Midterm Exam
Soft Consensed Matter Theory
April 16, 2014
12.00h-15.00h

This exam consists of 4 problems each worth 25 points.

THIS IS A CLOSED-BOOK EXAM. NO ADDITIONAL ELECTRONIC TOOLS SUCH AS CALCULATORS ARE ALLOWED.

PLEASE MAKE SURE THAT YOUR NAME IS WRITTEN ON EACH PAGE. ALSO MAKE SURE TO SPEND TIME ON ALL FOUR EXERCISES.

A few formulas that may or may not be useful in this exam:

$$B_2 = -\frac{1}{2} \int d\mathbf{r} \Big(\exp[-\beta u(\mathbf{r})] - 1 \Big); \qquad \text{2nd virial coefficient}$$

$$S(q) = \langle \frac{1}{N} \sum_{m,n}^{N} \exp[i\mathbf{q} \cdot \mathbf{r}_{mn}] \rangle;$$

$$p = \rho k_B T - \frac{\rho^2}{6} \int d\mathbf{r} g(r) r u'(r);$$

$$k_B T \left(\frac{\partial \rho}{\partial p} \right)_T = 1 + \rho \int d\mathbf{r}(g(r) - 1);$$

$$h(r) = c(r) + \rho \int d\mathbf{r}' c(r') h(|\mathbf{r} - \mathbf{r}'|).$$

Here $u(\mathbf{r})$ is the pair potential, $\beta = 1/k_B T$ with T the temperature and k_B the Boltzmann constant, p the pressure, ρ the number density, $g(r)$ the radial distribution function, $h(r)$ the total correlation function, $c(r)$ the direct correlation function, N the number of particles in the system, $\mathbf{r}_{mn}$ the center-to-center vector between particle m and n, $\langle .. \rangle$ a thermal average.

Problem 1

Consider a classical fluid of N point-particles in a volume V at temperature T with Hamiltonian $H = K + \Phi$ with kinetic energy $K = \sum_{i=1}^{N} \mathbf{p}_i^2/(2m)$ and potential energy $\Phi = \sum_{i<j} u(|\mathbf{r}_i - \mathbf{r}_j|)$. Here $\mathbf{p}_i$ and $\mathbf{r}_i$ denote the linear momentum and the center-of-mass position of particle i, respectively, m is the particle mass, and $u(r)$ the pair potential. For brevity we denote the set $\{\mathbf{r}_1, .., \mathbf{r}_N\}$ by $\mathbf{r}^N$ and likewise for $\mathbf{p}^N$. The fluid is in thermodynamic equilibrium.

(a) Give the properly normalized canonical probability distribution $f_c(\mathbf{r}^N, \mathbf{p}^N)$, and calculate the average kinetic energy $\langle K \rangle$.

(b) Show that the average potential energy can be written as
$\langle \Phi \rangle = \int_V d\mathbf{r}_1 ... d\mathbf{r}_N \Phi \exp(-\beta \Phi) / \int_V d\mathbf{r}_1 ... d\mathbf{r}_N \exp(-\beta \Phi)$, and simplify this expression (for a homogeneous fluid) as much as possible in terms of the radial distribution function $g(r)$.

Suppose now that the Helmholtz free energy $F(N, V, T) = V f(\rho, T)$ is given by

$$f(\rho, T) = k_B T \rho \left(\log \frac{\rho \Lambda^3}{1 - \rho b} - 1 \right) - a\rho^2, \tag{1}$$

with the thermal wavelength Λ and constants $a > 0$ and $b > 0$.

(c) Calculate the pressure $p(\rho, T)$ and sketch its ρ-dependence for (i) $T > T_c$, (ii) $T = T_c$, and (iii) $T < T_c$, where T_c is the critical temperature (that you do not need to calculate).

(d) Briefly describe the macroscopic states of the fluid upon increasing the density from $\rho b \ll 1$ to $\rho b \simeq 1$ in all three temperature regimes mentioned in (c).

(e) Calculate $B_2(T)$ for the square-well fluid with hard-core diameter σ, well depth $-\epsilon$, and well width δ (such that $u(r > \sigma + \delta) = 0$).

Problem 2

Consider a homogeneous fluid of N identical particles in a volume V. The density is $\rho = N/V$, and the temperature T. The pair distribution is defined as $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \langle \sum_{i \neq j}^{N} \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{r}_j - \mathbf{r}') \rangle$.

(a) Give arguments as to why one can write $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho^2 g(|\mathbf{r} - \mathbf{r}'|)$.

(b) Sketch $g(r)$ for dilute Argon far above the critical temperature, and also for triple-point Argon. Think of units on the axes.

(b) Prove that the structure factor can be written as $S(q) = 1 + \rho \int d\mathbf{r} g(r) \exp[i\mathbf{q} \cdot \mathbf{r}]$.

(c) Show from (c) for $q \neq 0$ that $S(q) = 1/(1 - \rho \hat{c}(q))$ with $\hat{c}(q)$ the Fourier transform of the direct correlation function $c(r)$.

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 $\int dx dy h(x, y) = 0$, we can write for the capillary-wave Hamiltonian $H_{cw} = (\gamma/2) \int dx dy [(\partial_x h)^2 + (\partial_y h)^2 + h^2/\ell^2]$.

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

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

Problem 3: *Liquid crystal phase transitions*

The compound p-etoxybenzoic acid exhibits, apart from the usual solid and liquid phases, two liquid-crystalline phases: the nematic and the smectic phase. The phase diagram of this compound is given below.
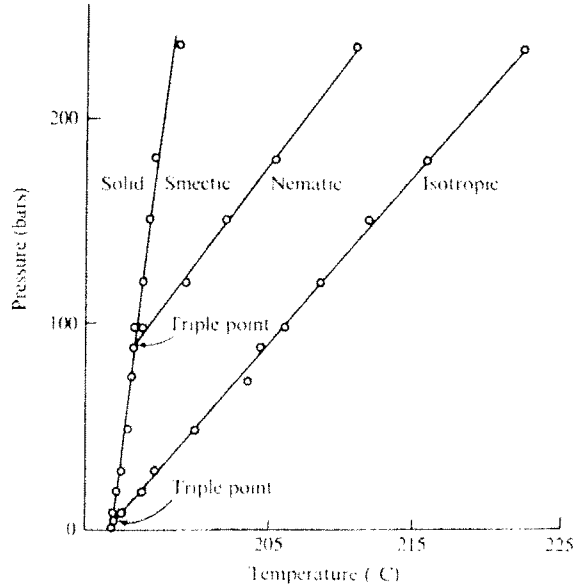
a) [2 pts] What precisely are nematic and smectic liquid-crystalline phases? Explain the three main differences between thermo- and lyotropic liquid crystals. Is p-etoxybenzoic acid a thermotropic or a lyotropic liquid crystal former?

b) [2 pts] What is meant by the *director* of a nematic liquid crystal and what is the definition of the (scalar) *nematic order parameter*?

The isotropic-nematic phase transition can be described by a Landau-de Gennes theory that says that the free energy difference per unit volume between a nematic and isotropic fluid, Δf_n [J m^{-3}], obeys

$$\Delta f_n = \tfrac{1}{2} a(T - T_*)S^2 - \tfrac{1}{3} BS^3 + \tfrac{1}{4} CS^4, \quad (1.1)$$

where $a > 0$ [J m^{-3} K^{-1}] and $B, C > 0$ [J m^{-3}] are material constants that plausibly depend on the pressure, T [K] is the absolute temperature and T_* [K] the spinodal temperature of the isotropic phase.

c) [3 pt] Explain <u>how</u> to calculate the clearing temperature T_{IN} [K] as well as the spinodal temperature of the nematic phase T_+ [K] from the Landau-de Gennes theory, eq (1.1). Give all required arguments for every step in this procedure. Note: no actual calculation is needed!

For p-etoxybenzoic acid both the isotropic-nematic and nematic-smectic transitions are first order transitions but this is not generally true as for some compounds the nematic-smectic transition is of second order.

d) [3 pts] Why is the isotropic-nematic transition sometimes called a weakly first order transition?

The spatial variation of the density of the smectic phase arguably obeys $\rho(\vec{r}) = \langle\rho\rangle(1 + \eta \cos(q_c \vec{n} \cdot \vec{r} + \varphi))$, where $\langle\rho\rangle$ [m^{-3}] is the average number density, η the relative variation of the density away from its average value, q_c [m^{-1}] the magnitude of the wave vector of the periodic density variation, $\vec{n}$ the director, $\vec{r}$ [m] the position in space and φ an arbitrary phase shift. The quantity q_c is roughly set by the length of the molecules that are somewhat elongated. Reasonably, η must be relevant smectic order parameter and MacMillan proposed in 1971 the following Landau free energy density Δf_s [J m^{-3}] in terms of that order parameter

$$\Delta f_s = \Delta f_n + \tfrac{1}{2}\alpha(T - T_0)\eta^2 + \tfrac{1}{4}\beta\eta^4 - \gamma\eta^2(S(\eta) - S), \quad (1.2)$$

where he also allowed the nematic order parameter $S(\eta)$ in the smectic phase to be different from that in the homogeneous isotropic and nematic phases. Here, α [J m^{-3} K^{-1}], and β and γ [J m^{-3}] are material constants that depend on pressure, all presumed to be positive, T_0 is a critical temperature. Note that $\eta = 0$ in the nematic and isotropic phases and that $S(0) \equiv S$.

e) [3 pts] Explain why we need to expect that the free energy is symmetric in the order parameter η.

f) [3 pts] Make plausible that if we insert the expectation value of $S(\eta)$, the free energy eq (1.2) reduces to

$$\Delta f_s = \Delta f_n(S) + \tfrac{1}{2}\alpha(T - T_0)\eta^2 + \tfrac{1}{4}\bar{\beta}\eta^4, \quad (1.3)$$

1

where

$$\bar{\beta} = \beta - 2\gamma^2(\partial^2 \Delta f_n / \partial S^2)^{-1}, \tag{1.4}$$

at least if we write

$$\Delta f_n\big(S(\eta)\big) = \Delta f_n(S) + \frac{1}{2}(\partial^2 \Delta f_n / \partial S^2)(S(\eta) - S)^2, \tag{1.5}$$

and ignore higher order corrections.

(g) [3 pts] Give the temperature dependence of the expectation values of η and $S(\eta)$ for the cases $T_0 < T_{IN}$ and $T_0 > T_{IN}$ presuming that $\bar{\beta} > 0$, [2 pts] as well as that of the variance of η. [1 pt] What can be said about the order of the transition and the accuracy of the Landau theory close to T_0?

(h) [3 pts] Argue why it may well be that $\bar{\beta} < 0$ even if $\beta > 0$, provided that $T_0 \uparrow T_{IN}$. Why do we need to amend the free energy eq. (1.3) if this happens to be the case, and what term consistent with the symmetry of the problem do we add to fix the problem?

(i) [3 pts] Amend the free energy eq. (1.3) and calculate the nematic-smectic transition temperature for the case $\bar{\beta} < 0$, and comment on the order of the transition.

Problem 4: *Macroscopic properties of liquid crystals*

Liquid crystals in contact with a solid surface, such as in a *twisted nematic cell* or in a nematic domain in *smart glass*, adjust their director field in response to their interaction with that solid surface.

a) [2 pts] Explain what is meant by *polar* and *azimuthal anchoring* of a nematic liquid crystal to a planar surface.

b) [2 pts] Describe what a twisted nematic cell entails, what its purpose is and how precisely use is made of a so-called *Frederiks transition*.

The deformation of a director field of a nematic due to the presence of surface goes at the expense of an elastic free energy cost. In the so-called equal-constant approximation, the Frank elastic free energy ΔF_E [J] can be written as

$$\Delta F_E = \frac{1}{2} K \int d^3 \vec{r} \left[\left(\vec{\nabla} \cdot \vec{n} \right)^2 + \left(\vec{\nabla} \times \vec{n} \right)^2 \right],$$ (2.1)

where K [N] is some average of the bulk elastic constants, the integration is over the entire volume of the material, $\vec{n}$ is the nematic director that depends on the spatial co-ordinate $\vec{r}$ [m].

c) [3 pts] What are the three bulk elastic deformation modes of a nematic, and which of those end up in the divergence and which in the rotation of the director field?

Presume that a semi-infinite nematic liquid crystal is in contact with a planar surface, and that the polar and azimuthal anchoring to that surface is rigid along the z direction in a Cartesian co-ordinate system. The surface is thought in the xz plane, and positioned at $y = 0$ [m] and the nematic fluid in the volume for $y > 0$. Let a magnetic field be switched on along the x direction. The magnetic field energy can, apart from an uninteresting constant, be written as

$$\Delta F_M = -\frac{1}{2} \Delta \chi \int d^3 \vec{r} \left[\left(\vec{H} \cdot \vec{n} \right)^2 \right],$$ (2.2)

where $\Delta \chi$ [J T^{-2} m^{-3}] is the magnetic susceptibility anisotropy of the nematic, presumed to be positive. Again, the integral is taken over the entire volume of the nematic.

d) [3 pts] Argue why, if the director field remains fixed in the xz plane, the overall free energy should obey

$$\Delta F_E + \Delta F_M = A \int_0^\infty dy \left[\frac{1}{2} K \left(\frac{d\theta}{dy} \right)^2 - \frac{1}{2} \Delta \chi H^2 \sin^2 \theta \right]$$ (2.3)

with A [m^2] the area of the planar surface and θ the polar angle of the director field.

e) [3 pts] Show that in thermal equilibrium, the polar angle obeys the following differential equation.

$$K \frac{d^2 \theta}{dy^2} + \Delta \chi H^2 \sin \theta \cos \theta = 0,$$ (2.4)

where have to impose the boundary conditions $\theta(0) = 0$ and $\lim_{y \to \infty} \theta(y) = \pm \frac{\pi}{2}$.

f) [3 pts] Even without explicitly solving eq. (2.4), we can deduce over what length scale the transition from $\theta = 0$ to $\theta = \pm \frac{\pi}{2}$ takes place. Give the functional dependence of that length scale on the magnetic field strength and discuss why this length scale diverges as the field strength goes to zero.

The elastic deformation of a smectic liquid crystal, pictured on the right in a polarisation micrograph, also gives rise to a free energy cost, but it obeys a different expression from that of the nematic due to the spatial organisation of the molecules in it. The particle density
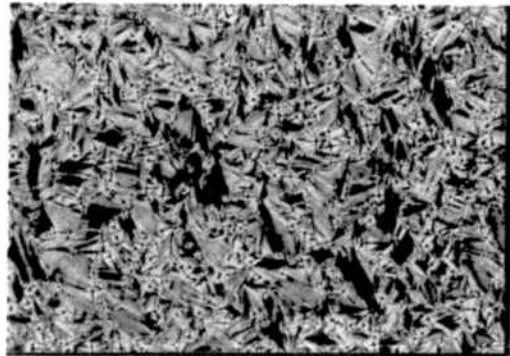
in the smectic phase approximately obeys $\rho(\vec{r}) = \langle\rho\rangle(1 + \eta\cos(q_c\vec{n}\cdot\vec{r} + \varphi))$, with $\langle\rho\rangle$ [m^{-3}] the average number density, η the relative variation of the density away from its average value, q_c [m^{-1}] the magnitude of the wave vector of the periodic density variation, $\vec{n}$ the director, $\vec{r}$ [m] the position in space and φ a phase shift. The quantity q_c is roughly set by the length of the molecules that are somewhat elongated.

In a perfect smectic the phase shift is a constant but in a deformed one, $\varphi = \varphi(\vec{r}) = q_c u$ where $u(\vec{r})$ [m] is a displacement field of the ideal, perfectly parallel layers of the molecules. It can be positive or negative. One can show that to lowest order in the deformation,

$$\Delta F_E = \int d^3\vec{r}\left[\frac{1}{2}B\left(\frac{\partial u}{\partial z}\right)^2 + \frac{1}{2}K\left(\left(\frac{\partial^2 u}{\partial x^2}\right) + \left(\frac{\partial^2 u}{\partial y^2}\right)\right)^2\right] \tag{2.5}$$

if we choose the director field along the z axis of our Cartesian co-ordinate system. Here, B is a bulk layer compression modulus and K an elastic constant for layer deformation.

g) [3 pts] Show that the expectation value of the amplitude of Fourier components $\hat{u}(\vec{q})$ of the spontaneous fluctuations of the displacement $u(\vec{r})$ around the value of zero, obeys

$$\langle|\hat{u}(\vec{q})|^2\rangle = \frac{k_B TV}{Bq_z^2 + Kq_\perp^4} \tag{2.6}$$

where $\vec{q} = (q_x, q_y, q_z)$ [m^{-1}] denotes the wave vector, and $q_\perp^2 = q_x^2 + q_y^2$ [m^{-1}], $k_B T$ [J] the thermal energy and V [m^3] the system volume.

h) [3 pts] What can be concluded about the amplitude of fluctuation modes on large length scales and about whether a smectic actually exhibits true long-range order?

i) [3 pts] Calculate the expectation value of the square of the amplitude of the layer fluctuations, $\langle u^2\rangle = V^{-1}\int d^3\vec{r}\langle u(\vec{r})^2\rangle$ and show that this requires introducing a short- and long-distance cut-off to prevent it from diverging logarithmically.