EXAM 1
SOFT CONDENSED MATTER
November 3th, 2014

- *The exam consist of 4 questions, total possible points is 200. Maximum number of credit points is indicated between square brackets.*
- *This is an open book exam. You may use anything you want; that is, handout, notes, books, etc. Except for calculator, no other electronic devices can be used.*
- *Use a new sheet of paper for each of the problems, with your name clearly written on every page.*
- *Exam is written in English. Please write clearly.*
- *Constants:* *Boltzmann:* $k = 1.38\times10^{-23}$ J/K
  vacuum permittivity: $\varepsilon_0 = 8.854\times10^{-12}\ \mathrm{C^2/N\cdot m^2}$
  Avogadro's number: $N_{\mathrm{Av}} = 6.022\times10^{23}\ \mathrm{mol^{-1}}$
  Elementary charge: $e = 1.602\times10^{-19}$ C

1. Consider a fluid of homogeneous monodisperse spheres interacting with the following pair potential

$$\phi(r) = \begin{cases} \infty & (r \le d) \\ \varepsilon \dfrac{\exp\left[-\kappa(r-d)\right]}{r/d} & (r > d) \end{cases},$$

where d is the diameter of the spheres and $\varepsilon > 0$ is the interaction strength and κ^{-1} is a measure for the range of the attractive part of the potential. Assume that $\varepsilon \ll kT$.

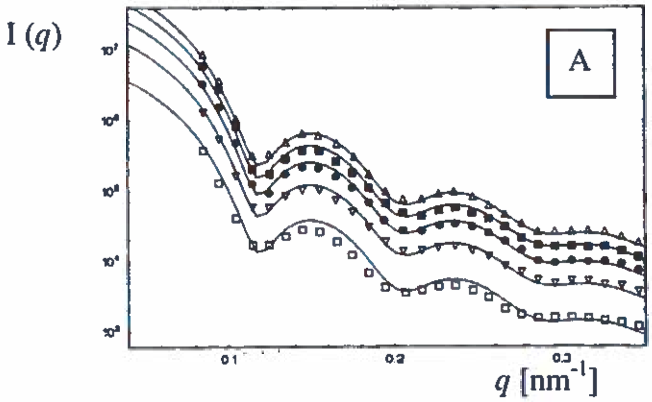
a. [10] Base on the *second virial coefficient* of this fluid, in which κd range (i.e. >>1, ~ 0, or << 1) will the system behave as in the hard sphere case?

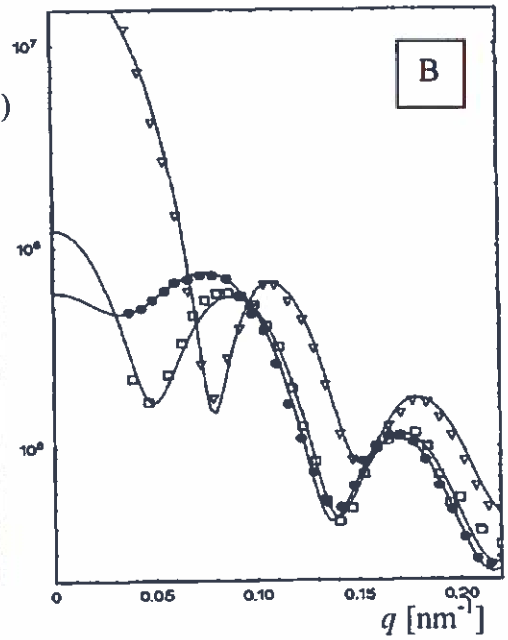
b. [10] Do you think such fluid has a liquid-gas phase separation? Give arguments for your answer.

c. [10] For sufficiently dilute fluids the *radial distribution function* can be approximated as $g(r) = \exp\left(-\phi(r)/kT\right)$. Assuming that $\varepsilon \ll kT$ and neglecting terms of order ε^2 and higher, what is the relative change in the internal energy per unit volume compare to the hard sphere case?

d. [10] In one graph sketch the *radial distribution functions* for this fluid at volume fractions of 0.01 and 0.40.

2. Researchers [Dingenouts and Ballauff, *Acta Polymer.*, (1993)] studied a core-shell latex consisting of spheres with a polystyrene (PS) core and a polymethylmethacrylate (PMMA) shell by small-angle x-ray scattering. Since the electron density, i.e., the contrast of both polymers, can be easily matched by addition of sucrose to the dispersing agent water, the internal structure of the particles can be studied by contrast variation. As a first step, the researchers determined size of homogeneous particles, which will be next coated to make the core-shell particles, using contrast variation. The scattering intensities of the homogeneous cores at different contrast are given in graph A.





a. [15] Estimate the average size of the PS cores from using graph A.

b. [10] Explain why the position of the minima in graph A does not depend on the dielectric contrast.

Next, the researchers measured the scattering intensities of the core-shell particle at different contrast (graph B). The researchers determined the total particle size following these steps:

- Write the scattering amplitude $f(q)$ for a spherical particle with a radius dependent electron density $\sigma(r)$ as $f(q) = 4\pi\int_0^R [\sigma(r)-\sigma_m]r^2 \frac{\sin(qr)}{qr}dr$, where σ_m electron density of the liquid phase.
- Define a volume averaged electron density $\sigma_{av}(R)$ for the particles and write the local electron density as $\sigma(r) = \sigma_{av}(R) - [\sigma(r) - \sigma_m]$.
- Split the scattering amplitude in a part which does *not* depend on the local electron density, $\sigma(r)$, and a part which does depend on the local electron density, $\sigma(r)$.
- Find what condition should q satisfy so that the scattering amplitude which does *not* depend on the local electron density is zero for all contrasts.
- Conclude what this will mean for the scattering amplitudes which do depend on the local electron density for all contrasts at this condition.

c. [25] Using the above steps, estimate the total size of the core-shell particles using the graph B.

d. [10] What other approaches can be used to determine the total particle size?

3. Consider a one-dimensional, binary lattice with *M* pairs of lattice sites (a, b). The lattice is in equilibrium with a solution of dimeric (macro) molecules as schematically depicted in Figure 1. A dimeric molecule may adsorb onto a site *a* of the lattice with energy ε_a , onto a site *b* with energy ε_b, or onto both sites at the same time with energy $(\varepsilon_a + \varepsilon_b)$. The total number of dimeric molecules in the system is *N*. There are no significant interactions other than the ones indicated between the lattice sites and the dimers.

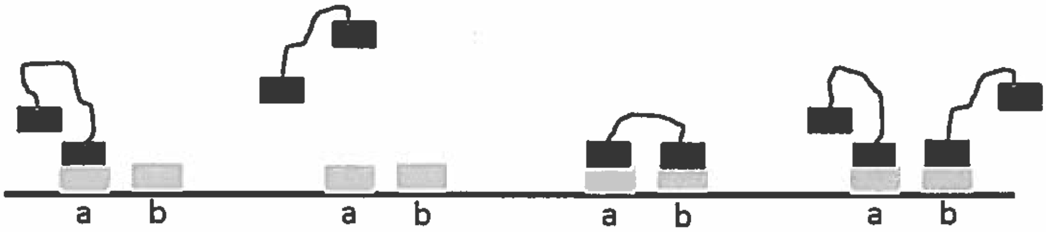


Figure 1: pairs of neighboring (a,b) lattice sites with several configurations of adsorbed dimeric molecule(s). Starting from the left: one adsorbed dimeric molecule onto lattice site *a*; no adsorption; one adsorbed dimeric molecule onto both site *a* and site *b*; two adsorbed dimers, each on one of the sites (a, b).

a. [10] Argue that the grand partition function in this situation is given by $\Xi = \left(\Xi_{pair}\right)^M$. Here, Ξ_{pair} refers to the grand partition function of a pair of lattice sites (a, b).

b. [20] Show that the grand partition function of a pair of lattice sites (a,b) is given by

$$\Xi_{pair} = 1 + \lambda(e^{-\varepsilon_a/kT} + e^{-\varepsilon_b/kT} + e^{-(\varepsilon_a+\varepsilon_b)/kT}) + \lambda^2 e^{-(\varepsilon_a+\varepsilon_b)/kT},$$

where the fugacity $\lambda = e^{\mu/kT}$, with μ the chemical potential of a dimeric molecule.

c. [15] Show that the average number of adsorbed dimers per (a,b) pair is given by

$$< N_{ads} >= \left(\lambda(e^{-\varepsilon_a/kT} + e^{-\varepsilon_b/kT} + e^{-(\varepsilon_a+\varepsilon_b)/kT}) + 2\lambda^2 e^{-(\varepsilon_a+\varepsilon_b)/kT}\right) / \Xi_{pair}$$

d. [20] Show that the average occupation number of sites *a* of an (a,b) pair is given by

$$< M_a >= \left(\lambda(e^{-\varepsilon_a/kT} + e^{-(\varepsilon_a+\varepsilon_b)/kT}) + \lambda^2 e^{-(\varepsilon_a+\varepsilon_b)/kT}\right) / \Xi_{pair}$$

- e. [10] Let p(a) be the grand canonical probability that a dimeric molecule binds to a site *a*, as depicted on the left configuration of Figure 1. Let $p(a \wedge b)$ be the grand canonical probability that a dimeric molecule adsorbs by making a bond with both an *a* and *b* site, as on the third configuration from the left of the Figure. Show that $\dfrac{p(a)}{p(a \wedge b)} = e^{\varepsilon_b/kT}$. Provide an interpretation for this result.

- f. [10] How would you determine λ in terms of M, total concentration of dimeric molecules, and interaction energies? You are not required to actually derive an explicit expression for λ, just write down the equation from which it is supposed to follow.

4. [15] Consider a surface in the form of a sphere of radius R, and another surface in the form of a cylinder of radius R and length L. The surfaces have zero preferred curvature ($c_0 = 0$).

Prove that the curvature free energy of a sphere for such a surface is given by $F_c(sphere) = 4\pi(2\kappa + \bar{\kappa})$, and that of the cylinder by $F_c(cylinder) = \pi\kappa\frac{L}{R}$.