EXAM 2
SOFT CONDENSED MATTER
July 2nd, 2013

- *This is an open book exam. You can use the syllabus and the handouts provided by the lecturers.*
- *Use a new sheet of paper for each of the problems.*
- *Constants:* *Boltzmann:* $k_B = 1.38\times10^{-23}$ 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 one-dimensional ideal polymer chain confined to an area between $x=0$ and $x=D$.

   a. Calculate which eigenfunctions and eigenvalues appear in the bilinear expansion of $G_N(x|x')$.

   b. When do you expect ground state dominance (and explain what that means)? Sketch the corresponding segment density profile.

   We now consider the situation of a polymer chain in 3 dimensions confined to a gap between two flat plates (placed at $x=0$ and $x=D$).

   c. Use scaling theory to predict the average end-to-end distance in this case for a very long polymer chain dissolved in an ideal solvent.

   d. How would the result for the average end-to-end distance change if the polymer is dissolved in a good solvent?

2. Consider one-dimensional aggregation without the presence of a template. The (short-range) binding energy is w and the total concentration (mole fraction) is x.

   a. Make use of paragraph 2.2 in the Handout to show that if $xe^{-w/kT} >> 1$, the average size of the aggregates is given by

   $$\langle n \rangle \approx e^{-w/2kT}\sqrt{x}\,.$$

   b. If w is independent of temperature and at constant overall concentration x, argue whether $\langle n \rangle$ increases, decreases, or remains constant with temperature. Provide an interpretation

   c. Now assume aggregation is driven by hydrophobic interactions: in that case argue that $w = -2\gamma(T)A$, with $2A$ the overlap area between two hydrophobic objects and $\gamma(T)$ the temperature-dependent interfacial tension between the monomers and the solvent.

   d. Show that the critical aggregate concentration as defined by $x_0 = e^{w/kT}$ is now given by

   $$x_0 = e^{-2Ah_0/kT}e^{2As_0/k}\,,$$

   and the average aggregate size by

   $$\langle n \rangle = e^{Ah_0/kT}e^{-As_0/k}\sqrt{x}\,.$$

   Here, h_0 and s_0 are the surface excess enthalpy and entropy, respectively, defined at a reference temperature T_0 and assumed independent of temperature in the interval $[T_0, T]$.

   Would you expect x_0 and $\langle n \rangle$ to increases, decreases, or remain constant with temperature?

   e. It is often observed that emulsions of oil drops in water are stabilized by nanoparticles or colloids that adsorb onto the oil-water interface. Provided the surface coverage of adsorbed species is f, show that *thermodynamically stable emulsion drops of radius R* can be expected if the 'bare' interfacial tension between oil and water, that is the tension of the interface that is uncovered by colloids, is given by

   $$\gamma \approx \frac{kT}{4\pi R^2(1-f)}\,.$$

   Discuss this result.

3. In a synthesis procedure for zinc sulfide (ZnS) colloidal particles two solutions of water soluble salts containing the zinc and sulfide ions separately are mixed rapidly in the presence of a polymeric surfactant. This makes the poorly soluble ZnS precipitate out to form monodisperse and spherical particles with a diameter close to a micrometer as demonstrated by static light scattering. X-ray scattering further demonstrates that these spherical particles are composed of crystalline ZnS with an average size of 15 nm. Under otherwise identical conditions the synthesis is repeated in the presence of 0.1 mM of NaCl in the water used. Now the spherical particle size comes out to be 2 μm, while the ZnS nanocrystal size remains unchanged.

   a. Explain in detail why the above observations are not compatible with a '*nucleation and growth only mechanism*'.

   b. What changes could be made to the above recipe to make it follow a *nucleation and growth mechanism,* or do you think this is not possible? In both cases also explain why.

   c. The two particles mentioned above are mixed (without any NaCl and in an equal molar ratio of the small and large particles) and used in a third 'seeded-growth' experiment in which new ZnS only grows on the seed mixture of spheres. The result is that the larger spheres with a diameter of 2 μm grew to a size of 3 μm, while the smaller ones grew to a size of 2.5 μm. What can be deduced from this experiment regarding the growth law/mechanism of the ZnS particles?
