Final Exam **Soft Condensed Matter Theory**, July 1, 2016, 13:30h-16:30.
This exam consists of 20 items divided into 3 problems. The maximum score for each item is 5 points. Write your name on each page and start every problem on a separate piece of paper please. This is a *closed-book* exam, and electronic tools are **not** allowed.

Problem 1: Isotropic to Smectic A phase transition.
Under atmospheric pressure, a compound such as 10CB (or decyl-cyanobiphenyl) exhibits a phase sequence of X-SmA-I with increasing temperature. Here "X" denotes the crystal phase, "SmA" the smectic A liquid crystal phase and "I" the isotropic fluid phase. These molecules are rodlike with a main body axis unit vector $\mathbf{u}$. In the SmA phase these molecules are not only aligned along some preferred direction $\mathbf{n}$ but in addition their centres of mass form layered structures along $\mathbf{n}$.

Here we view the SmA phase as a one-dimensional crystal; in the directions orthogonal to $\mathbf{n}$ the SmA phase remains fluid-like. The degree of orientational order can be described by the nematic scalar order parameter $S = (3/2)\langle(\mathbf{n}\cdot\mathbf{u})^2\rangle - 1/2$. In the isotropic liquid phase $S = 0$, whereas in the crystalline and smectic A phase $1 \geq S > 0$; if the particles are perfectly aligned, $S = 1$.

The density at position $\mathbf{r}$ can be written as $\rho(\mathbf{r}) = \langle\rho\rangle(1 + \eta\cos(q_c\mathbf{r}\cdot\mathbf{n} + \phi)$, where $\langle\rho\rangle$ is the average number density of molecules in the fluid, q_c is the magnitude of the wave vector of the periodic density modulation and ϕ an arbitrary phase shift. The quantity $2\pi/q_c$ is of the order of the length of the molecules. Here η is an order parameter that describes the degree of layering of the molecules. In the isotropic phase $\eta = 0$, whilst in the smectic and crystalline phases $\eta \neq 0$.

(a) Sketch three snapshots, each of about 10 molecules represented as $\mathbf{u}$, in the I, SmA, and X phase, respectively. Also argue why positive and negative values of η are equally likely in the smectic A phase.

The transition between the smectic A phase and the isotropic phase is of second order. A simple Landau theory describing this transition is based on a free energy density difference Δf [J m^{-3}] between the I and SmA phases of the form

$$\Delta f(S,\eta) = \frac{1}{2}aS^2 + \frac{1}{2}\alpha(T - T_0)\eta^2 + \frac{1}{4}\beta\eta^4 - \gamma\eta^2 S, \tag{1}$$

where a [J m^{-3}], α [J m^{-3} K^{-1}], β [J m^{-3}] and γ [J m^{-3}] are T-indendent positive phenomenological parameters. The I-SmA transition temperature is given by T_0.

(b) Argue why we only expect even orders in the order parameter η, calculate the expectation values of the two order parameters η and S, and sketch their temperature dependence.

(c) Verify the stability of the solutions of item (b). Hint: Use the trace and the determinant of the hessian matrix $\partial^2\Delta f/\partial\alpha\partial\beta$, with $\alpha, \beta = S, \eta$.

(d) Show that the entropy of the smectic A phase decreases for decreasing temperature $T < T_0$. Argue why this implies that energy (attractive interactions between the molecules) must drive the I-SmA transition.

(e) Explain the main difference between thermotropic and lyotropic liquid crystals, and to which of these two classes 10CB belongs.

Even though for $T > T_0$ the isotropic fluid is thermodynamically stable, fluctuations in the relevant order parameter(s) do herald the emergence of the SmA phase for $T < T_0$. These fluctuations can be incorporated in the theory by allowing for a non-local Landau free energy functional ΔF [J] of the form

$$\Delta F[S,\eta] = \int d\mathbf{r} \left[\Delta f(S,\eta) + \frac{1}{2} K_S (\vec{\nabla} S)^2 + \frac{1}{2} K_\eta (\vec{\nabla} \eta)^2 \right], \tag{2}$$

where K_S [J m^{-1}] and K_η [J m^{-1}] are "stiffness" parameters describing how strongly the fluid resists gradients in the order parameters.

(f) Show that the amplitudes $\hat{\eta}_{\mathbf{q}} = \int d\mathbf{r} \eta(\mathbf{r}) \exp(-i\mathbf{q}\cdot\mathbf{r})$ and $\hat{S}_{\mathbf{q}} = \int d\mathbf{r} S(\mathbf{r}) \exp(-i\mathbf{q}\cdot\mathbf{r})$ of the Fourier modes of the fluctuations of wave vector $\mathbf{q}$ obey

$$\langle |\hat{S}_{\mathbf{q}}|^2 \rangle = \langle \hat{S}_{-\mathbf{q}} \hat{S}_{\mathbf{q}} \rangle = \frac{V k_B T}{a + K_S q^2} \tag{3}$$

and

$$\langle |\hat{\eta}_{\mathbf{q}}|^2 \rangle = \langle \hat{\eta}_{-\mathbf{q}} \hat{\eta}_{\mathbf{q}} \rangle = \frac{V k_B T}{\alpha(T - T_0) + K_\eta q^2}, \tag{4}$$

where the brackets $\langle \cdots \rangle$ indicate a thermal (ensemble) average. Hint: Presume $S \ll 1$ and $|\eta| \ll 1$, discard all terms higher than quadratic order in the order parameters and make use of the identity $\int d\mathbf{r} \exp(-i\mathbf{q}\cdot\mathbf{r}) = V\delta_{\mathbf{q},0}$ with $\delta_{\mathbf{q},0}$ the usual Kronecker delta.

(g) Discuss what happens to the mean-square amplitudes of the Fourier transforms of the order parameters upon approach of the transition temperature T_0, and why S is called a non-critical order parameter and η a critical order parameter. Show that one length scale diverges, and give a physical interpretation of this length scale.

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Problem 2

We consider a three-dimensional polymer solution of M polymers of contour length Nb in a volume V. Here b is the length of a single bead, and $N \gg 1$ the degree of polymerisation. The volume fraction is ϕ, and the radius of gyration of a polymer is denoted by $R_g \simeq bN^{\nu}$.

(a) Give ν, in the dilute regime, for the cases that the solvent is (i) good, (ii) bad, and (iii) a Θ-solvent. Briefly explain your answer (derivations are not needed).

(b) Calculate the crossover volume fraction ϕ^* between the dilute and the semi-dilute concentration regime, as a function of N and ν.

(c) Derive, using a DeGennes scaling argument, that the osmotic pressure in the semi-dilute regime is proportional to ϕ^m and calculate/estimate the exponent m.

Within Flory-Huggins theory, the free energy F of the system is written as $F = (V/b^3)k_B T f(\phi)$ where

$$f(\phi) = \frac{\phi}{N}\ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi),$$

with χ the Flory-Huggins interaction parameter.

(d) Calculate the critical volume fraction ϕ_c, and the critical Flory-Huggins parameter χ_c.

(e) Describe in a few words the state of the system for $\chi \gg \chi_c$, assuming that $\phi = \phi_c$.

Consider a polymer solution in a good solvent in contact with an external hard wall.

(f) Explain if the local segment concentration close to the wall is higher or lower than that in the bulk far from the wall, or if it is the same. Is this similar or different from hard spheres close to a hard wall?

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Problem 3

Consider a planar electrode at $z = 0$ at a given potential ψ_0 in contact with an aqueous electrolyte of relative dielectric constant ϵ at room temperature T in the half-space $z > 0$. The electrolyte contains $n \geq 2$ ion species with charge $z_i e$, valency z_i, and concentration profiles $\rho_i(z)$, with $i = 1, 2, \cdots, n$. The electric potential is denoted by $\psi(z)$ and satisfies for $z > 0$ the Poisson equation $\psi''(z) = -\frac{4\pi}{(4\pi\epsilon_0)\epsilon} eQ(z)$ with $eQ(z)$ the charge density, ϵ_0 the vacuum permittivity, and e the proton charge.

(a) Express $Q(z)$ in terms of the profiles $\rho_i(z)$ and formulate the *bulk* neutrality condition in terms of the valencies z_i and the bulk concentrations $\rho_i(\infty)$.

(b) Derive an expression for the screening length κ^{-1} within linearised Poisson-Boltzmann (LPB) theory.

We now assume that $n = 2$ with $z_i = \pm 1$ with concentration profiles $\rho_\pm(z)$ for the cations ($z_+ = 1$) and anions ($z_- = -1$), with a known bulk concentrations $\rho_\pm(\infty) = \rho_s$ and $\psi(\infty) = 0$.

(c) Derive, for $z > 0$, the LPB equation $\psi''(z) = \kappa^2 \psi(z)$, solve for $\psi(z)$, and calculate $\rho_\pm(z)$.

(d) Calculate the areal charge density $e\sigma$ of the electrode for the case that $e\psi_0 \ll k_B T$.

We now assume that a cation C and an anion A can bind to form neutral pair AC according to the "quasi-chemical" reaction A+C↔AC with a known equilibrium constant K.

(e) Calculate the fraction $\alpha \in [0, 1]$ of ions that are part of a bound pair, far from any electrode, if the total concentration of ions (bound and free) equals 2ρ.

The stationary Stokes equation $-\nabla p + \mathbf{f} + \eta \nabla^2 \mathbf{u} = \mathbf{0}$ and $\nabla \cdot \mathbf{u} = 0$ describe the velocity $\mathbf{u}$ of an incompressible fluid subject to an applied pressure gradient ∇p and a body force density $\mathbf{f}$. Here η is the shear viscosity.

(f) Give an expression for $\mathbf{f}$ for the case of a constant applied electric field $\mathbf{E} = (E_x, 0, 0)$ in the x direction perpendicular to the normal $(0, 0, 1)$ of the charged electrode in the plane $z = 0$. The electrode is at a potential $\psi_0 \ll 25$ mV and in contact with an aqueous 1:1 electrolyte of Debye length κ^{-1} with $\psi(z \to \infty) = 0$, as treated in item (c).

(g) Solve for the case of item (f) the stationary Stokes equation for the flow profile under no-slip boundary conditions, assuming that: $\nabla p = 0$, only the x-component $u_x(z)$ is non-vanishing due to translational invariance in the y-direction $(0, 1, 0)$, and $u_x(\infty)$ is finite. How is such a fluid flow called?

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