Chalmers University of Technology Department of Applied Physics Aleksandar Matic/Per Jacobsson

Exam in Soft Matter Physics TIF015/FIM110

Time and place: Firday October 21st 2005 8.30-12.30 in M-building. **Examiners:** Aleksandar Matic (0730-346294), Per Jacobsson (070-3088200). **Allowed material:** Physics Handbook or equivalent, dictionary and pocket calculator **Grading:** 32 points, is required for a passed.

Solutions to the exam: Solutions will be put on the course home page after the exam. **Exam results:** Exam results are displayed at the Fysik entrance not later than Tuesday November 1st.

Review of the exam: Wednesday November 2nd 12.00-12.30 outside S2046

1. a) What is a Newtonian liquid? (2p)

b) What is shear thinning and shear thickening? Sketch diagrams to explain the two phenomena. (4p)

c) What is the typical energy of van der Waals and hydrogen bonds? Give it in relation to the thermal energy at room temperature. (4p)

2. In the regular solution model the free energy of mixing, F=U-TS, can be written as:

 $\frac{F_{\text{mix}}}{k_{\text{B}}T} = \phi_{\text{A}} \ln \phi_{\text{A}} + \phi_{\text{B}} \ln \phi_{\text{B}} + \chi \phi_{\text{A}} \phi_{\text{B}} ,$

where ϕ is the volume fraction of molecules of A and B type. In the graph on the right this model is shown for various values of the interaction parameter χ .

a) For what values of χ is mixing favoured and for what values will we have a phase separation? (2p)

b) What is a spinodal and binodal composition? (2p)



c) Sketch a metastable and an unstable situation in a free energy of mixing curve like the one for " χ =3". (3p)

d) Explain the difference between heterogeneous and homogeneous nucleation. (3p).

3. a) Sketch the behaviour of the volume and specific heat as a function of temperature around the glass transition. Compare to the case of crystallization. (3p)

b) The Vogel-Fulcher-Tamman equation describes well the behaviour of the viscosity, or the relaxation time, for a glass forming liquid:

$$\eta = \eta_0 \exp\left(\frac{DT_0}{T - T_0}\right)$$

Give a physical interpretation of the parameter T_0 . Where does the fragility of the system enter into this equation? Sketch in a scaled Arrhenius diagram the viscosity behaviour of a strong and a fragile glass (i.e. η/η_0 vs. T_g/T). (3p)

c) What is the value of η and τ at the glass transition? Give a motivation to your answer! (2p)

d) Sketch the pair distribution function, g(r), of a glass and a crystal built up of the same coordinating structure below, with $r_1=1.4$ Å and $\theta=135^{\circ}$. (2p)



4. a) In the figure below the curve of energy, E, as a function of separation, S, is given for two colloidal particles for a range of salt from 10^{-5} M to 10^{-2} M. Which are the two main contributions building up this curve? In a separate figure sketch the behaviour of each contribution. Why is the change in salt concentration reducing the maximum energy barrier (discuss this in term of parameters given in the figure)? (5)





b) Polymers can both stabilise and destabilise a colloidal solution. Based on the figure above discuss the mechanism for stabilisation and destabilisation of a colloidal solution. (3p)

c) A common way to destabilise a colloidal solution is to use the depletion mechanism. Explain the physics involved in this process. (2p)

5. a) The path of an ideal polymer chain can be described as a random walk. In real polymer chains constraints from definite bond angles give rise to short range correlations. Explain the meaning of The Flory characteristic ratio (C_{∞}) and the Kuhn length (l). (2p)

b) Excluded volume effects leads to long range correlations for real chains. Experimentally, for polymers in good solvents it is found that the end to end vector R is proportional to aN^x , where a is segment length and N is number of segments. The exponent x is experimentally found to be around 0.6. Using two contributions, one repulsive and one elastic, to the free energy of a single polymer coil:

 $F_{rep} = k_B T a^3 \frac{N^2}{2R^3}$, and $F_{el} = 3k_B T \frac{R^2}{2Na^2}$, it is possible to derive the exponent x.

Derive x and explain the origin of the two contributions F_{rep} and F_{el} . (5p)

c) The reptation model by de Gennes is a simple and successful description of the diffusion of a polymer chain in a melt. Explain the basic idea behind the tube-like motional constrains for a polymer chain in a melt (2p).

d) Given the additive resistance argument that the mobility of a chain in a tube, μ_{tube} , is equal to the mobility of a segment divided with number of segments μ_{seg}/N , and that a chain performs a random walk motion in order to escape from the tube, derive the relation between the escape time τ_r and the number of segments, N. Hint: Use the Einstein relation to relate the mobility with the diffusion coefficient. (6p)

6. a) Polymer in solutions can be described with a regular solution model according to Flory: $F_{rep} + U_{int} = k_B Ta^3 (1 - 2\chi) \frac{N^2}{2r^3} + constant$. Here F_{rep} is the same contribution as in (b) and U_{int} is the net interaction energy from solvent-solvent, solvent-polymer and polymer-polymer interactions. In terms of the Flory interaction parameter χ identify three different kinds of behavior. (3p)

b) For gel or for polymer networks we have two different classes Chemical and Physical gels. Explain the difference. (2p)

7. a) Derive the limits for formation of spherical and cylindrical micelles respectively of amphiphilic molecules in terms of characteristics of the molecule. (4p)b) What is the driving force behind the formation of infinite sheets of bilayers of

amphiphilic molecules? Give a motivation to your answer! (2p)

c) Very few homopolymers are miscible. Commonly a macroscopic phase separation is observed when a polymer A is mixed with another polymer B. Explain why this can be expected based on arguments from the regular solution model. (4p)

d) How is the situation in c) changed for the case of block copolymers AB? (2p)

8. a) Self assembled systems often show a very rich phase behaviour. Explain the why the transition between different phases occurs as a function of amphiphile concentration in the phase diagram given below (ignore the changes caused by temperature). (4p)

b) Explain how optical and mechanical properties can be expected to change as a function of amphiphile concentration in the figure below. (4p)



Fig. 9.7 The phase diagram of an amphiphilic copolymer in water, showing schematically the structures of the ordered phase. The material is a short triblock copolymer of ethylene oxide (EO) and propylene oxide (PO), with the structure $(EO)_{37}(PO)_{58}(EO)_{37}$. Data from P. Alexandris, D. Zhou, and A. Khan, *Langmuir*, **12**, 2690 (1996).