Study Guide

Soft Matter

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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, 08:30 – 10:15, HG00.622) 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, HG00.308) 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. Light scattering, optical microscopy and tweezing
    (a) Static and dynamic light scattering
    (b) Brightfield microscopy: image formation
    (c) Confocal microscopy
    (d) Optical tweezing
6. Mechanical properties of soft matter
    (a) Deformation of soft matter
    (b) Introduction to rheology

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:

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

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?).

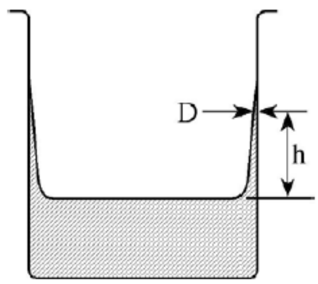
Problem 2

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, $\rho(x) \approx -2zen_0\Phi(x)$, 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 $R = 0.5\ \mu$m 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 $x dx = \frac{1}{2} dx^2$.

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.

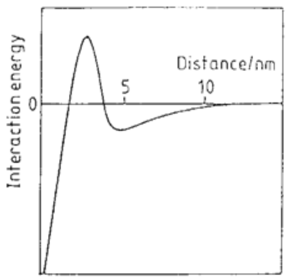
d) Explain why each of the following actions may lead to aggregation of the silica particles:

- 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

Isotropic phase: $V_{ex}^I \sim L^2 D$ 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 $m\langle\left(\frac{dx}{dt}\right)^2\rangle = k_BT$, show that one obtains

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

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

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

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:

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