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

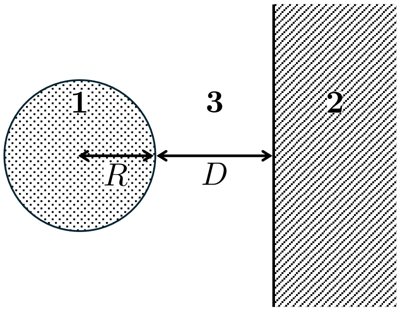
Elementary charge	e	1.602×10^{-19} C
Faraday's constant	F	9.648×10^{4} C mol^{-1}
Boltzmann's constant	k_{B}	1.381×10^{-23} J K^{-1} = 8.62×10^{-5} eV K^{-1}
Planck's constant	h	6.626×10^{-34} J s
Speed of light	c	3.0×10^{8} m s^{-1}
Atomic mass constant	m_{u}	1.661×10^{-27} kg
Avogadro's constant	N_{A}	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 $F_{\mathrm{int}}(R) = k_{\mathrm{B}}Tb^3 n$, 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, $\Pi \approx c k_{\mathrm{B}} T N_{\mathrm{A}}$, 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 $R = 1\ \mu\text{m}$) 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]**

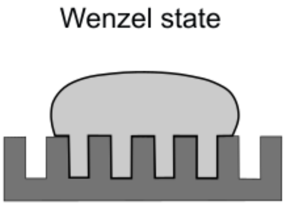
Question 4

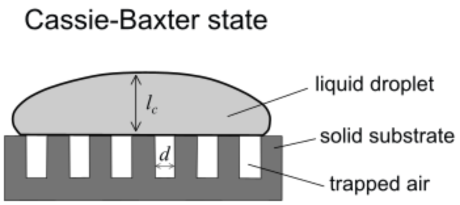
Wenzel's law describes the wetting of liquids on rough solid substrates:

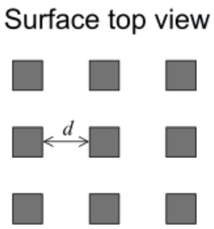
$$\cos\theta^* = r\cos\theta.$$

(a) Explain the meaning of the different symbols, and explain why Wenzel's law predicts that roughness can make hydrophilic surfaces superhydrophilic and hydrophobic surfaces superhydrophobic. **[4]**

Wenzel's law assumes that the liquid follows the roughness of the substrate, as shown below. For very hydrophobic surfaces, however, this is not a good assumption. Instead, air becomes trapped underneath the droplet and in between the texture on a surface. This state is called the Cassie-Baxter state (see figure below).


Wenzel state


Cassie-Baxter state


Surface top view

(b) The apparent contact angle of a droplet on a heterogeneous surface, containing substrates 1 and 2, can be approximated by $\cos\theta^* = \alpha_1\cos\theta_1 + \alpha_2\cos\theta_2$. Use this expression to derive Cassie-Baxter's law for the apparent contact angle θ^* on a rough surface with air trapped underneath the droplet: **[5]**

$$\cos\theta^* = -1 + \alpha_\mathrm{s}\left(\cos\theta + 1\right),$$

where α_s denotes the fraction of solid surface underneath the droplet.

(c) Compare the result of part (b) to Wenzel's law. Is it possible to make superhydrophobic surfaces with $\theta^* = 180°$ according to Wenzel's law and Cassie-Baxter's law? Explain. **[3]**

The Cassie-Baxter state of a droplet can be metastable if the distance between the pillars is large: if a droplet is placed on top of these pillars very carefully, it remains suspended and air remains trapped underneath the droplet, but if it is pushed, the liquid enters between the pillars and touches the bottom surface, resulting in a Wenzel state. The resistance is caused by the Laplace pressure, given by $\Delta p = \frac{2\gamma\cos\theta}{R}$, with R the radius of curvature and γ the surface tension.

(d) Explain why the Laplace pressure can resist a liquid from entering between the pillars. **[3]**

(e) Calculate the distance d between the pillars for which the droplet's own weight is sufficient to overcome this resistance. You may assume that the shape of a large droplet is approximately a disk with height $l_\mathrm{c} = \sqrt{\frac{\gamma}{\rho g}}$, with $\gamma = 72$ mN/m, $\rho = 1000$ kg/m^3 the liquid mass density and g the gravitational constant. The contact angle $\theta = 120°$. **[5]**