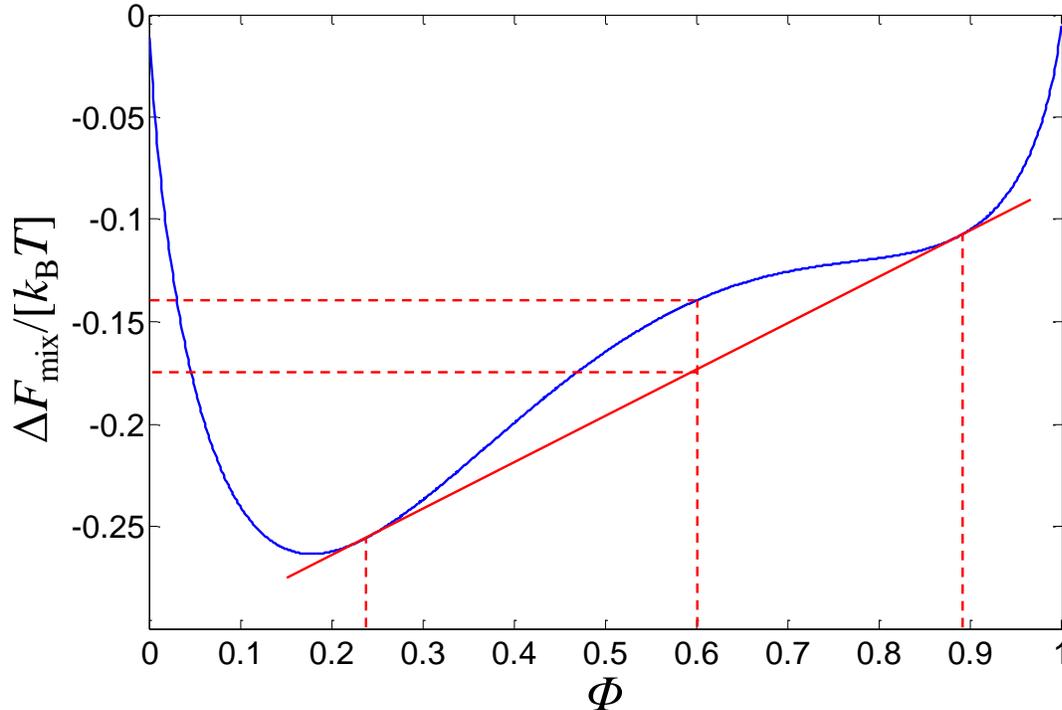


### Question 1

A (4p)

The graph shows the free energy of mixing for two liquids.



Estimate the coexisting compositions  $\Phi_1$  and  $\Phi_2$ !

Drawing a tangent to the curve gives  $\Phi_1 \approx 0.24$  and  $\Phi_2 \approx 0.89$  as the intersects.

Mean score: 3.9

B (4p)

Estimate the free energy of phase separation (to  $\Phi_1$  and  $\Phi_2$ ) at room temperature if  $\Phi_0 = 0.6$ !

Moving vertically from  $\Delta F_{\text{mix}}(\Phi_0)$  to the tangent corresponds to  $\sim 0.04k_B T$ . At 300 K this means the free energy of phase separation is  $-1.7 \times 10^{-22}$  J per molecular site.

Mean score: 2.9

C (2p)

Explain if the mixture is stable, metastable or unstable at  $\Phi_0$ .

Since the curvature is negative at  $\Phi_0$  the initial mixture is unstable.

Mean score: 1.7

## Question 2

A (4p)

One refers to most colloidal suspensions as metastable. Use DLVO theory to describe why! You should explain the forces involved and include a characteristic energy-distance graph at low ionic strength.

DLVO theory combines van der Waals attraction and repulsion due to the diffuse layer of ions close to the charged colloid interface. Since the repulsion decays exponentially with distance  $d$  and van der Waals attraction scales with the inverse of distance, the energy-distance curve will show a bump, an energy barrier, as  $d$  is reduced (at low ionic strength), followed by a rapid decrease at very short separation. The suspension is thus metastable because even though there is an overall energy reduction when  $d = 0$  a significant barrier must first be overcome for aggregation to occur.

Mean score: 1.2

B (6p)

Charged polystyrene colloids with radius 50 nm are dispersed at a volume fraction of 0.2 in a water solution of 1 mmolL<sup>-1</sup> NaCl. In order to cover a large oppositely charged surface with a monolayer of colloids the suspension is painted by hand. If the liquid film under the brush is 10 μm, what is the viscosity of the suspension during painting?

The following relations may be useful:

$$\kappa = \left[ \frac{2C_0 e^2}{\epsilon \epsilon_0 k_B T} \right]^{1/2} \quad \text{Pe} = \frac{6\pi\eta_0 R^3 \gamma}{k_B T} \quad \frac{\eta_{\text{high}}}{\eta_0} = \left[ 1 - \frac{\Phi}{0.71} \right]^{-2} \quad \frac{\eta_{\text{low}}}{\eta_0} = \left[ 1 - \frac{\Phi}{0.63} \right]^{-2}$$

To estimate the Peclet number, first make a rough estimate of how fast one moves a brush when painting (e.g. 10 cms<sup>-1</sup>). The shear rate is then the brush speed divided by 10 μm ( $\gamma = 10^4$  s<sup>-1</sup>). Now insert all values to see that Pe is above 1 (5.7 even without taking the Debye length into account). This means that we have shear thinning and that the formula with  $\eta_{\text{high}}$  should be used, but this is based on hard spheres. Calculate the Debye length for a monovalent salt at 1 molm<sup>-3</sup>. This should give  $\kappa^{-1} = 9.74 \dots$  nm. The volume fraction of hard spheres is then 0.2 multiplied with  $[(R + \kappa^{-1})/R]^3$ , which gives  $\Phi = 0.34 \dots$  Insert into the formula to get  $\eta_{\text{high}} = 3.7 \times 10^{-3}$  Pas.

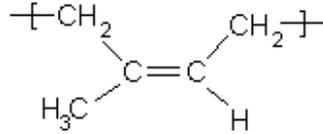
Mean score: 1.2

Note: In all formulas  $\eta_0$  is the (constant) viscosity of the pure solvent (here water). This should be clear if one has understood the theory.

### Question 3

A (3p)

A melt consists of poly(cis-isoprene) with molecular weight  $10 \text{ kgmol}^{-1}$ . The monomer is:



The  $-\text{CH}_3$  groups can cross-link through vulcanization. The probability that a  $\text{CH}_3$  group has reacted after time  $t$  is

$$1 - \exp(-t/\tau)$$

with  $\tau = 5 \text{ min}$ . How long (at least) should one run the vulcanization process to get a rubber?

The monomer weight is  $68 \text{ g mol}^{-1}$  which gives  $N = 147$ . Each monomer acts as a potential binding site to another coil so the percolation threshold is  $1/[N - 1]$ . This should be equal to  $1 - \exp(-t/\tau)$ , i.e. the fraction of reacted sites. Solving for  $t$  gives  $\sim 2 \text{ s}$ .

Mean score: 1.6

B (4p)

The density of a poly(cis-isoprene) melt is  $1.1 \text{ g cm}^{-3}$ . Young's modulus for a rubber is given by:

$$Y = \frac{3\rho k_B T}{mN_{\text{part}}}$$

Estimate the modulus of the product if the vulcanization (in A) runs for 20 s!

The challenge is to estimate  $N_{\text{part}}$ , all other parameters are given (assuming room temperature). After 20 s the probability of having a reacted  $-\text{CH}_3$  group is  $\sim 0.0645$ . To estimate how many monomers are in between cross-links points one can for instance calculate what number of monomers along the chain that are not cross-linked with a probability of 50%. One finds that the probability of not having any cross-link for 11 monomers in a row is  $[1 - 0.0645]^{10} = 0.51 \dots$  A reasonable value is thus  $N_{\text{part}} = 11$ . (Other types of statistical analysis can certainly be done with another probability distribution etc.) When inserting all values into the modulus the result should be  $Y \approx 1.1 \times 10^7 \text{ Pa}$ . (A quite heavily cross-linked rubber.)

Mean score: 2.0

Comment: It seems everybody assumed that  $N$  was 147 also here and used this number to estimate  $N_{\text{part}}$  to 16 based on the number of cross-links in one molecule. The intention was actually that  $N$  should be arbitrary, but I considered this solution to be acceptable. However, it is not OK to multiply the fraction of reacted bonds with  $N$  because in principle this gives the number of cross links per molecule, not the distance between them. In the end you should somehow show that you know the physical meaning of  $N_{\text{part}}$ .

C (3p)

Vulcanization is an example of a chemical gelation. Explain the difference compared with a physical gelation process! Give one example of the nature of the cross-links in physical gelation!

Physical gelation, unlike chemical, is not based on generating covalent bonds. The cross-links are based on weaker interactions which are reversible with temperature. Examples are lamellae or self-assembled domains in copolymers.

Mean score: 1.3

Comments: Many wrote that physical gelation is “reversible” but without explaining that it is with respect to changing temperature! Also, many give “gelatin” as an example but without explaining what the cross-links in this gel consist of!

#### Question 4

A (3p)

Many hydrophilic polymers have a so called lower critical solution temperature (LCST). Why is an upper critical solution temperature behavior physically more intuitive and why does one still sometimes observe an LCST?

Due to the entropy of mixing, higher temperature should normally promote solvation of the polymer as it does for mixtures in general. However, the hydrophobic effect can dominate such that the total entropy of mixing, including the solvent, is negative (as for amphiphilic self assembly). Then raising the temperature does not promote solvation in water. Instead, one must stay below an LCST to ensure solvation.

Mean score: 0.5

B (4p)

Diapers contain pulp fibers and polymer particles. What are the functions of these two components in the product?

The fibers promote fast liquid spreading by capillary transport in microscale networks. The polymer particles are superabsorbents that take up and store the liquid efficiently.

Mean score: 2.9

C (3p)

A polymer is in a good solvent. A hydrodynamic diameter of 10 nm was measured with light scattering for coils in a dilute solution. What will the hydrodynamic diameter be if the molecular weight is doubled?

The hydrodynamic diameter must be linearly related to the Flory radius, which is proportional to the molecular weight to the power of  $3/5$ . Doubling the molecular weight thus gives a new hydrodynamic diameter of  $10 \times 2^{3/5} \approx 15$  nm.

Mean score: 2.0

Comment: Many solutions were very unclear here, but I gave full points as long as the factor  $2^{3/5}$  was somehow included because that shows the main idea.