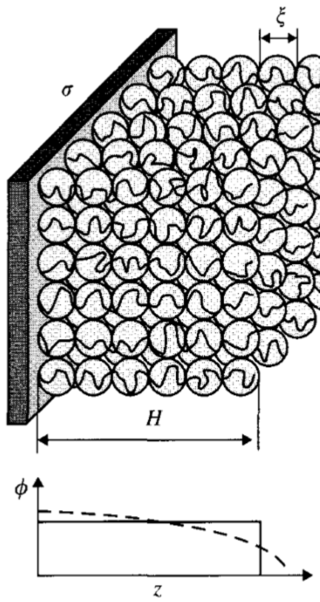
Soft Matter Problem set 3 – Polymers

Problem 9

Consider the polymer brush shown below. Each chain is grafted by one end to a substrate (for instance, the surface of a colloidal particle), and has a length of N (Kuhn) monomers. The layer contains σ chains per unit area, and has a total height h. We will analyze the properties of this brush by scaling arguments, making use of blobs.



a) Give an expression for the blob size ξ as a function of σ. Hint: what is the length scale at which the polymer chain is unperturbed by its neighbours?

b) Give an expression for the number of monomers g inside a blob for an ideal polymer chain. Use the answer from a) to express g in terms of σ.

c) The brush height h is the product of the number of blobs per chain N/g and the blob size ξ. How does h depend on σ for a brush of ideal chains (in a theta solvent)?

d) The chains in a brush are stretched away from the surface. Give an expression for the stretching free energy F_{str} per chain in a brush.

e) The reason for the chain stretching in a brush is the osmotic pressure inside the brush layer. Show that the osmotic pressure has the same dimensions as $F_{\mathrm{str}}/V_{\mathrm{chain}}$ with V_{chain} the volume of a single chain. Use this to derive an expression for the osmotic pressure inside the brush layer.

f) When two surfaces with a polymer brush are pushed together, they repel because of this osmotic pressure. Estimate the force required to push two surfaces of 1 cm^{-2} together. Does this force depend on the brush height? Please explain.

g) (To be completed after lecture 4) Repeat steps b) to f) for a polymer brush in a good solvent ($\nu = 3/5$).

Problem 10

When a polymer chain is stretched to an end-to-end distance $R > R_0$, the conformational entropy decreases according to: $S(N,R) = -3k_{\mathrm{B}}R^2/2Nb^2$. The force required to stretch the polymer to an end-to-end distance R is given by: $f(R) = -3k_{\mathrm{B}}R/Nb^2$.

a) Give an expression for the spring constant of an ideal polymer chain from the expression of the force $f(R)$, and calculate the spring constant for a polymer of length $N = 1000$ and Kuhn length $b = 1$ nm.

b) Give a thermodynamic explanation why the spring constant of an ideal polymer chain *decreases* with increasing length of the polymer.

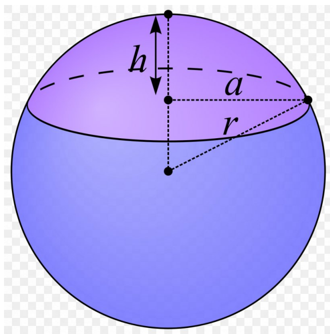
c) A rubber band (Dutch: 'elastiekje') is a crosslinked polymer network of ideal chains. The force to extend it slightly (linear regime) has the same form as $f(R)$ above for a single ideal chain. Suppose that a weight is attached to the rubber band. What happens to the position of the weight if the temperature is increased?

Problem 11

(You can use the lecture notes on depletion attraction to answer this question before week 4.) Depletion interactions arise when a solution of suspended (colloidal) particles contains other particles (such as polymer coils) that have an intermediate size between the suspended particles and the solvent molecules. The intermediate particles are also called depletants. The most common depletants are polymers (of radius R_p) that do not adsorb on the surface of the colloidal particles. It is assumed they interact only via a hard-core interaction. As shown in the previous problem, these polymers are then excluded from a region of thickness R_p away from the surface of the colloidal particle, which is called the depletion zone.

As two colloidal particles approach, their depletion zones overlap, with the result that there is a volume of the solution between the particles in which the concentration of the polymer molecules is less than in the bulk solution. This means that the difference in osmotic pressure between the bulk solution and the depletion zone leads to a force that pushes the colloidal particles together: the depletion force.

a) How large is the depletion volume V_{dep} for two colloidal particles of radius $a = 1$ μm that touch each other? Hint: make a drawing, and use the spherical cap formula to calculate the volume of a spherical cap with height h and radius r: $V_{\mathrm{cap}} = \frac{\pi h^2}{3}(3r - h)$.



b) For arbitrary distance r between the centers of the colloidal particles, the depletion volume is given by:

$$V_{\mathrm{dep}}(r) = \frac{4\pi}{3}\left(a + R_p\right)^3 \left(1 - \frac{3r}{4(a + R_p)} + \frac{r^3}{16(a + R_p)^3}\right)$$

Make a sketch of $V_{\mathrm{dep}}(r)$. At what distance r is $V_{\mathrm{dep}} = 0$?

c) The interaction free energy between the particles is given by $F_{\text{dep}}(r) = -\Pi V_{\text{dep}}(r)$ with Π the osmotic pressure of the polymers. The osmotic pressure is given by the ideal gas expression: $\Pi = nk_{\text{B}}T$ with n the number concentration of polymer molecules (in m^{-3}). We have a polymer with a molecular weight $M = 135$ kg mol^{-1}, a radius $R_p = 30$ nm. Calculate the osmotic pressure of the solution for concentrations of 2 and 20 g/L.

d) Estimate the interaction free energy between the particles at contact for these polymer concentrations.

e) How does the depletion interaction depend on temperature? Explain why.

f) Two different solutions both containing 20 g/L of polymer are prepared, one with an ionic strength of 0.1 M, the other with an ionic strength of 10^{-5} M. The colloidal particles are found to aggregate with the polymer solution at 0.1 M ionic strength, but not at 10^{-5} M. Explain why.

Problem 12

Real polymer chains in a good solvent are easier to stretch than ideal polymers.

a) Use a scaling approach to derive an expression for the force required to stretch a real polymer chain in a good solvent.

b) Is a real polymer chain also a Hookean spring? Explain why (not).

c) At what extension is the stretching force of an ideal polymer equal to the stretching force of a real polymer in a good solvent?