Final Exam **Soft Condensed Matter Theory**, June 30, 2017, 9:00h-12:00. This exam consists of 20 items, the maximum score for each item is 5 points. Write your name on each page. This is a *closed-book* exam, and electronic tools are **not** allowed.

Problem 1 Uniaxial nematic liquid-crystalline states have been observed in many different kind of fluid, lyotropic and thermotropic. For both cases, molecular statistical mechanical theories have been proposed to explain the spontaneous alignment of the (usually rod-like) nematogenic particles. Maier-Saupe theory is designed to apply to thermotropic nematics, whilst Onsager theory describes lyotropic nematics.

(a) Explain (i) the main difference between thermotropic and lyotropic nematic liquid crystals, and (ii) what drives the spontaneous ordering in these two types of liquid crystal.

Some compounds also exhibit a so-called smectic A phase under conditions in between those where the nematic and the crystal phases are stable. The smectic A phase resembles the nematic in that the particles that make up the fluid are aligned along a director, but differ in the sense that the particle density is not uniform but modulated along the director. This is caused by the freezing out of one positional degree of freedom of the particles. In a sense, particles attain crystalline order along the director but remain fluid-like perpendicular to that.

The typical wavelength of the density modulation is the size of the molecules, d, and the density variation is proportional to $\cos(2\pi z/d)$ with z the spatial co-ordinate along the director. A simple theory proposed by MacMillan and Maier, which has the same ingredients as that of Maier and Saupe describing the nematic transition in thermotropics, is based on the following Helmholtz free energy functional

$$\frac{\beta \Delta F[\psi]}{N} = \int_{-d/2}^{+d/2} dz \left[\psi(z) \ln(\psi(z) d) + \frac{1}{2} \psi(z) \beta \Delta U(z) \right]. \tag{1}$$

Here, N is number of particles in a slab of thickness d, reflecting the periodicity of the density modulation, $\psi(z)$ the positional distribution function of the centres of mass of the particles in the slab, ΔU is the excess molecular field not captured by that driving the nematic transition. Obviously, the distribution function is normalised, $\int_{-d/2}^{+d/2} dz\, \psi(z) = 1$; $\beta = 1/k_B T$ is as usual the reciprocal thermal energy, with k_B Boltzmann's constant and T the absolute temperature.

(b) Describe the physical background of the two ingredients in this free energy functional.

A sensible trial molecular field is

$$\Delta U(z) = -\epsilon \sigma \cos\left(\frac{2\pi z}{d}\right), \tag{2}$$

where ϵ is the strength of the van der Waals interaction between the particles driving the transition to the smectic A phase. Arguably, this is strongest for particles in register, that is, for particles that line up perfectly. The degree of positional ordering is described by the smectic order parameter σ, defined as

$$\sigma = \int_{-d/2}^{+d/2} dz\, \psi(z) \cos\left(\frac{2\pi z}{d}\right). \tag{3}$$

(c) Show that the most probable distribution of material in the smectic A phase obeys the following self-consistent field equation,

$$\psi(z) = \frac{1}{Z} \exp\left[-\beta\epsilon\sigma \cos\left(\frac{2\pi z}{d}\right)\right], \tag{4}$$

where Z acts as a normalisation constant.

(d) Show that the uniform distribution, describing the nematic phase, is a solution to equation (4) for all temperatures T, and that the associated free energy obeys $\Delta F = 0$, implying that the free energy functional describes the difference in free energies of the smectic phase and the reference nematic phase.

The self-consistent field equation can be solved by presuming the ordering is weak and $\sigma \ll 1$. In that case we find for the order parameter a second solution

$$\sigma = \frac{1}{2}\sqrt{\frac{\beta\epsilon}{4} - 1}, \tag{5}$$

which becomes relevant if $\beta\epsilon \geq 4$, i.e., for $T \leq \epsilon/4k_B$. This fixes the nematic-smectic A transition temperature at $T_{N-SmA} = \epsilon/4k_B$. According to the model, the transition is second order.

(e) Describe how we can verify that for $T < T_{N-SmA}$ the smectic A phase is indeed the thermodynamically stable phase, and that the nematic phase must be thermodynamically unstable.

Problem 2

Consider a single ideal polymer of $N+1$ beads at positions $\mathbf{r}_i$ with fixed bond length $b = |\mathbf{r}_{i+1} - \mathbf{r}_i|$. The end-to-end vector is $\mathbf{R} = b\sum_{i=1}^{N} \mathbf{u}_i$ with $\mathbf{u}_i$ the unit vector pointing from bead i to bead $i+1$. The chain is long, hence $N \gg 1$.

(a) Give the molecular reason for chain flexibility, and argue why thermal averaging is needed in the description of a typical polymer such as polyethylene at room temperature T.

(b) Calculate the thermally averaged end-to-end vector $\langle \mathbf{R} \rangle$ and its mean-square $\langle \mathbf{R} \cdot \mathbf{R} \rangle$ for a so-called flexible chain that satisfies $\langle \mathbf{u}_i \rangle = \mathbf{0}$ and $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle = \exp(-|i-j|b/\ell)$ with $\ell \ll Nb$ the (presumably known) persistence length of the chain. Simplify your final result for the case $\ell \gg b$.

The probability distribution $P(\mathbf{R}, N)$ for a perfectly flexible ideal chain (with $\ell \ll Nb$) with its first segment in the origin satisfies $P(\mathbf{R}, N) = (4\pi)^{-1} \int d\mathbf{u} P(\mathbf{R} - b\mathbf{u}, N-1)$.

(c) Give a physical motivation for this relation and use it to derive a diffusion-like equation for $P(\mathbf{R}, N)$.

The diffusion-like equation of (c) predicts for the radius of gyration $R_g \propto \langle \mathbf{R} \cdot \mathbf{R} \rangle^{1/2} \propto N^{1/2}$, but experimetally it is found that $R_g \propto N^{\nu}$ with $\nu \neq 1/2$.

(d) Give the numerical value of ν in (i) good and (ii) bad solvents, and discuss in a few words the origin and the consquences of the deviation from $\nu = 1/2$.

(e) Derive an expression (in terms of N and ν) for the volume fraction ϕ^* that separates the dilute from the so-called semi-dilute regime for polymers in a good solvent.

Problem 3

We consider a one-component fluid of number density $\rho(\mathbf{r}, t)$ and fluid velocity $\mathbf{u}(\mathbf{r}, t)$ at position $\mathbf{r}$ at time t.

(a) Use the continuity equation to show that $\nabla \cdot \mathbf{u}(\mathbf{r}, t) = 0$ if the fluid is incompressible.

The Navier-Stokes equation for an incompressible fluid with mass density ρ_m and viscosity η reads $\rho_m(\partial \mathbf{u}/\partial t) + \rho_m(\mathbf{u} \cdot \nabla)\mathbf{u} = \eta\nabla^2\mathbf{u} - \nabla p + \mathbf{f}$, where p is the hydrostatic pressure and $\mathbf{f}$ an external body force.

(b) Simplify the incompressible Navier-Stokes equation as much as possible for the case of stationary and slow laminar flow conditions (i.e. at low Reynolds number Re) without body forces, in the geometry of a narrow slit of height H and lenghth $L \gg H$ such that $z \in [0, H]$ and $x \in [0, L]$, with an applied pressures p_0 at $x \leq 0$ and $p = p_L$ at $x \geq L$ such that the fluid is pushed through the slit in the x-direction; the width in the y-direction can be taken as infinity.

In the geometry of (b), but now in the case of two identical *charged* surfaces $z = 0$ and $z = H$, and in absence of any pressure gradient (so $p_0 = p_L = 0$), an electric field $\mathbf{E} = (E_x, 0, 0)$ is applied. Hence the body force is $\mathbf{f} = q(z)\mathbf{E}$ with $q(z)$ the charge density *in the fluid*. The stationary Stokes equation can then be written as $\eta d^2u_x(z)/dz^2 = q(z)E_x$.

(c) Where does the body force come from in the case that the fluid is an electrolyte?

(d) Use the Poisson equation $\nabla^2\psi(z) = -\epsilon_0\epsilon q(z)$ with $\psi(z)$ the potential and $\epsilon\epsilon_0$ the dielectric permittivity of the fluid to show that the electric field causes the fluid in the middle of the slit, at $z = H/2$ far from the walls, to flow with velocity $u_x(H/2) = -\epsilon\epsilon_0\psi(0)E_x/\eta$, provided no-slip boundary conditions $u_x(0) = u_x(H) = 0$ are used.

(e) Argue in a few words why the result of (d) is an example of linear response, and give two other linear-response examples of transport phenomena.

Problem 4

(a) Describe in a few words what could happen if enough polymers with a radius of gyration of 100 nm are added to a suspension of hard spheres of diameter 200 nm at a packing fraction of, say, 0.10, under good solvent conditions. Motivate your answer.

(b) Describe in a few words what could happen if an aqueous suspension of highly charged colloidal spheres (diameter 100 nm, packing fraction 0.3, zeta potential 100 mV) slowly gets de-ionised from an initial NaCl concentration of 100mM to a final NaCl concentration of 0.01mM. Motivate your answer.

(c) Describe in a few words what structures you would expect to self-assemble in a melt of block-copolymers composed of two mutually immiscible blocks of monomer A and B if (i) the two blocks are equally long, and (ii) block A is much longer than block B.

(d) Explain why and how the surface charge of a colloidal sphere in water can change with pH.

(e) Derive Fick's law from Dynamic DFT at the ideal-gas level.