EXAM 2
SOFT CONDENSED MATTER
January 25th, 2016

- *The exam consist of 5 questions; total possible points is 200. Maximum number of 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.*
- *Start a new sheet of paper at problem 4, with your name clearly written on every page.*
- *Exam is written in English. Please write clearly.*
- *Constants:*

Boltzmann:	$k = 1.38 \times 10^{-23}$ J/K
Vacuum permittivity:	$\varepsilon_0 = 8.854 \times 10^{-12}$ C^2/N·m^2
Avogadro's number:	$N_{Av} = 6.022 \times 10^{23}$ mol^{-1}
Elementary charge:	$e = 1.602 \times 10^{-19}$ C
Acceleration of gravity on the earth	$g = 9.8$ m/s^2.

1. Properties of Gaussian and excluded volume chains [36 points]

The most probable end-to-end distance R_{mp} of an ideal Gaussian chain consisting of N segments is the value of the end-to-end distance R at which $R^2 P(R,N)$ maximizes. Here $P(R,N)$ is defined as:

$$P(R,N) = \left(2\pi b^2 N/3\right)^{-3/2} \exp\left(-3R^2/2b^2 N\right) \tag{1.1}$$

a. What is the meaning of equation (1.1) and explain why the segment size b is a variable. [10 *points*]

b. Show that $R_{mp} = 2R_g$, where the radius of gyration $R_g = b\sqrt{(N/6)}$. [14 *points*]

For a self-avoiding random walk (SAW) generated on a lattice by a Monte Carlo computer simulation, the radius of gyration R_g of the polymer chain depends on chain length N as follows:

$$R_g = 0.4205 b N^{0.5934} \tag{1.2}$$

c. Interpret the values 0.4205 and 0.5934 and discuss analogies and differences with the properties of an ideal Gaussian chain. [12 *points*]

2. Osmotic pressure from Flory-Huggins theory [24 points]

In a virial expansion the Flory-Huggins result for the osmotic pressure Π of a polymer solution reads at low concentration:

$$\frac{\Pi v_c}{k_B T} = \frac{\phi}{N} + \left(\frac{1}{2} - \chi\right)\phi^2 + \dots \tag{2.1}$$

a) Use equation (2.1) to discuss the deviation from ideal behavior in terms of $\Pi - \Pi_{ideal}$ as a function of χ [12 *points*]

b) Show that $\Pi > \Pi_{ideal}$ for $\chi < 1/2$ when taking the full Flory-Huggins expression for the osmotic pressure [12 *points*]

3. Polymer solution near a single wall [40 points]

A polymer solution is in contact with a single wall. The adsorbed amount Γ is defined as:

$$\Gamma = \int_0^\infty dz \, [\phi(z) - \phi_b], \tag{3.1}$$

where z is the distance from the wall, $\phi(z)$ is the local segment density profile and ϕ_b is the bulk polymer segment concentration.

    a. What determines whether polymers in solution adsorb (positive adsorption) or are depleted (negative adsorption) and how is this translated into the local polymer density profile? [10 *points*]

In case of positive adsorption describe how an adsorbed polymer looks like in case of

    b. a very low polymer bulk concentration ϕ_b [8 *points*]
    c. a high polymer bulk concentration ϕ_b [8 *points*]

In case of negative adsorption an accurate expression for the polymer concentration at the wall is

$$\phi(z) = \phi_b \tanh^2(z/\delta) \tag{3.2}$$

Note that $\tanh(x) = (e^x - e^{-x})/(e^x + e^{-x})$.

    d. Show that the adsorbed amount in case of negative adsorption reads $\Gamma/\phi_b = -\delta$. [14 *points*]

Hint: use $\int dx \tanh^2(qx) = x - \tanh(qx)/q + $ integration constant, where q is a constant.

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4. Colloidal interactions problems [50 points]

Consider a spherical particle of density $\rho_p = 1025$ kg/m^3, and a zero surface potential ψ_p. The particle is made of material A with a non-retarded Hamaker constant $A_{AA} = 1 \times 10^{-20}$ J in a vacuum at room temperature. The particle is dispersed in a solvent B with density $\rho_s = 1000$ kg/m^3, and with a non-retarded Hamaker constant $A_{BB} = 9 \times 10^{-20}$ J in a vacuum at room temperature. The particle is located near a flat substrate C with zero surface potential ϕ_s and with a non-retarded Hamaker constant $A_{CC} = 16 \times 10^{-20}$ J in a vacuum at room temperature.

    a. Calculate the Hamaker constant for the interaction between the particle and the substrate. [*10 points*]
    b. Providing that you can change the material properties of the substrate, what Hamaker constant should you choose to minimise the interaction between the particle and the substrate. [*5 points*]
    c. Please write down an analytical expression of the total potential energy of the particle as a function of height above the surface h. **Hint:** Use supporting information on the last page. [*5 points*]
    d. Provide an analytical expression for the equilibrium distance between the particle and the substrate in the case of short distance. What is the total potential energy at this distance? How would the equilibrium total energy be affected if the particle and the wall both had an electric double layer? [*15 points*]

In an experiment by Walz and Prieve, the total potential energy profiles measured for a sphere interacting with a substrate across a solution. The three sets of data (see Fig. 1A)

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correspond to different power levels for a laser beam focused on the bottom of the sphere, producing an upward optical force (i.e. against the gravity). Fig. 1B summarizes the results of a systematic study of how the apparent weight (i.e. force of gravity minus optical force) depends on the laser power when the beam is incident either on the top or bottom of the sphere.
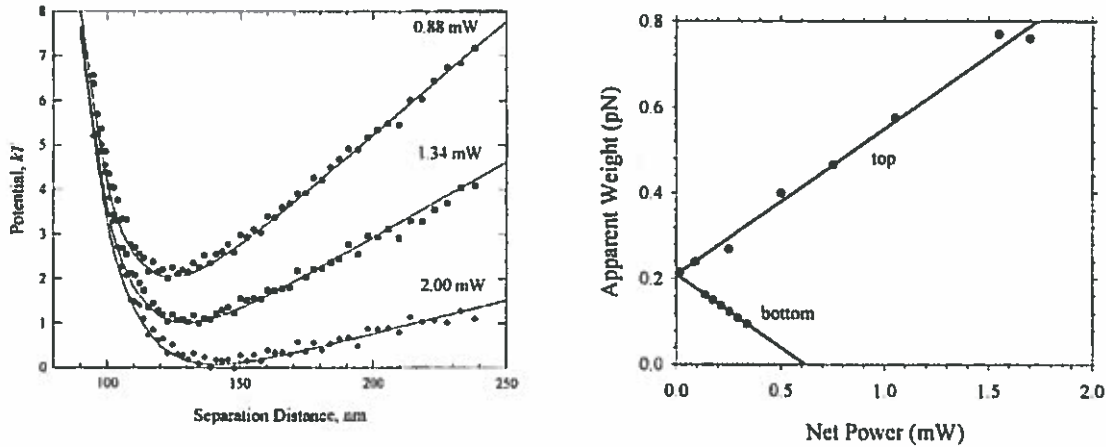

Figure 1 (A) Total potential profiles measured for a sphere interacting with a glass slide across a solution. The three sets of data correspond to different power levels for a laser beam focused on the bottom of the sphere, producing an upward optical force. (B) Effect of the intensity of a laser beam measured in pico Newtons ($1 pN = 10^{-12} N$), incident on either the top or bottom of a particle in solution, on the apparent weight of the particle.

  e. Explain why at large distances the potential energy profile is linear. [*5 points*]
  f. Using Fig. 1B, please estimate the size of the particle assuming a density difference between particle and solvent of $\Delta\rho = 25$ kg/m^3. [*10 points*]

5. Synthesis problems [50 points]

Consider the formation of a nucleus of an amorphous phase "c" on a curved interface "s" with a radius R^s from a fluid phase "f" containing a solution of molecules forming the nucleus. Let's denote by V_c the volume of the nucleus, by S_{cf} the surface area of the nucleus in contact with the solution, and by S_{sc} the surface are of the nucleus in contact with the curved solid substrate. $\Delta\mu$ defines the difference between the chemical potentials of the molecule in the solution μ_f and in the nucleating amorphous phase μ_{fc}. γ_{ij} is the interfacial tension between phases i and j (i.e. interfacial tension of the substrate-nucleus, γ_{sc}, the substrate-solution, γ_{sf}, and solution – nucleus, γ_{cf}) and v_m is the molar volume of the nucleating molecule. ΔG_V is the Gibbs free energy difference per unit volume of the nucleus phase "c" between matter in solution "f" and matter in state "c", which can be expressed by $\Delta G_V = -\dfrac{\Delta\mu}{v_m}$. Assume that the concept of contact angle can be applied.

  a. Write an expression for the free energy of formation of such a nucleus of radius r in terms of the interfacial tensions. Describe the contribution of each term. [*15 points*]
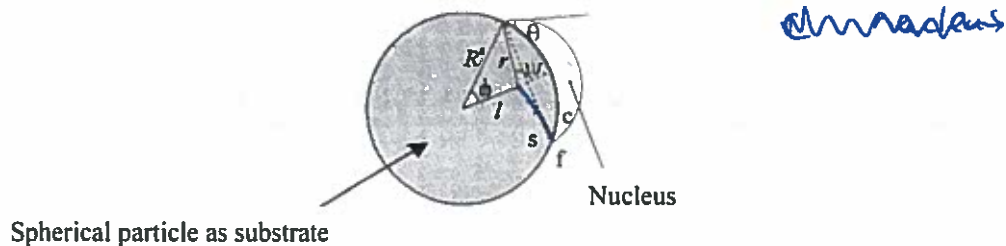

Spherical particle as substrate

Figure 2 Schematic illustration of nucleation of an amorphous phase "c" on a spherical particle "s" with a radius of R.

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In the case of nucleation on a sphere with a radius R^s (see Fig. 2), the volume of the nucleus V_c, the surface area of the nucleus in contact with the solution S_{cf}, and the surface area of nucleus in contact with the curved substrate S_{sc} are given by the following expressions:

$$m = cos\theta = (\gamma_{fs} - \gamma_{cs})/\gamma_{cf} \qquad (5.1)$$

$$\left.\begin{aligned}
S_{cf} &= 2\pi r^2(1-cos\psi), \\
S_{sc} &= 2\pi R^2(1-cos\varphi), \\
V_c &= \tfrac{1}{3}\pi r^3(2-3\,cos\psi+cos^3\psi) \\
&\quad -\tfrac{1}{3}\pi R^3(2-3\,cos\varphi+cos^3\varphi),
\end{aligned}\right\} \qquad (5.2)$$

and

$$\left.\begin{aligned}
cos\varphi &= (R-r\,cos\theta)/d = (R-rm)/d, \\
cos\psi &= -(r-R\,cos\theta)/d = -(r-Rm)/d,
\end{aligned}\right\} \qquad (5.3)$$

where

$$d = (R^2+r^2-2rRm)^{\frac{1}{2}}. \qquad (5.4)$$

b. Argue that the radius of the critical nucleus is given by $r^* = -2v_m\gamma_{cf}/kT\ln S = -2\gamma_{cf}/\Delta G_V$. [15 points]

c. Show/explain that the critical free energy of nucleation is given by the following expression:

$$\Delta G^* = -\frac{8\pi\left(\gamma_{cf}\right)^3}{3(\Delta G_V)^2} f(m,x),$$

where $x = R^s/r^*$ and

$$f(m,x) = 1 + \left(\frac{1-mx}{g}\right)^3 + x^3\left[2 - 3\left(\frac{x-m}{g}\right) + \left(\frac{x-m}{g}\right)^3\right]$$
$$+ 3mx^2\left(\frac{x-m}{g}-1\right),$$

and

$$g = (1+x^2-2mx)^{\frac{1}{2}}.$$

Researchers have designed a new class of colloidal particles in the shape of hemispherical caps (see Fig. 3A-B). As a next step they were coated with amorphous silica. If the free energy of a critical nucleus on the convex substrate can be written as $\Delta G^* = -\frac{8\pi\left(\gamma_{cf}\right)^3}{3(\Delta G_V)^2} f(m,x)$ and the free energy of formation of a critical nucleus on the concave substrate can be evaluated to be $\Delta G'^* = -\frac{8\pi\left(\gamma_{cf}\right)^3}{3(\Delta G_V)^2} f'(m,x)$, where the value of the functions $f(x,m)$ and depend on $x = R^s/r^*$ and $m = cos\theta$. The values of the two functions are given in Figs. 3C and 3D.

d. On which surface, concave or convex, will the energy for nucleus formation be lower? Give an argument to support your answer. [10 points]
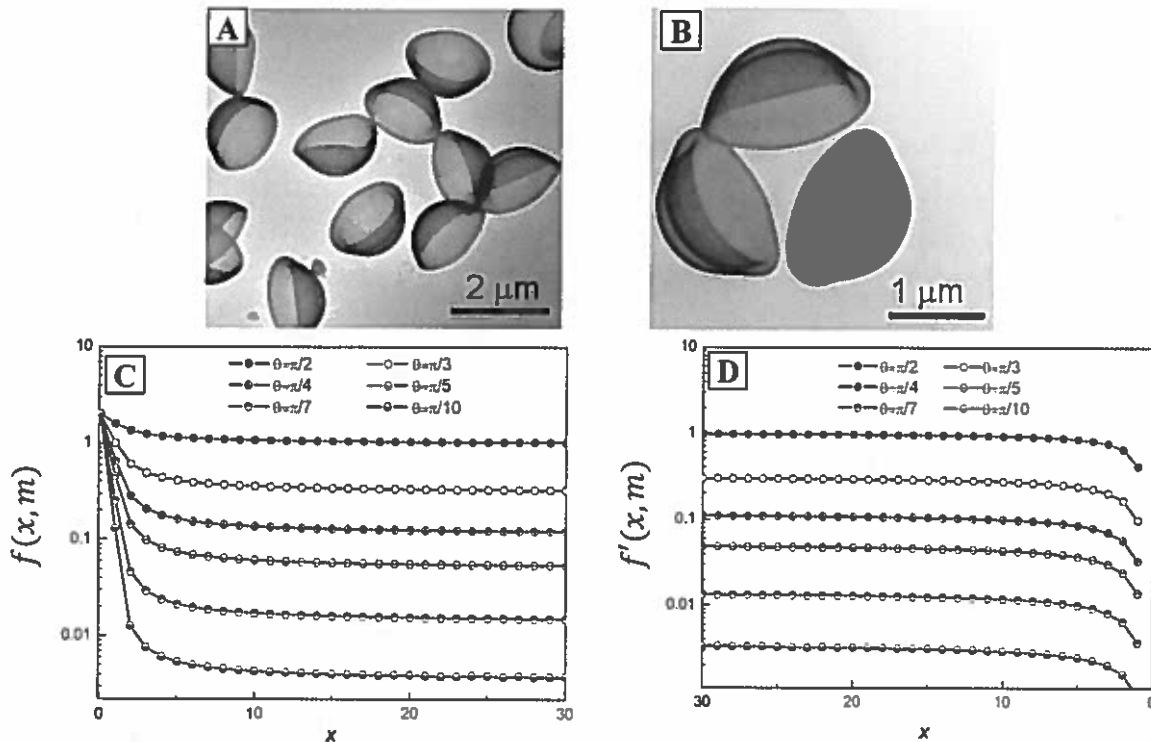
Figure 3 Scannign elelctron micrographs of hemispherical caps (A-B). Dependence of the factor: (C) $f'(m,x)$ and (D) $f(m,x)$ on the relative particle size $x = R^s/r^*$ and the contact angle θ.

Researchers have observed that upon storage a colloidal dispersion of the so called snowman-like shape (i.e. a large sphere on which a smaller sphere is attached like a "head"; see Fig. 4) colloidal particles made of two materials (A and B) having low, but nonzero solubility in the continuous phase, turn into a mix of spherical particles and snowman-like shape particles with larger "head". Schematically:
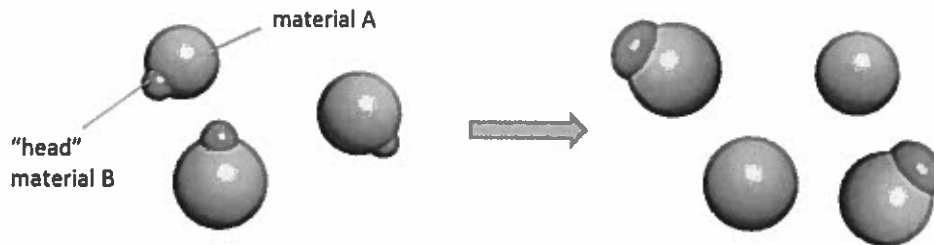

Figure 4

e. What is the most likely mechanism explaining this change? Assuming that the rate of disappearance of the "heads" is the rate limiting step (i.e. the slowest process), estimate how the reaction speed will change if the size of the "head" is increased by a factor of two. [*10 points*]

Supporting Information

Table 1: van der Waals interactions between different objects.

Configuration	All distances	Short distances	Large distances
Sphere-sphere Two spheres with radii a_1 and a_2 interacting at distance h.	$\begin{aligned} -A\,\frac{1}{6}\Bigg(&\frac{2a_1a_2}{(2a_1+2a_2+h)h} \\ &+\frac{2a_1a_2}{(2a_1+h)(2a_2+h)} \\ &+\ln\frac{h(2a_1+2a_2+h)}{(2a_1+h)(2a_2+h)}\Bigg) \end{aligned}$	$-A\,\dfrac{1}{6h}\left(\dfrac{a_1a_2}{a_1+a_2}\right)$ a_1 or a_2 $\ll a_1+a_2+h$ $\approx h$	$-A\,\dfrac{16}{9}\left(\dfrac{a_1^3a_2^3}{h^6}\right)$ a_1 or $a_2 \gg h$
Sphere-plane Sphere with radius a interacting at distance h.	$-A\,\dfrac{1}{6}\left(\dfrac{a}{h}+\dfrac{a}{2a+h}+\ln\dfrac{h}{2a+h}\right)$	$-A\,\dfrac{a}{6h}$ $a+h\sim a\gg h$	$-A\,\dfrac{2}{9}\left(\dfrac{a^3}{h^3}\right)$ $a+h\ll a$