp\left(-\frac{r_{\text{max}}}{l_p}\right) \right] \right] \right]^{1/2}$$

Here r_{max} is the contour length and l_p is the persistence length (half of the Kuhn length). Calculate R_{WLC} for the same nylon as in part A!

The contour length is $r_{\text{max}} = aN$ and $l_p = 4 \text{ nm}$. Insertion of values then gives $R_{\text{WLC}} = 45.8 \text{ nm}$.

C (2p)

Comment on the results from A and B with respect to the two models used. (When do they give similar results?)

The WLC model is intended for stiff polymers that do not bend so much. It gives an end to end distance which is lower than the random walk result, but they converge to the same values when the polymer is long enough to be flexible, which is the case here. The contour length is over 33 Kuhn lengths. (However, this normally means that overlap needs to be considered and the Flory radius should in fact be used.)