# Suspensions and polymer solutions

Home Examination

7 July 2011

Please solve the following two problems. You are required to do the examination on your own. You can consult notes, books, the internet, mathematical software, etc.. Of course, you may also ask the lecturer questions. There is no need to repeat calculations that were performed in class or in the exercises. The solutions should be e-mailed or handed by Thursday night, July 14, 2011, unless you have contacted the lecturer concerning a different arrangement.

## Problem 1: Charge-stabilized suspension with depletion interaction

Consider a dilute suspension containing large spherical particles of radius $a_\ell$ and small ones of radius $a_\mathrm{s}$. The host liquid is a salt solution of Debye screening length $\kappa^{-1}$ and dielectric constant $\epsilon$. The large spheres have a surface charge density $\sigma$. The concentration of small particles is $c_\mathrm{s}$, corresponding to an osmotic pressure $p_\mathrm{s} = k_\mathrm{B}Tc_\mathrm{s}$.

Now consider an isolated pair of large particles, whose center-to-center distance is $r = 2a_\ell + d$. The aim is to characterize their effective pair potential, arising from their interaction free energy as a function of the separation $d$. Assume $\kappa^{-1} \lesssim (d, a_\mathrm{s}) \ll a_\ell$, and that at such separations the van der Waals interaction is negligible.

(a) Show that, under the aforementioned assumptions, the free energy of interaction for $d < 2a_\mathrm{s}$ is given by

$$F_\mathrm{int}(d) \simeq \frac{8\pi^2 a_\ell \sigma^2}{\epsilon\kappa^2} e^{-\kappa d} - \frac{\pi}{2} k_\mathrm{B}Tc_\mathrm{s}a_\ell(2a_\mathrm{s} - d)^2 \tag{1}$$

(and by the first term alone for $d > 2a_\mathrm{s}$).

(b) Show that the qualitative shape of this potential depends only on the following two dimensionless parameters:

$$\alpha \equiv 2\kappa a_\mathrm{s}, \quad \gamma \equiv \frac{8\pi\sigma^2}{\epsilon k_\mathrm{B}Tc_\mathrm{s}}.$$

(c) Discuss the possible qualitative shapes of the potential. Analyze the exact regions of values for $\alpha$ and $\gamma$ that yield the different potential shapes. (Hint: there should be five such cases.)

(d) What are the conditions under which you expect that the large particles might form crystals with a stable, finite inter-particle distance?

## Problem 2: Swelling of a 2D polymer ring

Consider a two-dimensional polymer chain whose ends are linked to form a ring. (Such systems are achieved, for example, by depositing DNA plasmids onto a surface.) The ring is made of $N$ segments of length $a$ each. The statistics of the unperturbed chain is characterized by a swelling exponent $\nu$.

A 2D pressure difference is introduced between the inner and outer parts of the ring, $\Delta p = p_{\mathrm{in}} - p_{\mathrm{out}}$, causing the ring to swell. The aim is to analyze the mean area of the ring, $A$, as a function of $N$, $a$, $\nu$, $\Delta p$, and the temperature $T$. All calculations should be made up to unknown prefactors. Assume that the ring's area $A$ always depends on its typical radius $R$ in the usual way, $A \sim R^2$.

(a) (i) Use a Flory-like argument to obtain the Gibbs free energy of an ideal (Gaussian) ring.

(ii) Show that the mean area of this ring is expected to drastically change at a critical pressure difference, $\Delta p_{\mathrm{c}} \sim k_{\mathrm{B}}T/(Na^2)$.

(b) (i) Use again a Flory-like argument to obtain the Gibbs free energy of a real chain (i.e., for a general $\nu$). (Hint: recall the probability distribution function derived for a real chain.)

(ii) Show that the mean area satisfies the following relation:

$$\frac{A}{(Na)^2} \sim \left(\frac{Na^2\Delta p}{k_{\mathrm{B}}T}\right)^{\frac{2(1-\nu)}{2\nu-1}} . \tag{2}$$

(iii) What is predicted by this relation for an ideal chain? Compare to the results of item (a).

(iv) What is predicted by this relation for a 2D self-avoiding chain? At what values of $\Delta p$ does $R$: (1) scale linearly with $N$; (2) is approximately equal to the unperturbed value, $R_0 \sim aN^{\nu}$? Are these two results consistent? How does $R$ scale with $N$ for $\Delta p \sim k_{\mathrm{B}}T/a^2$? Is this result reasonable? Why?

(c) (i) Perform a scaling ('blob') analysis for a real chain. Hint: assume that because of the pressure difference the ring is under tension $f \sim R\Delta p$ (Laplace' law). Show that the number of monomers in a blob satisfies the relation

$$g \sim \left(\frac{k_{\mathrm{B}}T}{Na^2\Delta p}\right)^{\frac{1}{2\nu-1}} . \tag{3}$$

(ii) Calculate the area and compare to Eq. (2) from the Flory argument.

(iii) Find the limits of this scaling behavior. Use them to explain the results of item (b)(iv).

(d) Briefly summarize your conclusions concerning the qualitative swelling behaviors of ideal rings and self-avoiding rings.