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Exam in Soft Matter Physics TIF015/FIM110

Time: Monday October 21, 2013, 8.30-12.30.
Examiner: Aleksandar Matic (0730-346294) and Andreas Dahlin (0707632779)
Allowed material: Physics Handbook or equivalent, dictionary and pocket calculator approved by Chalmers (Chalmersgodkänd räknare)
Grading: 24 points, is required for a passed.
Note: All answers must be in English. **Motivate all answers carefully. Answers without motivation give no credit.**

1a) The random walk or freely jointed chain segment model is a very simple way to predict the size of a polymer. It contains only one contribution to the free energy. What is the physical meaning of that term? Which two important terms (physical effects) are ignored in this simplified model? (Describe qualitatively with a few sentences per term, no need for equations.) Also, explain two relatively common situations in which the random walk model actually gives an accurate measure of coil size. (5p)

b) Describe (without equations) how polymers crystallize. The description can be brief, but make sure the following questions are answered: What process corresponds to the activation energy? Why does one observe a characteristic thickness of lamellae? How can one influence this thickness in a simple manner? (3p)

c) A polymer has a special end group that attaches spontaneously to a surface. How could one prepare a brush using such polymer molecules? (2p)

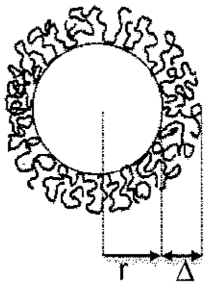
2. Consider a supercooled liquid at room temperature.
a) Write an expression for the change in free energy $\Delta G(r)$ on forming a spherical nucleus of crystal of radius r as a function of the change in Gibbs free energy on going from the liquid to the solid, ΔG_{bulk}, and the crystal/liquid surface tension is γ_{lc}. Motivate the different terms in the expression. (4p)

b) Given that the crystal/liquid surface tension $\gamma_{lc}= 0.03$ J/m^2 and the change in free energy per unit volume, if the whole sample would crystallize, $\Delta G_{bulk}=-10^7$ J/m^3.

What is the critical radius of the nucleus in order for it to spontaneously grow? Don't forget to motivate your answer. (3p)

c) Discuss qualitatively if the liquid is likely to crystallize at room temperature via homogeneous nucleation at room temperature. (3p)

3. A colloidal suspension consist of spherical particles with a solid core of radius r=100 nm coated with a polymer layer of thickness Δ=10 nm in an aqueous solution of sodium chloride. The suspension is at room temperature and the salt concentration in the solution is $5 \cdot 10^{-2}$ mol/dm^3.



a) Draw the diagram of interaction energy as a function of the distance from the center of the particle for this system. Do this quantitatively by providing a scale on the x-axis in the diagram and also motivate carefully why you obtain this shape of the interaction as a function of distance. (6 p)

b) If the suspension is destabilised so that the system is dominated by attractive interactions different types of aggregate structures are formed in the case of strong or weak attraction. Describe the difference in the structure of the aggregates in the two cases and why they are formed in that way. (4 p)

4. a) Discuss why glasses both can be considered to belong to and not to belong to soft matter materials. (2 p)

b) Estimate the instantaneous shear modulus, G_0, for a glass-forming liquid at the glass transition. (3 p)

c) For a glass forming liquid the temperature dependence of the relaxation time is given by the Vogel-Fulcher-Tamman equation

$$\tau = \tau_0 \exp\left(\frac{D}{T - T_0}\right)$$

with the D=710 K and T_0=323 K.

Using a certain cooling rate, ΔT_1, in a calorimetric experiment we obtain a glass transition temperature T_g=348 K. Is this to be considered a rapid or a slow quench? Carefully motivate your answer! (5p)

5. In a solution of the amphiphilic molecule Sodium dodecyl sulphate (SDS, chemical formula $C_{12}H_{25} - OSO_3Na$) in water, at room temperature, the amphiphlic molecules are either present as monomers or in micelles of aggregation number M.

a) What is the shape of the micelles in the solution? Carefully motivate your answer. For a linear hydrocarbon chain you can assume that the volume is given by v=(27.4+29.9n)·10^{-3} nm^3 and that the critical chain length is given by l_c=(0.154+0.1265n) nm and that SDS has a head group are a0=0.65 nm^2 in an aqueous solution. (2p)

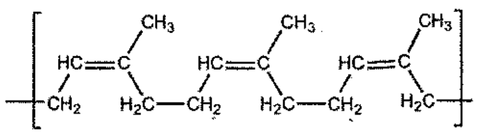
b) The volume fraction of amphiphilic molecules in the micelles, X_M, is given in terms of the volume fraction of monomers, X_1, by

$$X_M = M\left[X_1 \exp\left(\frac{\varepsilon_1 - \varepsilon_M}{k_B T}\right)\right]^M$$

The energy difference between a molecule as a monomer in the solution and a molecule belonging to a micell is determined to 21.25 kJ/mol. Estimate the critical micellar concentration (CMC). (5 p)

c) At concentrations above CMC we can regard this as a colloidal suspension. Discuss the mechanism stabilizing the solution and how we can destabilize solution. (3p)

6a) Poly(cis-isoprene), also known as natural rubber, has the chemical formula:



Assume the Kuhn length is twice the monomer length, which is 4.0 Å. Calculate the size (distance between end points) of a coil in a solution with $\chi = 0$ if M = 10 kg/mol. (5p)

b) The solvent evaporates and the resulting melt has a density of 1.08 g/cm^3. The plateau value of the stress relaxation modulus at room temperature is 4.86 MPa. How many monomers are between entanglement points on average? (3p)

c) The melt undergoes "vulcanization" during which cross-links to other chains can be formed at the methyl ($-CH_3$) groups. Estimate the percolation threshold! (2p)

Some useful relations

Debye screening length:

$$\kappa^{-1} = \left(\frac{2e^2 n_0 z^2}{\varepsilon \varepsilon_0 k_B T} \right)^{-\frac{1}{2}}$$

Polydispersity index (M_w/M_n):

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i} \qquad M_w = \sum_i w_i M_i = \frac{\sum_i n_i M_i M_i}{\sum_i n_i M_i}$$

Random walk:

$$R = aN^{1/2}$$

Entropy:

$$S = k_B \log(W)$$

Gibbs' free energy change:

$$\Delta G = \Delta H - T\Delta S$$

Flory radius (in solvent):

$$R_F = [1 - 2\chi]^{\frac{1}{5}} aN^{\frac{3}{5}}$$

Alexander - de Gennes polymer brush height:

$$H = \left[\frac{1-2\chi}{3} \Gamma \right]^{\frac{1}{3}} a^{\frac{5}{3}} N$$

Reptation theory terminal time:

$$t_T = \frac{[aN]^2}{2D_{CiT}} = \frac{\zeta_{segment} aN^3}{2k_B T}$$

Gelation threshold and gel fraction:

$$f_c = \frac{1}{z-1} \qquad p_{gel} = 1 - p_0^z \qquad p_0 = 1 - f + fp_0^{z-1}$$

Rubber elasticity modulus:

$$Y = \frac{3\rho k_B T}{mN_{part}} \qquad G_e = \frac{\rho k_B T}{M_{eff}}$$

Oscillatory deformation $e(t) = e_0 \sin(\omega t)$ stress response and dynamic modulus:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \qquad \tan(\delta) = \frac{\mathrm{Im}(G_{DM})}{\mathrm{Re}(G_{DM})} \qquad G_{DM}(\omega) = \mathrm{i}\omega \int_0^\infty \exp(-\mathrm{i}\omega t) G(t) \mathrm{d}t$$