Experimental and Theoretical Physics Part II
Soft Condensed Matter Lectures 1-11

Question Sheet 2

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SCM Problems part II

These are the questions on the second part of the Part II soft condensed matter course by Keyser and Knowles.

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II-Q 1   The concentration of aqueous solutions of butanol, and their surface tension with air were measured at 20^oC with the following results:

c/mol dm^{-3}	0.0264	0.0536	0.1050	0.2110	0.4300
γ/ mN/m	68.00	63.14	56.31	48.08	38.87

Determine the surface area available per molecule of butanol.

II-Q 2

(a) The amphiphilic molecule sodium dodecyl sulphate (SDS) has the following dimensions: length of hydrophobic tail $l_c = 1.67$ nm, volume of hydrophobic tail $v = 0.35$ nm^3, area per head group $a = 0.57$ nm^2. Assuming that SDS forms spherical micelles, calculate the micelle radius and the mean aggregation number. What does your result suggest for the formation of micelles of SDS? Briefly discuss your conclusion.

(b) Show that for a lipid bilayer made by surfactant molecules with effective tail length l, volume v and head group area a:

$$\frac{1}{2} < \frac{v}{al} < 1.$$

II-Q 3   Ignoring any effect from gravity, the amplitude spectrum of thermal fluctuations of the interface between two fluids, as a function of the wavevector **q**, is approximately:

$$\langle h^2(\mathbf{q}) \rangle = \frac{k_B T}{A(\gamma q^2)}.$$

where γ is the interface tension and A is the area of the interface. This interface is in a square container with $A = 1\,\mathrm{cm}^2$.

At room temperature, what is the average undulation amplitude due to thermal fluctuations for the interface between water and hexane, which has an interface tension of $38 \times 10^{-3}\,\mathrm{N/m}$?

[*Hint: Assume a small wavelength cutoff at the molecular scale of 0.2 nm.*]

II-Q 4

(a) At room temperature, water wets a clean glass surface almost completely. Water is observed to rise to a height of 4.7 cm in a capillary tube of 0.8 mm diameter. Calculate the surface tension of water.

(b) Liquid of viscosity η is taken up by a capillary of radius R at a rate given by the Poiseuille equation. If the contact angle for the liquid on the capillary surface is θ, and the surface energy is γ, show that the distance, L, the liquid has traveled up the capillary in time t is given by:

$$L(t) = \sqrt{\frac{R\gamma \cos(\theta) t}{2\eta}}.$$

II-Q 5   Calculate the variation of energy δW needed to move the contact line between a solid, vapour and a partially wetting liquid. You may assume that the system is in equilibrium. Your answer should yield Young's equation.
Now use the wetting parameter S as defined in the lectures to derive a relationship between S and $\cos\theta$ to relate contact angle to surface tension and S.

II-Q 6

(a) Explain how a surfactant can be used to stabilise an emulsion between water and oil. You may use a sketch.

(b) A water-in-oil emulsion is stabilised by a surfactant. The surfactant is only present in the aqueous phase at concentration c_0 (by volume). The surfactant

concentration in the oil phase is $c = 0$. Now an emulsion of water in oil is formed. The concentration of surfactant on the droplet surface is given by c_S while its concentration in the aqueous droplet is c_v. Find an equation that connects the starting (bulk) concentration c_0 with the surfactant concentration c_s (droplet surface) and c_v (droplet volume). How does c_s scale with the droplet size?

(c) Discuss the challenges for stabilising shrinking droplets given your result from part (b)?

II-Q 7 Assuming that the interatomic potential between two atoms a distance r apart is given by $-L/r^6$, show that the attractive potential per unit area between two semi-infinite plates (i.e. blocks facing each other, semi-infinitely deep and infinitely wide and high) a distance h apart is given by $-A/(12\pi h^2)$, where the Hamaker constant A is given by $\pi^2 n^2 L$ and n is the number of atoms per unit volume.

II-Q 8 In the Debye-Hückel approximation the Poisson-Boltzmann equation for the potential of charges in electrolyte near a surface is solved by linearisation.

(a) Obtain the variation of the potential as a function of distance from the surface and discuss the role of the Debye-Hückel approximation.

(b) What is the physical meaning of the Debye screening length?

(c) How does the Debye screening length and the validity of the Debye-Hückel approximation change if salt is added to the solution?

II-Q 9 Solve the Poisson-Boltzmann equation (Eq. (5.6) in the notes) for the spherically symmetric situation:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \frac{e^2\beta\psi(r)}{\epsilon}\sum_i c_{0,i}z_i^2 \tag{11.1}$$

II-Q 10

(a) Ions are not point-like and have a finite radius a. The Debye-Hückel theory can be expanded to include finite ion size. Assume that ions are hard spheres with radius a and charge q. For simplification the dielectric constant of ion and solvent are the same. Calculate the potential around the ion for $r > a$ and $0 < r < a$.

(b) Calculate the charge distribution around and sketch the distribution as a function of distance. Determine the maximum of the distribution.

II-Q 11 A charged particle with radius R and charge Q is immersed in aqueous solution containing monovalent ions. Assume that the ions have a radius a_i. You may start from the Debye-Hückel potential around the particle

$$\phi(r) = \frac{Q}{4\pi\epsilon_0\epsilon}\frac{\exp(-\kappa(r-a))}{r(1+\kappa a)}, r > a$$

where $a = R + a_i$ the effective radius of the spherical particle. κ is the inverse of the Debye screening length. Determine the surface potential of the particle at $r = R$ and interpret your result.

II-Q 12 The electric double layer (EDL) can be seen as a capacitor.

(a) Calculate the capacitance of the EDL in concentrated electrolytes for an electrode with area of 1 cm^2 in water ($\epsilon = 80$) when the radius of a hydrated ion is 0.2 nm. In experiments the capacitance is found to be 10 μF. Explain the discrepancy between your result and the experimental result.

(b) Calculate the electric field strength in the system given in (a) when the surface potential is 100 mV.

(c) What happens with the capacitance in dilute electrolyte solutions?
   [*Hint: Consider the full structure of the double layer and what determines the capacitance.*]

II-Q 13

(a) Consider charged spherical colloid particles of radius a, with their surface carrying a charge σ per unit area, in an ionic solution with the equilibrium ion concentration is n_0. Find the electrostatic potential at the surface of a colloidal particle ψ_0.

(b) To obtain the interaction between two charged colloid particles, you should consider the electrostatic repulsion between them, and the osmotic pressure at the mid-point plane between them. Compare the two effects for the case of two spherical particles at significant separation, and also for the case of two planar (half-space) parallel surfaces a distance h apart.

(c) Sketch the combined interaction energy between two colloidal particles as a function of their separation (DLVO). Explain the relative energy scales of the contributions to interaction. Describe an experiment whereby the force of this interaction can be measured.

II-Q 14

(a) Electrophoresis is a process frequently used to separate proteins of slightly differing charge or size, dispersed in water. Obtain an expression for the drift velocity for capillary electrophoresis, modeling the protein as a sphere of radius R and charge Ze.

The mutant and native forms of a protein, both with radius 3nm, differ in charge by e. If an electric field of $500\,\mathrm{Vm^{-1}}$ is applied, and the minimum separation of the two bands produced by the two species which can readily be detected is 1mm, how long will the electrophoresis experiment need to be carried out to differentiate the two species?

[Take $\eta_{water} = 1 \times 10^{-3}\,\mathrm{Pa\,s}$ at room temperature.]

(b) If we take diffusion into account, what is the broadening of the bands at the end of the experiment?

II-Q 15   Assume that the surface of a cylindrical capillary of radius r is charged and has a fixed surface potential $\phi_0 < 0$. Under the assumption that $r \gg \lambda$ show that the fluid velocity v of the electro-osmotic flow in the centre of the capillary can be written as

$$v = -\frac{\epsilon_0 \epsilon_r \phi_0 E}{\eta}$$

where η is the fluid viscosity and E the applied electric field along the capillary. Explain why this velocity does not depend on r.

[*Hint: You may assume low Reynolds number i.e. laminar flow conditions. Boundary conditions on the capillary surface are no-slip, which means velocity $v = 0$ at $x = 0$. This calculation is done in the thin Debye layer limit which means $\partial v / \partial x = 0$ for distances from the surface larger than the Debye length. You will need to combine the Poisson equation linking surface potential and charge density*

$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{\rho(x)}{\epsilon_r \epsilon_0}$$

with the Stokes equation

$$-\eta \frac{\partial^2 v}{\partial x^2} = \rho(x)E$$

and solve the resulting differential equation by integration and taking the boundary conditions into account.]

II-Q 16 Consider a spherical particle in water with radius $r = 2$ μm held in an optical trap far from any surface. The charged particle is in an homogeneous electric field $E = 10$ V m^{-1} in aqueous solution with the viscosity of water $\eta = 0.001$ kg m^{-1}s^{-1}.

(a) Assuming a surface potential $\phi = -20$ mV calculate the expected electrophoretic force F_e and displacement from the centre of the optical trap Δx. You may assume that the optical trap forms a harmonic potential with linear force distance relation $F = -\kappa \Delta x$ where $\kappa = 0.1$ pN nm^{-1}. What is the maximum velocity of the counter ions in the EDL around the particle at $E = 10$ V m^{-1}?

(b) Sketch the forces acting on the particle in (a).

(c) A particle in an optical trap undergoes Brownian motion. The variance of the fluctuations $\langle x^2 \rangle$ are linked to the stiffness κ of the optical trap by the equipartition theorem. In a real experiment, $\langle x^2 \rangle$ is found to be 4.14×10^{-17} m^2 at $E = 0$ and 3.52×10^{-17} m^2 at $E = 10$ V m^{-1}. Estimate the stiffness of the optical trap. Is the trap harmonic?

[*Hint:* $\gamma = 6\pi\eta r$ *is the Stokes friction coefficient of the particle.*]

II-Q 17 A flexible polymer with N Kuhn segments of length b is moving inside a gel. The gel fibers are spaced far enough apart to only marginally affect the conformation of the polymer chain.[1]

(a) Assume that the polymer has a drag coefficient of $\gamma = \eta N b$ in the gel, with η the viscosity of water and b the segment length. Find an expression for the time, τ, it takes for the polymer to diffuse a distance equal to its contour length $L = Nb$. Using this expression, estimate τ for double-stranded DNA ($b = 100$ nm) with a length of 30,000 basepairs.

(b) An uniform electric field E is applied in the gel which leads to a total force $F = fN$ on the polymer. Assume that the polymer moves through the gel by reptation only and hence show that the drift velocity v_d of the polymer in the gel is now depending on N

$$v_d = \frac{f}{\eta b N}.$$

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[1]Part of this question is based on Zimm and Levene, "Problems and prospects in the theory of gel electrophoresis of DNA" Quart. Rev. Biophys (1992). Can be downloaded from the course webpage.

(c) Estimate the electric field E that you need to drive DNA molecules with 30,000 basepairs through a gel of 10 cm length in 1 hour. Calculate the distance DNA molecules with 25,000 basepairs would have traveled in the same amount of time. In both cases you may assume that the DNA has a charge of $600e$ per 100 nm segment.