Study Guide

Soft Matter

(NWI-MOL178) 2026/2027

Evan Spruijt
Physical Organic Chemistry
HG03.020, tel. 52455, email: evan.spruijt@ru.nl

Roel Dullens (coord.)
Physics & Chemistry of Soft Matter
HG03.061, tel. 53669, email: roel.dullens@ru.nl



Introduction

Soft Matter is a class of matter that is governed by weak interactions, relatively large length scales (nm $-$ μm) compared to atomic and molecular system, and long time scales (seconds). As a result of this, soft matter systems such as toothpaste, paint, beer froth, colloids, soap solutions or mayonnaise are easily deformable, hence the term *soft matter*, and readily studied using optical microscopy techniques. In this course, the fundamentals of soft matter will be introduced, which includes the main classes of soft matter, their interactions, phase behaviour, dynamics and mechanical properties.

Recommended course material

- Book: Soft Matter Physics by M. Doi, Oxford University Press
- Book: Molecular Driving Forces by K.A. Dill and S. Bromberg, Garland Science
- Book: Soft Matter, Concepts, Phenomena and Applications by W. van Saarloos, V. Vitelli and Z. Zeravcic, Princeton University Press
- Book: The Colloidal Domain by D. Fennell and H. Wennerström, Wiley
- All info will be available via **www.dullenslab.com/teaching/softmatter/** and/or in Brightspace

Aim

- After this course, the students will have
  1. gained a general understanding of fundamental characteristics of soft matter
  2. learned to understand and quantify interactions relevant in soft matter
  3. learned to describe the phase behaviour of soft matter
  4. obtained a quantitative understanding of wetting phenomena and the dynamics and mechanical properties of soft matter
  5. become familiar with the most common optical techniques to visualise and manipulate soft matter

Organisation

- **Lectures**

  During the lectures (Tuesday, 13:30 – 15:15, HG00.062) the main contents of this Soft Matter course will (obviously) be discussed and explained. Please bring a notebook (and an active mindset) to the lectures so that you can write (and think) along. Note that the lectures and the suggested literature supplement each other, and some topics will be presented differently than in the books.

- **Problem Classes**

  The problems for the problem classes (Thursday, 15:30 – 17:15, HG00.071) will appear online (**www.dullenslab.com/teaching** or Brightspace); answers will be available online after the problem classes. **The problems in the classes will be representative for the exam**.

- **Examination**

  The evaluation will consist of a 3-hour written exam.

  Graphical calculators are NOT allowed during the exam (regular ones are).

- **Video recordings**

  The lectures will be recorded and will be available on Brightspace.

Contents of Soft Matter

Synopsis

1. Introduction to Soft Matter
2. Colloids
   (a) Van der Waals interactions
   (b) Double layer interactions
   (c) DLVO potential
   (d) Brownian motion
   (e) Phase behaviour
3. Polymers
   (a) Dimensions of polymers: ideal and real chains
   (b) Phase behaviour: Flory-Huggins theory
   (c) Polymer solutions: dilute, semidilute and entangled
   (d) Dynamics
4. Interfaces and surfactants
   (a) Interfacial tension
   (b) Wetting: Laplace and Young equations
   (c) Capillary rise
   (d) Surfactants: micelles and Gibbs adsorption equation
5. Mechanical properties of soft matter
   (a) Deformation of soft matter
   (b) Introduction to rheology
6. Light scattering, optical microscopy and tweezing
   (a) Static and dynamic light scattering
   (b) Brightfield microscopy: image formation
   (c) Confocal microscopy
   (d) Optical tweezing

Problem set 1 – Soft Matter

Problem 1

Due to gravity colloidal particles in suspension form of a sedimentation equilibrium, which is characterised by a height-dependent number density $n(z)$. The (osmotic) pressure at a height h (w.r.t the bottom of the container) at low concentrations (i.e. assuming no interactions) is given by $\Pi(h) = n(h)k_BT$.

a) Explain what is meant by the buoyant mass of a colloidal particle of mass density ρ_c in a solvent of mass density ρ_s? Write down the expression for the gravitational force acting an a particle in terms of the particle volume V and the mass density difference $\Delta\rho = \rho_c - \rho_s$.

b) The upward force, due to the osmotic pressure gradient, acting on a particle in a sedimentation equilibrium is given by

$$F_{up} = -\frac{1}{n(h)}\frac{d\Pi}{dh}.$$

Verify by dimensional analysis that this expression indeed has the units of a force.

c) Balance the forces from parts a) and b) and solve the resulting differential equation to obtain the so-called *barometric height distribution* for the particle density n as a function of height h:

$$n(h) = n(0)\exp\left(\frac{-\Delta\rho V g h}{k_BT}\right).$$

d) Calculate the decay length – which is often referred to as the *gravitational length* – of the exponential function (i.e. the height at which $n(h)/n(0) = e^{-1}$) for polystyrene particles of diameter

- 0.1 μm
- 1 μm
- 10 μm

in water at 300 K. Note that the density of polystyrene = 1.05 g cm^{-3}.

Comment on the values you obtain, especially in relation to the extent of the Earth's atmosphere (what would be the gravitational length of an oxygen molecule?).

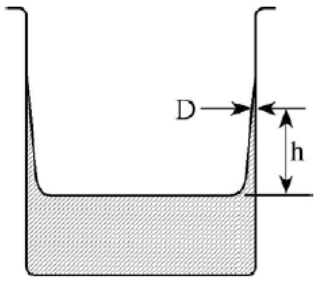
Problem 2

When octane is placed in a quartz vessel, the octane wets the walls of the vessel as schematically shown in the figure below.

The energy, U, per unit area of a film of octane of thickness, D, due to van der Waals interactions can be described by

$$U(D) = \frac{-A}{12\pi D^2},$$

where the Hamaker constant $A = -7 \cdot 10^{-21}$ J.
The gravitational potential energy per unit area of the film at a height, h, above the liquid surface is given by $U = \rho g h D$, with ρ the density of the liquid (= 703 kg m^{-3} for octane) and $g = 9.81$ m s^{-2}.



a) Sketch the form of each of these two potentials (for $A < 0$), and of their sum, as a function of D.

b) Evaluate the equilibrium thickness of the film at $h = 1$ cm.

The Hamaker constant for water interacting with itself across a vacuum is $A_{ww} = 3.7 \cdot 10^{-20}$ J while for a typical hydrocarbon oil, $A_{oo} = 5.1 \cdot 10^{-20}$ J.

c) Estimate the Hamaker constant, A_{wo}, for water interacting with oil across a vacuum.

d) Determine the sign of the Hamaker constant for a film of oil on water in air. Note that the combining relation for medium 1 interacting with medium 2 across medium 3: $A_{132} \approx A_{12} + A_{33} - A_{13} - A_{23}$.

e) Hence predict whether oil will spread on water.

Problem 3

The Debye length depends on the salt concentration via the bulk number density n_0 as given by

$$\kappa^{-1} = \sqrt{\frac{\epsilon\epsilon_0 k_B T}{2e^2 n_0 z^2}},$$

where ϵ is relative permittivity, ϵ_0 the permittivity in vacuum ($\epsilon_0 = 8.85 \cdot 10^{-12}$ C^2/N m^2), z the valency of the ions and e the elementary charge.

a) Calculate the Debye length in 1.00 mM KNO_3 (for water at $T = 298$ K and $\epsilon = 78$).

b) Explain whether the Debye length will be smaller or larger in a solution of (i) 1.75 mM KNO_3 and (ii) 1.00 mM K_2SO_4?

The exact solution of the Poisson-Boltzmann equation for a charged surface is given by the Gouy-Chapman equation for the dimensionless electrostatic potential:

$$\Phi(x) = 2 \ln \left[\frac{1 + \tanh(\Phi_0/4) e^{-\kappa x}}{1 - \tanh(\Phi_0/4) e^{-\kappa x}} \right].$$

c) Show that for small dimensionless surface potentials, i.e. $\Phi_0 \ll 1$, the solution to the linearised Poisson-Boltzmann equation is recovered ($\Phi(x) = \Phi_0 e^{-\kappa x}$).

Hint: Use that for $x \ll 1$ $\tanh x \approx x$ and $\ln(1 + x) \approx x$ (also in that order actually!)

d) Explain what is meant by the electric double layer and what the significance of the Debye length κ^{-1} is in this respect?

The relation between the thickness of the double layer and κ^{-1} can also be demonstrated using the condition for electro-neutrality. The surface charge density (of the charged surface), σ, must be exactly matched by the integrated charge density in the solution, $\rho(x)$:

$$\sigma = -\int_0^\infty \rho(x) dx.$$

e) Given that for small surface potentials, $\rho(x) \approx -2ze n_0 \Phi(x)$, show that

$$\sigma = \epsilon\epsilon_0 \kappa \phi_0.$$

Note that this result is identical to that for a dielectric-filled capacitor with charge σ, potential ϕ_0 and a plate–plate separation of κ^{-1}; hence the analogy between the thickness of the electrical double layer and the separation between the oppositely charged plates of the capacitor.

f) Calculate ϕ_0 for a typical surface charge density of colloids in water, $\sigma = 1$ e/nm^2, and a salt concentration of 0.1 M NaCl. Is the linear Poisson-Boltzmann equation, valid for $\phi_0 < 26$ mV, typically applicable for colloidal particles?

Problem 4

a) The Van der Waals interaction between two spheres of radius R and separated by a distance D is given by $U = -AR/12D$, where A is the Hamaker constant.

- Calculate U between two $R = 0.5$ μm silica spheres ($A_{11} = 6 \cdot 10^{-20}$ J) separated by 100 nm in vacuum.
- Repeat the calculation for silica in water, where $A_{131} = 0.8 \cdot 10^{-20}$ J.
- Compare both values to the thermal energy of the particles at room temperature.

In the lectures, the Van der Waals interaction (per unit area) between two half spaces was calculated. Here, we will follow the same strategy to calculate the Van der Waals interaction (per unit area) between two plates of finite thickness T at a separation D, as shown in the diagram below.

b) Starting from the interaction between two atoms being $U = -C/r^6$, first show that the interaction between 1 atom and a plate of thickness T and number density ρ, separated by a distance D, is

$$U(D) = -\frac{\pi C \rho}{6}\left(\frac{1}{D^3} - \frac{1}{(D+T)^3}\right).$$

Hint: use that $xdx = \frac{1}{2}dx^2$.

Note that for $T \to \infty$ the 'atom – half space' interaction is recovered ($-\pi C\rho/6D^3$) .

c) Next, calculate the interaction between two plates by integrating over the second plate of thickness T and number density ρ and express your answer in terms of the Hamaker constant $A = \pi^2 C \rho^2$. Hence, show that the Van der Waals interaction (per unit area) between two plates of thickness T at a separation D is

$$U(D) = -\frac{A}{12\pi}\left(\frac{1}{D^2} - \frac{2}{(D+T)^2} + \frac{1}{(D+2T)^2}\right),$$

Note again that for $T \to \infty$ the 'half space – half space' interaction is recovered ($-A/12\pi D^2$).

Problem set 2 – Soft Matter

Problem 5

Two sapphire surfaces in a 1 mM NaCl solution ($\kappa^{-1} \approx 10$ nm, $\epsilon = 78$) are separated by $D = 20$ nm. The Hamaker constant for sapphire–water-sapphire is $A_{131} = 6.7{\cdot}10^{-20}$ J and surface charge $\sigma = 1.5$ mC m^{-2}.

a) Given that calculate the *attractive* pressure, $\Pi = -dU/dD$, due to the attractive van der Waals interaction, $U = -A/12\pi D^2$.

b) Calculate the *repulsive* pressure between the sapphire surfaces, $\Pi(D) = \frac{2\sigma^2}{\epsilon\epsilon_0} e^{-\kappa D}$, and compare the value you obtain to your answer in part a): is the repulsive pressure enough to prevent the sapphire surfaces from sticking to each other or not? ($\epsilon_0 = 8.85 \cdot 10^{-12}$ C^2 N^{-1}m^{-2})

The interaction energy between spherical silica particles in a stable colloidal suspension at pH 7 in an aqueous NaCl solution is shown in the diagram below.

c) Explain the factors that determine the shape of the curve.

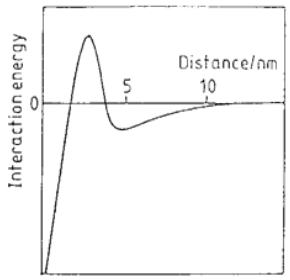
d) Explain why each of the following actions may lead to aggregation of the silica particles:

- increasing the NaCl concentration.

- adding a divalent electrolyte.

- adding methanol to the solution.

- reducing the pH (note: the isoelectric point of silica is around pH = 2).



Problem 6

The one-dimensional (1D) motion of a colloidal particle with mass m and radius a in a fluid medium is described by the Langevin equation,

$$m\frac{dv(t)}{dt} = F - \xi v(t) + f(t),$$

where v is the instantaneous velocity, ξ the friction coefficient, F the external force on the particle and $f(t)$ the fluctuating force.

a) Carefully explain the origin of Brownian motion and why $\langle f(t)\rangle = 0$.

Consider the steady-state diffusion of spherical particles down a concentration gradient, dc/dx. The force on a single particle is given by $F = -d\mu/dx$, in which the chemical potential has the form $\mu = \mu^{\ominus} + k_B T \ln c/c^{\ominus}$, where $\mu^{\ominus}$ and $c^{\ominus}$ are constants.

b) Find an expression for F and hence show that

$$\langle v\rangle = -\frac{k_B T}{\xi c}\frac{dc}{dx}.$$

c) Write an expression for the flux J (units mol m^{-2} s^{-1}) in terms of $\langle v\rangle$, and by comparing it with Fick's First Law, $J = -D\, dc/dx$, show that the diffusion coefficient D is given by (Stokes-Einstein)

$$D = \frac{k_B T}{\xi}.$$

Consider a suspension of N colloidal particles of radius $R = 1$ μm in water ($\eta = 0.89 \cdot 10^{-3}$ Pa s) in a volume V at $T = 298$ K. The volume fraction ϕ is defined as $\phi = \rho v_p$, where $\rho = N/V$ (number density) and v_p the particle volume. The Stokes friction factor for a sphere of radius R in a solvent of viscosity η is $\xi = 6\pi\eta R$.

d) The mean squared displacement is given by $\langle r^2(t)\rangle = 6Dt$ (see also problem 8). Calculate the time it takes for a single colloidal particle (i.e. in the limit of $\phi \to 0$) to diffuse a distance equal to its own diameter (in 3D). How does this so-called 'Brownian time' vary with R?

e) Show that the typical time τ for a particle to travel the mean distance between the particles is proportional to $\phi^{-2/3}$ and calculate τ for a suspension with $\phi = 0.3$.

Problem 7

In this problem, we will look at the entropy-driven transition from the isotropic to the nematic phase in suspension of hard colloidal rods, as first described by Lars Onsager (in the 1940s): "*The isotropic-nematic transition in a suspension of rods is driven by the loss of orientation entropy and the gain of free volume entropy.*"

a) Explain the differences between the isotropic and nematic phase in terms of ordering of the centres and orientations of the rods in both phases.

b) Now, we consider the *orientational* entropy of the isotropic and nematic phases. Using the Boltzmann equation for the entropy, $S = k_B \ln \Omega$, show that the change in orientational entropy for the isotropic-to-nematic transition can be estimated as

$$\Delta S_{or} = k_B \ln \frac{\Omega_N}{\Omega_I} \sim k_B \ln \frac{1}{4\pi} \sim -k_B.$$

Next, we consider the change in entropy due to the change in the excluded volume going from the isotropic to the nematic phase. To this end, we need the Gibbs-Duhem relation (from thermodynamics):

$$N d\mu = -S dT,$$

and the following expression for the chemical potential

$$\mu = \mu_0 - k_B T \ln \frac{V_i}{V},$$

where μ_0 is a constant, V the volume and V_i the volume available to insert an extra particle. Note that $V_i = V - V_{excl}$, where V_{excl} is the *excluded volume*, i.e. the volume where no extra particle can be inserted (due to the presence of another rod), and at low concentrations $V \gg V_{excl}$.

c) Show that at low concentrations the 'excluded volume entropy' (per particle) is given by

$$\frac{S_{excl}}{N} = k_B \ln \frac{V_i}{V} \approx -k_B \frac{V_{excl}}{V}.$$

Hint: $\ln(1 - x) \approx -x$.

d) Make a sketch to explain that the excluded volumes between two rods (length L and diameter D) in the isotropic and nematic phases are (approximately) given by

$$\text{Isotropic phase: } V_{ex}^I \sim L^2 D \qquad \text{Nematic phase: } V_{ex}^N \sim D^2 L.$$

e) Show that the change in S_{excl} for the isotropic-to-nematic transition, $\Delta S_{excl} = S_{excl}^N - S_{excl}^I$, is

$$\Delta S_{excl} = k_B \rho L^2 D, \quad \text{where } \rho = N/V \text{ is the number density.}$$

f) Finally, the isotropic-nematic transition occurs at the number density (ρ^*) where the loss of orientational entropy is balanced by the gain of excluded volume entropy:

$$\Delta S_{or} + \Delta S_{excl} = 0.$$

Show that $\rho^* = 1/(L^2 D)$, which is equivalent to a volume fraction of $\phi^* = \rho^* v_p = D/L$, where v_p is the volume of a rod, $D^2 L$. This explain that for rods with $L/D = 10$ (which is not even that long) this *entropy-driven* transition already happens at very low concentrations!

Problem 8

Here, we follow Langevin's original paper (see the translation by D.S. Lemons and A. Gythiel, Am. J. Phys. 65, 1079 (1997)) to derive an expression for mean squared displacement of a Brownian particle of mass m. The Langevin equation in 1D is given by:

$$m\frac{d^2x}{dt^2} = F - \xi\frac{dx}{dt} + f(t),$$

where F is an external (driving) force, ξ is the Stokes friction factor and $f(t)$ is a fluctuating random force with $\langle f(t)\rangle = 0$.

a) Multiply both sides of the Langevin equation by x and then use the hint below to show that

$$\frac{m}{2}\frac{d^2x^2}{dt^2} - m\left(\frac{dx}{dt}\right)^2 = Fx - \frac{\xi}{2}\frac{dx^2}{dt} + xf(t).$$

Hint: Note that $\frac{d^2x^2}{dt^2} = \frac{d}{dt}\left(\frac{dx^2}{dt}\right) = 2\left[x\frac{d^2x}{dt^2} + (\frac{dx}{dt})^2\right]$ as is easily shown using $dx^2 = 2xdx$.

b) Next, by (i) assuming that there is no external force, (ii) taking the ensemble average and (iii) then applying the equipartition theorem $m\langle\left(\frac{dx}{dt}\right)^2\rangle = k_B T$, show that one obtains

$$\frac{m}{2}\left\langle\frac{d^2x^2}{dt^2}\right\rangle - k_B T = -\frac{\xi}{2}\left\langle\frac{dx^2}{dt}\right\rangle.$$

c) By taking $z = \langle dx^2/dt\rangle$, integrate the above equation to obtain

$$z = \frac{2k_B T}{\xi} + A\exp\left(-\frac{\xi t}{m}\right),$$

where A is a constant that does not depend on t.

Hint: take the indefinite integral, i.e. no integration boundaries, just add an integration constant.

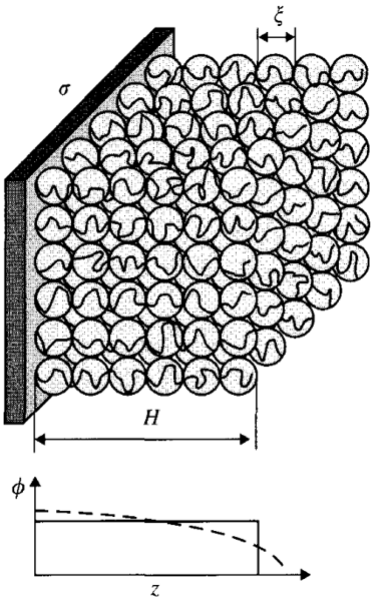
d) For long times, i.e. $t \gg m/\xi$, show this equation can be solved to obtain the mean squared displacement in one dimension:

$$\langle x^2\rangle = \frac{2k_B T}{\xi}t = 2Dt.$$

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.

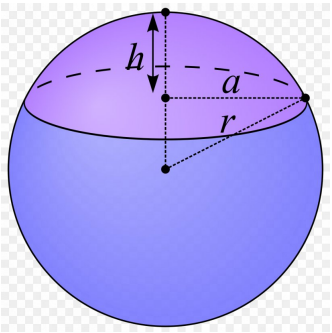
c) A rubber band (Dutch: 'elastiekje') is a crosslinked polymer network of ideal chains. The force to extend it slightly (linear regime) has the same form as $f(R)$ above for a single ideal chain. Suppose that a weight is attached to the rubber band. What happens to the position of the weight if the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

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

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?

Soft Matter Problem set 4 – Interfaces and surfactants

Problem 13

Use the molecular view of interfacial tension ($\gamma \approx u/2a^2$) to explain which of the following interfaces have a higher interfacial tension.

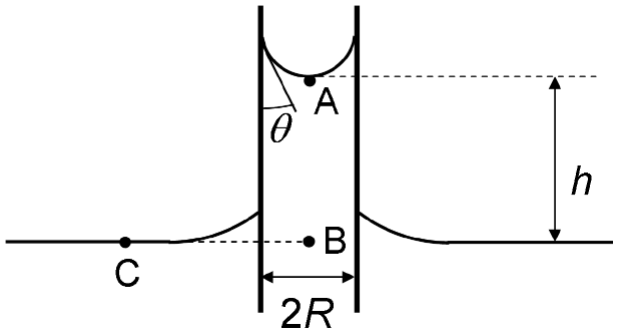
a) Water-air and water-ice.

b) Water-air and water-toluene.

c) A colloidal liquid-colloidal gas interface with particles of radius $a = 200$ nm and $a = 1$ μm.

Problem 14

We will derive the equation for capillary rise $h = 2\gamma \cos\theta/\rho g h$.



a) What is the Laplace pressure ($\Delta p = p_A - p_0$) according to the Young-Laplace equation?

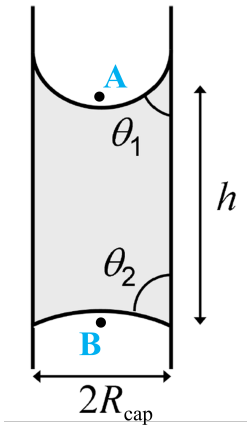
b) What is the pressure at points B and C? The interface at B is flat, and C is at the same height as B.

c) The pressure difference between points A and B is purely hydrostatic, i.e., the weight of the water column. Give an expression for the force per unit area ($f/A = \delta p_{AB} = p_B - p_A$) due to the weight of the water column above B.

d) Use your answer to a, b and c to derive the capillary rise equation. What size of capillary is required to rise a liquid by 100 m (the height of the tallest trees)?

Problem 15

Contact angle hysteresis makes it possible to capture a liquid column of height h suspended in a vertical capillary of radius R_{cap}, as shown in the figure below.



a) What is the microscopic origin of the contact angle hysteresis?

The Laplace pressure at a curved interface is given by: $\Delta p = \dfrac{2\gamma \cos\theta}{R}$, with R the radius of curvature.

b) What is the pressure difference between points A and B in the drawing? Use this pressure difference to derive an expression for the maximum height h of the capillary plug that can remain inside the capillary without falling down due to gravity.

Problem 16

The formation of micelles starts quite abruptly at a threshold concentration, known as the critical micelle concentration (CMC). Above the CMC, the number of micelles increases approximately linearly with increasing surfactant concentration. To explain the abrupt formation and linear dependence of micelle concentration on surfactant concentration, we will consider the formation of micelles as a reversible reaction between n surfactants:

$$n\ \mathrm{A} \rightleftharpoons \mathrm{A}_n$$

See also the lecture notes.

a) At what total mole fraction of surfactant is the amount of free surfactant x_1 equal to the amount of surfactant in micelles x_n?

b) Make a sketch of x_n as a function of x_1. How could you estimate the aggregation number n (the average number of surfactants per micelle) and the difference in standard chemical potentials, $\mu_1^0 - \mu_n^0$, from a plot of x_n versus x_1?

c) Another way to estimate the aggregation number, is to look at the shape of the surfactant molecules. A typical surfactant, sodium dodecyl sulfate or SDS ($C_{12}H_{25}SO_3^-\ Na^+$), forms spherical micelles. The length ℓ of an SDS molecule is about 12×1.3 Å (per C-C bond) plus 1.5 Å $= 17, 1$Å, which is the radius of the spherical SDS micelle. The effective area of the polar sulfate head group $a_0 = 60$ Å^2. The molecular volume v of a single SDS molecule is about 360 Å^3. Estimate the maximum number of SDS molecules per spherical micelle.

d) What would happen to the CMC and the aggregation number n of SDS when salt is added to the solution? Explain your answer.

Problem set 5 – Soft Matter

Problem 17

Viscosity measurements can be used to determine the volume fraction, density or size of colloidal particles, and the molecular weight and degree of swelling of polymers by making use of the Einstein relation for suspension viscosity.

a) Describe how one could determine the effective density of a colloidal material from measuring its viscosity?

b) Is this method also accurate for polydisperse colloids (i.e., where the colloidal particles have different sizes)?

c) How would a polymer brush (with thickness h) on the surface of the colloidal particles influence the calculated density?

Problem 18

Similar viscosity measurements can be used to determine the molecular weight of polymers. In this case, the Mark-Houwink-Sakurada relationship is used.

a) Start from the Einstein expression for intrinsic viscosity (slide 13), and assume that the polymers are effective spheres with a radius R_h (h for hydrodynamic radius) and a volume $V_h = 4\pi R_h^3/3$. Derive the Mark-Houwink-Sakurada relationship.

b) Do the Mark-Houwink-Saturada parameters K_M and a depend on temperature?

c) For rigid rods, such as Tobacco mosaic virus, the Mark-Houwink-Saturada parameter $a = 2$. Also for very strongly charged polyelectrolytes in low salt concentration $a = 2$ (they behave like rigid rods), so $[\eta] = K_M\, M_w^2$. What do you conclude from this about the hydrodynamic radius of a strongly charged polyelectrolyte of length L?

d) What is the Mark-Houwink-Saturada parameter a for solid spherical particles, such as latex colloids?

Problem 19

The Maxwell model is the simplest model of the linear viscoelastic response of soft materials. It is a combination of an elastic spring and a viscous dashpot.

a) Sketch a graph for the extension length Δx as a function of time for a single spring, a single dashpot and a Maxwell element that contains both a spring and a dashpot, if at time $t = t_1$ a constant force is suddenly exerted, which is removed abruptly at time $t = t_2$.

b) Compare the expression for stress of an elastic solid (slide 7) and force in the elastic spring of a Maxwell material (slide 17). How is the constant k_e related to the modulus G? Do the same for the constant k_v and the viscosity η by comparing the force in the viscous dashpot and the stress of a Newtonian liquid (slide 7)?

c) Derive the equation for creep of a Maxwell material (slide 18). Start from the expression of the force in the spring and dashpot (slide 17). In a creep experiment, the applied force F is kept constant. Rewrite $x_e = F/k_e$ and $dx_v/dt = F/k_v$, and find the expression for $\gamma = x_t/L0$.

Problem 20

Many soft materials show nonlinear viscoelastic behavior: they have strain or shear-rate dependent moduli or viscosities, or time-dependence. Let us consider here the viscoelastic *liquids* that have a terminal viscous behaviour (i.e., they flow at long timescales), and their behaviour in an experiment where the shear rate ($\dot{\gamma}$) is gradually increased. For each of the materials below, draw the following two diagrams: (1) the viscosity η as a function of the shear rate $\dot{\gamma}$, and (2) the shear stress σ as a function of shear rate $\dot{\gamma}$.

a) A concentrated polymer solution that shows strong shear thinning behaviour at high shear rates.

b) A suspension of colloidal particles that shows shear thickening behaviour (e.g., like corn starch).

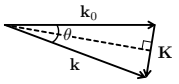
c) A dense emulsion of polymer-stabilized oil droplets in water (e.g., mayonaise) that exhibits a yield stress, followed by medium shear thinning.

d) The sample under b) can become thixotropic upon the addition of salt, meaning that they exhibit a time-dependent shear thinning effect, and return to a tick viscous state at rest over time. Explain what could be the microscopic origin of this effect.

Problem set 6 – Soft Matter

Problem 21

a) Show that magnitude of the scattering vector is $K \equiv \mid \vec{K} \mid = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$ using the figure below.



$|\mathbf{k}| = |\mathbf{k}_0| = k$

The form factor $P(K)$ for a homogeneous (i.e. $\zeta(\mathbf{r}) = \zeta$) sphere of radius a – in spherical coordinates – is

$$P(K) = \left| \frac{\int_0^a \frac{\sin(Kr)}{Kr} 4\pi r^2 dr}{\int_0^a 4\pi r^2 dr} \right|^2 . \qquad \text{(Eq. 1)}$$

b) Show that the form factor for homogeneous spherical particles is given by

$$P(K) = \left(3\, \frac{\sin(Ka) - Ka\cos(Ka)}{(Ka)^3} \right)^2 .$$

Hint: make the variable substitution $x = Kr$ and then integrate by parts $\int f'g\, dx = [fg] - \int fg' dx$.

c) The first minimum of $P(K)$ is located at $Ka = 4.49$ (which follows from the numerical solutions of $\tan x = x$). Calculate the scattering angle corresponding to this first minimum for a sphere of $a = 1$ μm, and $\lambda = 532$ nm. Does this scattering angle increase or decrease for smaller particles?

d) Explain why the minima in the form factor become less sharp for polydisperse particles.

Problem 22

The position autocorrelation function for a Brownian particle in a harmonic optical trap is given by

$$\langle x(t')x(t) \rangle = \frac{k_B T}{\kappa} e^{-|t'-t|/\tau},$$

where $\tau = \xi/\kappa$ is the relaxation time of the particle in the trap, ξ the drag coefficient and κ the (harmonic) trap stiffness.

a) Show that the mean squared displacement (MSD), defined as $\langle [x(t') - x(t)]^2 \rangle$, is given by

$$\langle [x(t') - x(t)]^2 \rangle = \frac{2k_B T}{\kappa} \left(1 - e^{-\Delta t/\tau} \right),$$

with $\Delta t = |t' - t|$ the lag time (the MSD depends on the time difference, not on the absolute time).

b) Determine the following two limits for the MSD:

i) For $\Delta t \ll \tau$ $\quad \rightarrow \quad$ $\text{MSD}(\Delta t) = \frac{2k_B T}{\xi} \Delta t$.

ii) For $\Delta t \gg \tau$ $\quad \rightarrow \quad$ $\text{MSD}(\Delta t) = \frac{2k_B T}{\kappa}$.

c) Sketch the MSD as a function of the lag time (Δt) and also indicate the limits from part b).

d) For a 1.0 μm radius polystyrene particle in water ($\eta = 0.98$ mPa s) at $T = 298$ K in an optical trap with a stiffness of $\kappa = 34.95$ fN/nm, the long-time plateau value of the MSD is 231 nm^2 and the initial slope $\approx 400 \cdot 10^{-15}$ m^2/s. Determine Boltzmann's constant (k_B), and hence Avogadro's number, and discuss how else you could determine k_B from a measurement of the MSD of a particle in an optical trap (you could try it, which one is easier/works better?).

Problem 23

For small scattering vectors, the form factor $P(K)$ is well-described by Guinier's law

$$P(K) = \exp\left(-\frac{1}{3}K^2R_G^2\right), \qquad \text{with} \qquad R_G^2 = \frac{\int_0^a r^4 dr}{\int_0^a r^2 dr},$$

the radius of gyration (as seen in lecture 3 on polymers). In this problem we will derive Guinier's law.

a) Starting from the definition of the form factor (Eq. 1 from problem 19) and given that $\frac{\sin Kr}{Kr} \approx 1 - \frac{1}{6}K^2r^2 + \ldots$, show that $P(K)$ can be written as

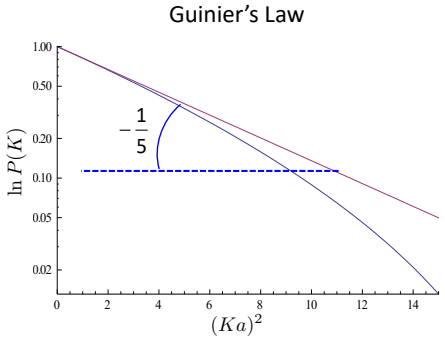
$$P(K) = 1 - \frac{1}{3}K^2\frac{\int_0^a r^4 dr}{\int_0^a r^2 dr} + \mathcal{O}(k^4)$$

b) Neglecting the higher-order terms ($\mathcal{O}(k^4)$), show that for small K Guinier's law is obtained

$$P(K) = 1 - \frac{1}{3}K^2R_G^2 = \exp\left(-\frac{1}{3}K^2R_g^2\right).$$

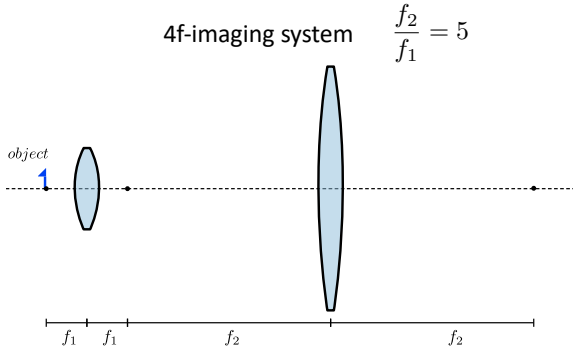
c) Calculate the radius of gyration for a homogeneous sphere of radius a.

d) Using your answer to part (c), verify that a plot of $\ln(P(K))$ vs $(Ka)^2$ has a slope of $-1/5$ in the limit of small K as shown in the figure below.

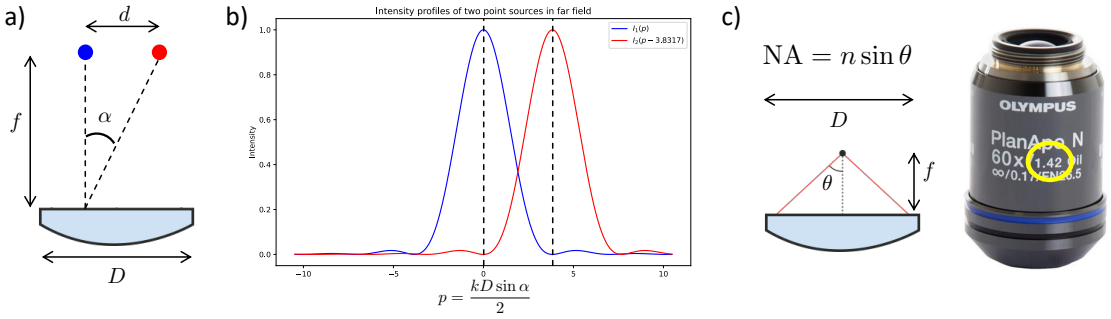


Problem 24

a) The figure below shows a $4f$–imaging system with a magnification $M = f_2/f_1 = 5$. Draw the ray tracing and construct the image of the object.



Next, we will 'derive' Abbe's diffraction limit, which sets the resolution of an optical microscope. To this end, we will consider the intensity profiles $I(\theta)$ of two emitting point sources separated by a distance d at a focal distance f away from the imaging lens (see panel a) in figure below)). These point sources can be resolved if the (minimum) distance between them corresponds to the intensity maximum of the first point source overlapping with the first intensity minimum of the second one, as shown in panel b) of the figure below). For this situation, $p_{min} = \frac{1}{2}kD\sin\alpha = 3.8317$, where D is the diameter of the imaging lens, $k = 2\pi/\lambda$ (wavevector) and α the angle between the point sources (see panel a)).



Panel a) Two point sources separated by a distance d in the focal plane of the lens.
Panel b) The intensity profiles of two point sources separated by $p_{min} = 3.8317$.
Panel c) The geometry for the numerical aperture for an objective lens.

b) Show that the diffraction limit of the lens is given by $d = 1.22f\lambda/D$. Note that $f \gg d$.

c) Next, we relate the diffraction limit to the numerical aperture (NA) of a lens: $\text{NA} = n\sin\theta$, with n the refractive index of the medium and θ is the collection angle of the objective (see panel c) in the figure above). Using that $f \gg D$ and $n = 1$, show that the diffraction limit can be written as

$$d = \frac{1.22\lambda}{2\ \text{NA}} \approx \frac{\lambda}{2\ \text{NA}} \qquad \text{(as it is often seen in textbooks)}$$

Note that the assumption $f \gg D$ is actually not necessarily true for microscopes.

d) Calculate the diffraction limit for a microscope objective with NA=1.42 and a wavelength of 532 nm.