

### Question 1

The free energy of mixing for a binary liquid mixture is given by:

$$\Delta F_{\text{mix}} = k_{\text{B}}T[\Phi_{\text{A}} \log(\Phi_{\text{A}}) + 3\Phi_{\text{B}} \log(\Phi_{\text{B}}) + 3\Phi_{\text{A}}\Phi_{\text{B}}\chi]$$

A (6p)

Is the mixture stable, unstable or metastable for  $\chi = 5/3$  and  $\Phi_{\text{A}} = 0.2$ ? (Motivate your answer by a calculation.)

Set  $\Phi = \Phi_{\text{A}} = 1 - \Phi_{\text{B}}$ . Derive  $\Delta F_{\text{mix}}$  twice with respect to  $\Phi$ :  $k_{\text{B}}T[1/\Phi + 3/[1 - \Phi] - 6\chi]$  Insert  $\Phi = 0.2$  and the value for  $\chi$  into this expression and you get a negative number, which means that the curvature is negative, which means the mixture is unstable.

Mean score: 4.4

Comment: Many people drew nice symmetric curves around  $\Phi_{\text{A}} = 1/2$  to illustrate where the unstable region is. This is not true because the equation is not the regular solution model. (No points were lost because of such drawings though.)

B (4p)

Estimate what values of  $\chi$  that always result in stable mixtures (for any volume fractions)!

A stable mixture must have positive curvature for all values of  $\Phi$  (zero to one). From part (A) you have an expression for the curvature which is essentially a function of  $\Phi$ . For negative curvature  $1/\Phi + 3/[1 - \Phi] - 6\chi > 0$  must hold, which means that  $\chi < 1/[6\Phi] + 1/[2[1 - \Phi]]$ . You need to find the minimum of the expression, which should be approximately 1.24 (for  $\Phi = 0.37$ ). Thus  $\chi < 1.24$  means all mixtures are stable.

Mean score: 1.7

Comment: Again this is obviously not the regular solution model so  $\chi < 2$  is not the limit we are looking for.

#### Question 4

A (2p)

A rubber band is taken into a sauna. Assume the density remains the same. Will it be easier or harder to pull the band? (You need to give a brief motivation, but you do not have to refer to any equation.)

A rubber consists of cross-linked polymers. Stretching a polymer means countering an entropic restoring force. Since the effect is entropic it will become more pronounced at higher temperatures and hence it should be harder to pull the band. (Less elegantly, one can also refer to the equation for the modulus, which is proportional to  $T$ .)

Mean score: 0.5

Comment: A lot of people seem to think the rubber band is just a polymer melt and that the coils need to get free from entanglement, as in reptation theory. But a rubber band has covalent cross-links between coils and can never behave as a liquid.

B (4p)

Silly Putty or “bouncing clay” is viscoelastic: It bounces when dropped on the floor, but it also behaves as a highly viscous liquid which settles down by gravity. If the degree of polymerization is increased, will Silly Putty bounce higher, lower or the same? Will it take shorter, longer or about the same time for it to settle as a liquid? Motivate your answers briefly.

The elasticity (plateau modulus) is determined by the degree of entanglement of the polymers, which does not change much with  $N$ , so the bouncing will be about the same. For liquid behavior, the polymers must become unentangled. The time this takes (terminal time) scales with  $N^3$  according to reptation theory. So the time to settle will increase. One can also argue that the viscosity increases, since it can be approximated by the plateau modulus multiplied with the relaxation time, which means low shear rate.

Mean score: 2.4

C (4p)

Polyethylene can be a hard and stiff material even above the glass transition temperature. Why? Give one example of how the stiffness of the final plastic can be varied by changes during the synthesis of the polymer!

The crystalline domains (lamellae) makes the material hard and brittle. PE has a relatively high degree of crystallinity, but it can be controlled primarily by branching during synthesis since branched polymers crystallize less.

Mean score: 1.0

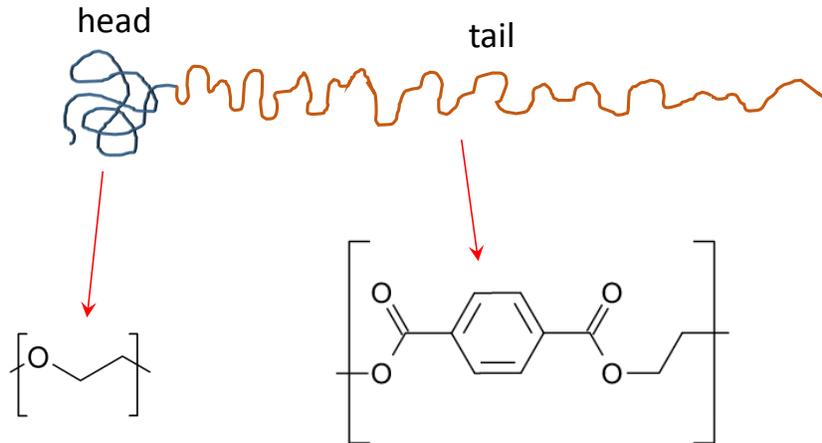
Comment: A lot of people discussed “cross-links” in their answer but without explaining what they mean with it! Strictly, the plastic has no cross-links (covalent bonds between coils), but entanglement points and in the case of PE also lamellae can of course act as a type of effective

cross-links but this must be explained. (The funniest answer I got was that the stiffness can be varied “by hiring a chemist”.)

### Question 5

A (3p)

Various aggregates can be formed in water with block copolymers that have a hydrophilic and a hydrophobic part. Assume we have a small but flexible head consisting of poly(ethylene glycol) (PEG) with  $M = 2$  kDa connected to a hydrophobic poly(ethylene terephthalate) (PET) “tail”:



Estimate the “optimal head area” by assuming it is simply the square of the end to end distance of the PEG in water (ignore the PET). PEG has a monomer ( $CH_2-CH_2-O$ ) of size 0.28 nm and Kuhn length 0.72 nm in water.

Use the Flory radius  $R_F = aN^{3/5}$ . Get  $N$  from molecular weight divided by monomer weight of 44, which gives  $N = 45$ . Rescale to  $R_F = b[aN/b]^{3/5}$  with  $a = 0.28$  nm and  $b = 0.72$  nm. This gives  $R_F = 4$  nm so the “head area” is  $16$  nm<sup>2</sup>.

Mean score: 2.1

Comment: Many people use the random walk model instead, but a polymer in a good solvent obeys Flory’s scaling law. (I gave one point for using the random walk accurately.)

B (3p)

Assume the characteristic size of the PET monomer is 2.0 nm. Show that the block copolymer should form spherical micelles!

Hint: You may use the combination parameter from self assembly principles.

The combination parameter is  $v_t/[A_h l_t]$  where you have  $A_h$  from part (A),  $v_t$  as the volume of the PET “tail” and  $l_t$  as the maximum extension of the PET. If the characteristic size of the monomer is 2 nm we have  $l_t = N \times 2$  nm (contour length) and  $v_t = N \times 2^3$  nm<sup>3</sup>. The combination parameter is then  $8N/[16 \times 2N] = 1/4$ , i.e. below  $1/3$  (the value of  $N$  is not relevant in this model).

Mean score: 1.5

Comment: If you at least write down the combination parameter correctly and explain that it should be below 1/3 you get one point.

C (4p)

The interior of the micelle can be thought of as a homogenous melt of PET, where the PET part of each molecule starts at the surface and ends somewhere in the interior. However, some molecules might have to stretch so that the whole interior is properly “filled up” with PET. If  $N = 50$  for the PET block, what is the free energy cost in  $k_B T$  for a molecule to stretch out in order to reach the center of the micelle? You may use a Kuhn length of 4 nm.

Hint: The configurational entropy contribution to the free energy of a coil is given by:

$$G(r) = \frac{3k_B T r^2}{2Na^2} + \text{constant}$$

If the interior is treated like a melt, the initial “relaxed” state for the PET is to have an end to end distance of  $r_i = aN^{1/2}$  (random walk), rescaled into  $[abN]^{1/2}$ . The final state has an end to end distance equal to the radius of the micelle, which we can get from  $4\pi r_f^2 = MA_h$  and  $4\pi r_f^3/3 = Mv$ , where  $M$  is the aggregation number. Combining the expressions gives  $r_f = 3Na^3/A_h$ . (This is an actual radius, it should not be rescaled.) Now we can write  $\Delta G = 3k_B T/[2Nab] \times [r_f^2 - r_i^2]$  (rescaling also the first factor). Inserting all values ( $a = 2$  nm,  $b = 4$  nm,  $N = 50$  and  $A_h = 16$  nm<sup>2</sup>) gives  $\Delta G = 20k_B T$ .

Mean score: 0.8

Comment: Only one person got the right answer so perhaps this question was a bit too difficult. I gave one point to those who showed some kind of calculation containing a  $\Delta G$  and some initial and final value for  $r$  which are not too strange.