

Midterm Exam **Soft Condensed Matter Theory**, April 19, 2017, 13:30h-16:30. 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

The Helmholtz free energy $F(N, V, T)$ of some homogeneous classical fluid of N identical spherical particles in a volume V (density $\rho = N/V$) at temperature T is assumed to be given by

$$F(N, V, T) = Nk_B T \left(\log \frac{Nc}{V - Nb} - 1 \right) - \frac{aN^2}{V}, \quad (1)$$

with non-negative constants a , b , and c , which are all independent of ρ , while a and b are also independent of T . Here k_B is the Boltzmann constant.

- (a) Calculate the pressure $p(\rho, T)$ and the chemical potential $\mu(\rho, T)$.
- (b) Calculate c by comparing the low- ρ limit of F (or μ) with that of an ideal gas.
- (c) Give an interpretation of the constants a and b in the case that the system is (i) a Lennard-Jones fluid and (ii) a colloid-polymer mixture (of N colloidal spheres).

We now wish to describe the *same* fluid, but now at a given chemical potential μ and temperature T , in a given external potential $V_{ext}(\mathbf{r})$, i.e. the fluid is no longer assumed to be homogeneous but has, in equilibrium, a spatially varying density profile $\rho_0(\mathbf{r})$. The intrinsic Helmholtz free-energy functional is assumed to be given within the local-density approximation $\mathcal{F}[\rho] = \int d\mathbf{r} f_{hom}(\rho(\mathbf{r}), T)$ with $f_{hom}(\rho, T)$ the Helmholtz free energy per unit volume of the homogenous fluid at density ρ at temperature T .

- (d) Give the variational grand potential functional $\Omega_V[\rho]$ in terms of $\mathcal{F}[\rho]$ and the external potential at the imposed chemical potential.
- (e) Give the Euler-Lagrange equation for $\rho_0(\mathbf{r})$ as explicitly as possible.

Problem 2

Consider a single colloidal sphere of radius a , mass m , position $\mathbf{R}(t)$, and velocity $\mathbf{v}(t)$ in water at room temperature T , with t the time. The particle performs Brownian motion, is in the origin at $t = 0$, and the velocity auto correlation function (vacf) is given by $\langle \mathbf{v}(t) \cdot \mathbf{v}(t') \rangle = A \exp[-\xi|t - t'|]$ with amplitude $A > 0$, friction constant $\xi > 0$, and the square brackets denoting an average over many trajectories.

- (a) Calculate A , e.g. using equipartition of energy.
- (b) Use the Langevin equation to explain in a few words how to derive the vacf.
- (c) Express the mean-squared distance $\langle \mathbf{R}(t)^2 \rangle$ in terms of the vacf and calculate $\langle \mathbf{R}(t)^2 \rangle$ in the ("ballistic") short-time limit $t \ll \xi^{-1}$.
- (d) For $t \gg \xi^{-1}$ we have $\langle \mathbf{R}(t)^2 \rangle = 6Dt$, with $D = k_B T / (6\pi\eta a)$ where $\eta = 10^{-3} \text{Pa}$ s the viscosity. Estimate the time t_D it typically takes to diffuse over a distance a , for $a = 1 \mu\text{m}$.
- (e) Explain in a few words how Jean Perrin could measure Avogadro's number from colloidal diffusion.

Problem 3

Consider a classical fluid composed of N identical particles at positions \mathbf{r}_i for $i = 1, \dots, N$, in a volume V at temperature T . The potential energy is $\Phi = \sum_{i < j}^N \phi(r_{ij})$ with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ with $\phi(r)$ the pair potential. The canonical ensemble average is denoted by $\langle \dots \rangle$, and the pair-distribution function is defined as $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \langle \sum_{i \neq j}^N \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') \rangle$.

- Express the average potential energy $\langle \Phi \rangle$ in terms of (an integral of) $\rho^{(2)}$.
- If the fluid is homogeneous and isotropic with density $\rho = N/V$, give arguments as to why one can then write $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g(r_{12})$ with $g(r)$ the radial distribution function. Rewrite $\langle \Phi \rangle$ in terms of g .
- Sketch $g(r)$ of a Lennard-Jones fluid (diameter σ and well depth ϵ) for $T = \epsilon/k_B$ at (i) $\rho\sigma^3 = 0.001$ and (ii) $\rho\sigma^3 = 1$. Think of units on the axes.
- Describe in a few words and with a few formulas how knowledge of the radial distribution function $g_{HS}(r)$ of a hard-sphere fluid can be used to accurately obtain the free energy of dense Lennard-Jones fluids.

The Ornstein-Zernike equation $h(r) = c(r) + \rho \int d\mathbf{r}' c(r') h(|\mathbf{r} - \mathbf{r}'|)$ relates the total correlation function $h(r) \equiv g(r) - 1$ to the direct correlation function $c(r)$. We define $S(q) = \langle N^{-1} \sum_{i,j}^N \exp[i\mathbf{q} \cdot \mathbf{r}_{ij}] \rangle$ as the structure factor for wave number $q = |\mathbf{q}|$.

- Show for $q \neq 0$ that $S(q) = (1 - \rho \hat{c}(q))^{-1}$ where $\hat{c}(q) = \int dr c(r) \exp[i\mathbf{q} \cdot \mathbf{r}]$ is the Fourier transform of $c(r)$.

Problem 4

Consider a 1:1 electrolyte (dielectric constant ϵ , temperature T , ion charges $\pm e$) in the half-space $z > 0$ in contact with a planar electrode at a given potential ψ_0 at $z = 0$. The ion concentrations are $\rho_{\pm}(z)$ and the bulk ion concentrations are given by $\rho_+(\infty) = \rho_-(\infty) \equiv \rho_s$. In SI units the Poisson equation reads $\psi''(z) = -Q(z)/(\epsilon_0 \epsilon)$ with ϵ_0 the vacuum permittivity and $Q(z)$ the total charge density. We wish to calculate the electric potential $\psi(z)$ within (linearised) Poisson-Boltzmann theory.

- For $z > 0$, write the ion concentrations as Boltzmann distributions, express $Q(z)$ in terms of $\rho_{\pm}(z)$, and combine all this into the Poisson-Boltzmann equation for $\psi(z)$.
- Show for $z > 0$ that a dimensionless, properly scaled and sufficiently small potential satisfies $\phi''(z) = \kappa^2 \phi(z)$. Give the relation between $\psi(z)$ and $\phi(z)$ and derive an expression for κ .
- Solve the equation of (b) for $\phi(z)$ and use the result to give an expression for the surface charge density of the electrode. How small should $|\psi_0|$ be for this result to be accurate?

A mixture of N colloidal spheres at positions \mathbf{R}_i and N_s solvent molecules at positions \mathbf{r}_j has potential energy $\Phi(\{\mathbf{R}\}, \{\mathbf{r}\})$ composed of colloid-colloid, colloid-solvent, and solvent-solvent interactions, and has effective solvent-induced interactions $\Phi_{eff}(\{\mathbf{R}\}; \mu_s, T)$ between the colloidal spheres with μ_s the solvent chemical potential.

- Show how $\Phi_{eff}(\{\mathbf{R}\}; \mu_s, T)$ can be derived from $\Phi(\{\mathbf{R}\}, \{\mathbf{r}\})$.
- Give *two* examples of medium-induced interactions between colloidal spheres, and two techniques to experimentally measure them.