Final Exam **Soft Condensed Matter Theory**, June 29, 2019, 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
Consider a gas-liquid interface with surface tension γ and mass density difference $\Delta\rho$ between the bulk liquid and bulk gas phase, in the Earth's gravity field with acceleration g pointing in the negative z-direction. Denoting the horizontal position by (x, y) and the local height of the interface by $z = h(x, y)$ (so we ignore overhangs), with $\int dxdyh(x, y) = 0$, we can write for the capillary-wave Hamiltonian $H_{cw} = (\gamma/2)\int dxdy[(\partial_x h)^2 + (\partial_y h)^2 + h^2/\ell^2]$.

(a) Explain the physics behind the terms in H_{cw} and derive an expression for the capillary length ℓ.

(b) Diagonalize H_{cw} by a Fourier analysis, and explain *how* the roughness $\langle\int dxdyh^2(x, y)\rangle$ can be calculated from the Fourier representation.

Problem 2
We consider a one-component 3D fluid at chemical potential μ at temperature T in an external potential $V(\mathbf{r})$, such that the density profile $\rho(\mathbf{r})$ is inhomogeneous. The intrinsic Helmholtz free-energy functional $\mathcal{F}[\rho]$ of this system is written as the sum of an ideal-gas contribution $\mathcal{F}_{id}[\rho]$ and an excess part that we assume to be given by
$\mathcal{F}_{ex}[\rho] = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'W(|\mathbf{r} - \mathbf{r}'|)\rho(\mathbf{r})\rho(\mathbf{r}')$ with some known function $W(r)$.

(a) Give an expressison for $\mathcal{F}_{id}[\rho]$.

(b) Give, as explicitly as possible, a condition for the equilibrium density profile $\rho_{eq}(\mathbf{r})$.

(c) Give an expression for the equilibrium grand potential of this inhomogeneous fluid.

(d) Calculate the direct correlation function $c^{(2)}(\mathbf{r}, \mathbf{r}')$ of this fluid.

(e) If the pair potential between the particles of this fluid at center-to-center separation r is denoted by $u(r)$, give $W(r)$ for the case of a second-virial approximation.

(f) Calculate the pressure $P(\rho_b)$ as a function of the bulk density ρ_b of this fluid for the case that $W(r) = 2k_BT$ for $0 < r < \sigma$ and $W(r) = 0$ for $r \geq \sigma$, where σ is a measure for the linear dimension of the particles.

Problem 3
The Gibbs free energy of a thermotropic 3D nematic liquid crystal at temperature T is assumed to be given by the (truncated) Landau expansion $G = G_0 + a(T - T^*)S^2 - bS^3 + cS^4$, with a, b, c, T^* given and fixed material-specific positive constants and S the uniaxial nematic order parameter.

(a) Give the interpretation of G_0, and argue why G can contain a cubic S^3 term but *no* linear term in S.

(b) Calculate the temperature T_{IN} at which the phase transition takes place. Hint: you may use that one can rewrite $G - G_0 = [a(T - T^*) - b^2/4c]S^2 + cS^2(S - b/2c)^2$.

(c) Argue whether the transition is first or second order, and sketch the temperature dependence of the order parameter $S(T)$ with T^* indicated on the T-axis.

Problem 4

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

(a) Derive an expression for the Reynolds number Re, and show that the Navier-Stokes equation reduces, in a stationary state with Re $\ll 1$, to the Stokes equation $\eta\nabla^2\mathbf{u}-\nabla p+\mathbf{f}=0$.

We consider a long cylindrical channel of length L and radius $R \ll L$ with symmetry axis $\hat{z}$ along the z-direction and radial coordinate r, and with an inlet at $z=0$ at pressure $p_0+\Delta p$ and an outlet at $z=L$ at pressure p_0. The pressure drop Δp is small enough for the flow between inlet and outlet to be in the Re $\ll 1$ regime. Because of the long length of the channel we may also assume that the only non-zero component of $\mathbf{u}$ is its z-component, denoted by u_z. We first consider the case $\mathbf{f}\equiv 0$.

(b) Show that u_z does not depend on z, that p does not depend on r, and that $p=p_0+(1-z/L)\Delta p$ for $z\in[0,L]$.

(c) Use that $\nabla^2=\frac{\partial^2}{\partial z^2}+r^{-1}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}$ in cylinder coordinates with azimuthal symmetry to find $u_z(r)$ for no-slip boundary conditions $u_z(r=R)=0$.

We now consider a slit-like channel with height H; bottom and top are in the two planes $z=\pm H/2$, both at zeta-potential ψ_s. The channel has length $L \gg H$ and connects the inlet at $x=0$ to the outlet at $x=L$. Now there is *no* applied pressure drop, so $\nabla p\equiv 0$, but there is a weak applied electric field $\mathbf{E}=(E_x,0,0)$ in the x-direction, which gives rise to a body force $\mathbf{f}=q(z)\mathbf{E}$ where $q(z)=-\epsilon\epsilon_0 d^2\psi(z)/dz^2$ is the electric charge density due to a diffuse cloud of ions for $|z|<H/2$. Here $-xE_x+\psi(z)$ is the electrostatic potential in the channel.

(d) Calculate the x-component $u_x(z)$ of the fluid velocity profile $\mathbf{u}=(u_x,0,0)$ in terms of $\psi(z)$, in the stationary state under no-slip boundary conditions, and give the velocity $u_x(0)$ in the middle of the slit for the case that the Debye length is much smaller than the height H.

The equation $\mathbf{J}=-D(\nabla\rho+\rho\beta\nabla U))+\rho\mathbf{u}$ expresses the flux $\mathbf{J}(\mathbf{r},t)$ of an uncharged solute species of density $\rho(\mathbf{r},t)$ in a static external potential $U(\mathbf{r})$ and in a fluid of velocity $\mathbf{u}(\mathbf{r})$.

(e) Give a motivation for all three terms in this equation, and give an expression for the *equilibrium* density profile $\rho_{eq}(\mathbf{r})$.

Problem 5

(a) Sketch, in a single graph, the equilibrium density profile $\rho(z)$ as a function of the distance $z>0$ from a planar hard wall, for a hard-sphere fluid (diameter σ) at a bulk packing fraction far from the wall given by (i) 0.01 and (ii) 0.48.

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

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

—THE END—