Examination

Soft Matter

(NWI-MOL178)

Thursday, 16th January 2025, 12:45 – 15:45
Time allowed: **three hours**.

The exam consists of 4 questions

Please hand in your answers to each question on SEPARATE sheets.

Clearly write your name and student number on each sheet.

The marks in [ ] are only indicative of the weight given to each (sub)question.

A list of constants is included below.

List of constants

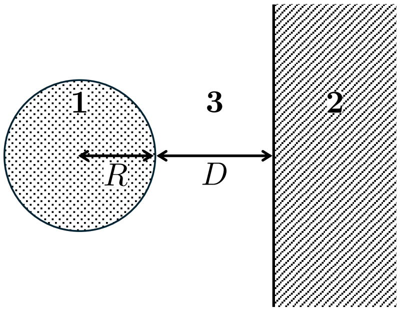
Elementary charge	e	1.602×10^{-19} C
Faraday's constant	F	9.648×10^{4} C mol^{-1}
Boltzmann's constant	k_B	1.381×10^{-23} J K^{-1} = 8.62×10^{-5} eV K^{-1}
Planck's constant	h	6.626×10^{-34} J s
Speed of light	c	3.0×10^{8} m s^{-1}
Atomic mass constant	m_u	1.661×10^{-27} kg
Avogadro's constant	N_A	6.022×10^{23} mol^{-1}
Gas constant	R	8.314 J K^{-1} mol^{-1}
Gravitational acceleration	g	9.807 m s^{-2}
Unit of energy		1 eV = 1.602×10^{-19} J
Standard pressure	$p^{\ominus}$	1 bar = 1×10^{5} Pa = 0.9869 atm
Unit of pressure		1 atm = 101.3 kPa

Question 1

Consider a spherical colloidal particle of radius R near a wall. The particle is made of material 1, the wall of material 2, and they are immersed in a medium 3. The van der Waals interaction energy between the particle and the wall is given by

$$U(D) = -\frac{A_{132}R}{6D},$$

where D is the surface-to-surface separation. See also the figure below.



(a) Briefly explain the origin of the Van der Waals interaction and the meaning of A_{132} (a derivation is *not* required). **[4]**

(b) For a polystyrene particle and a glass wall immersed in water, $A_{132} = 1.19 \cdot 10^{-20}$ J. Calculate the Van der Waals interaction energy and the force acting on a sphere with a radius of $R = 1$ μm at a separation of $D = 0.1R$. Comment on the magnitude of U relatively to the thermal energy at a temperature $T = 298$ K. **[4]**

(c) Now consider the situation that the colloidal particle and the wall are made of the *same* material. Show that the Van der Waals interaction is always attractive in this case. Note that $A_{132} = A_{12} + A_{33} - A_{13} - A_{23}$ and $A_{ij} \approx \sqrt{A_{ii}A_{jj}}$. **[4]**

For a system of spherical colloidal particles of radius R dispersed in an aqueous electrolyte solution the total (DLVO) interaction energy between two particles as a function of the surface-to-surface distance D is given by

$$U(D) = \frac{BTR\,c}{\kappa^2}e^{-\kappa D} - \frac{AR}{12D}.$$

Here, c the concentration of electrolyte, κ^{-1} the Debye length and B a constant.

(d) Sketch the total interaction energy as a function of D as well as the separate contributions to $U(D)$ due to the double layer and Van der Waals interactions. Explain why changing the salt concentration may lead to aggregation of the particles. **[4]**

(e) The critical aggregation concentration (c_0) is defined by the distance at which both the energy, $U(D)$, and force, $F(D)$, are zero. Show that at this concentration $D = 1/\kappa$ and comment on this result. **[4]**

Question 2

Consider a solution containing colloidal particles and polymers that do not adsorb onto the colloids. The polymers induce a depletion interaction between the colloids:

$$F_{\mathrm{dep}}(h) = -\Pi\, V_{\mathrm{ov}}(h), \qquad \text{where} \qquad V_{\mathrm{ov}}(h) = \frac{\pi}{6}\,(2R_{\mathrm{p}} - h)^2 \left(3a + 2R_{\mathrm{p}} + \frac{h}{2}\right).$$

Here, Π is the osmotic pressure of the polymer solution, V_{ov} the overlap volume, a the particle radius, R_{p} the radius of the polymers, and h the surface-to-surface separation between the particles.

(a) Briefly explain the origin of the depletion interaction and the meaning of the overlap volume V_{ov}. **[4]**

(b) Calculate the maximum overlap volume and the range of the depletion interaction for a colloid with $a = 500$ nm and two polymer sizes: $R_{\mathrm{p}} = 50$ and 100 nm. Make a sketch of V_{ov} as a function of h for these two polymer sizes in one plot. **[5]**

The size of a polymer depends on the quality of the solvent. The root mean squared end-to-end distance of a polymer is described by Flory's expression: $\sqrt{\langle R^2 \rangle} = bN^{\nu}$, where b is the Kuhn length and N the number of Kuhn monomers. The exponent $\nu = 0.5$ for a polymer in a theta solvent (ideal chain), and $\nu = 0.6$ for a polymer in a good solvent.

(c) Derive Flory's expression for a polymer in a good solvent from the balance between the excluded volume interaction between monomers and the entropic stretching of the chain. Note that the energy of the excluded volume interaction per monomer is $F_{\mathrm{int}}(R) = k_{\mathrm{B}}Tb^3n$, with n the number density of monomers in a polymer coil. The free energy required to stretch a polymer chain to an end-to-end distance R is given by $F_{\mathrm{ent}}(R) = k_{\mathrm{B}}T\frac{R^2}{Nb^2}$. **[5]**

At low polymer concentrations the osmotic pressure, $\Pi \approx ck_{\mathrm{B}}TN_{\mathrm{A}}$, is linearly proportional to the polymer concentration c (in mol/L). Above the overlap concentration, the osmotic pressure is no longer proportional to the polymer concentration.

(d) Derive an expression for the overlap concentration of a polymer in a good solvent. Comment on the meaning of the overlap concentration for the osmotic pressure. **[3]**

Two different types of non-adsorbing polymers of equal length N are added to two identical solutions containing colloidal particles and salt. One polymer is in a good solvent, the other one is in a theta solvent. The colloidal particles alone interact through a DLVO potential, and are stable without polymer.

(e) The sample to which the polymer in a good solvent is added aggregates instantaneously, but the other sample does not. Explain why this happens. **[3]**

Question 3

The (1D) motion of a colloidal particle in a solvent is described by the Langevin equation,

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

where m is the mass of the particle, v the instantaneous velocity, ξ the (Stokes) friction factor, F the external force on the particle and $f(t)$ the fluctuating thermal force.

(a) Explain the origin of Brownian motion and why $\langle f(t)\rangle = 0$. **[3]**

Consider the steady-state diffusion of spherical particles down a concentration gradient, dc/dx, where $c = c(x)$. The force on a single particle is $F = -d\mu(x)/dx$, with the chemical potential $\mu(x) = \mu^{\ominus} + k_BT\ln(c/c^{\ominus})$. Here, $\mu^{\ominus}$ and $c^{\ominus}$ are constants.

(b) (i) Find an expression for F and show that **[4]**

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

(ii) Combine the flux $J = c\langle v\rangle$ with Fick's First Law, $J = -D\ dc/dx$, to show that the diffusion coefficient D is given by, **[1]**

$$D = \frac{k_BT}{\xi}.$$

Consider a suspension of colloidal spheres (radius $R = 1\ \mu$m) in water ($\eta = 0.89\cdot 10^{-3}$ Pa s) at a volume fraction ϕ and $T = 298$ K. The friction factor is $\xi = 6\pi\eta R$.

(c) The mean distance between the particles is approximately given by $r_m \approx (v_p/\phi)^{1/3}$, with v_p the particle volume. Given that the mean squared displacement in 3D is $\langle r^2(t)\rangle = 6Dt$, show that the typical time τ_m for a particle to diffuse the mean distance r_m is proportional to $\phi^{-2/3}$ and calculate τ_m for a suspension with $\phi = 0.3$. **[4]**

(d) Discuss whether for a particle in a suspension of volume fraction ϕ, the diffusion coefficient, $D(\phi)$, will be smaller, the same or larger compared to the diffusion coefficient for a single particle, D, for times $t \ll \tau_m$ and $t \gg \tau_m$. **[4]**

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

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

where $\tau = \xi/\kappa$ is the relaxation time of the particle in the trap and κ the trap stiffness.

(e) (i) Show that the mean squared displacement, defined as $\langle [x(t') - x(t)]^2\rangle$, for a particle in an harmonic optical trap is given by **[2]**

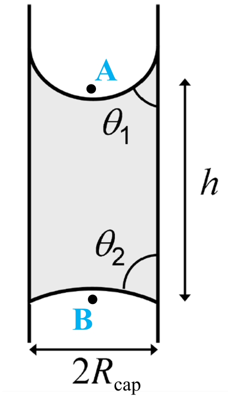
$$\langle [x(t') - x(t)]^2\rangle = \frac{2k_BT}{\kappa}\left(1 - e^{-\Delta t/\tau}\right),$$

with $\Delta t = |t' - t|$ the lag time. Note that due to equipartition $\langle x^2\rangle = k_BT/\kappa$.

ii) Explain how Boltzmann's constant may be determined from the mean squared displacement of a particle in an optical trap of known stiffness κ. **[2]**

Question 4

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? **[3]**

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. **[5]**

If the surface of the tube is not smooth but rough, for example a drinking straw made of paper, the contact angles in the image above are modified. Wenzel's law describes the wetting of liquids on rough solid substrates: $\cos\theta^* = r\cos\theta$, where θ^* is the contact angle on the rough surface and r is the roughness factor.

(c) Derive Wenzel's law by considering the change in surface energy when the contact line between solid, liquid and air is moved along a rough surface. **[5]**

(d) Explain what happens to the maximum height h that can remain inside the capillary when the walls are slightly rough ($r > 1$) using Wenzel's law and the contact angle hysteresis in (b)? **[3]**

(e) Explain why there is an optimal roughness beyond which the maximum height h no longer increases but decreases when further increasing the roughness. **[4]**