

Midterm Exam **Soft Condensed Matter Theory**, April 12, 2019, 09:00-12:00. This exam consists of 17 items, the maximum score for each item is 6 points. Write your name on each page. This is a *closed-book* exam, and electronic tools are **not** allowed. Give arguments for your answers and write clearly -unreadable answers are no answers. You may use that the viscosity of water is $\eta = 10^{-3}\text{Pa s}$, the Bjerrum length in vacuum at room temperature is 56nm, the Stokes-Einstein equation for the diffusion coefficient of a sphere of radius a reads $D = k_B T / 6\pi\eta a$ with T the temperature and $k_B = 1.38 \cdot 10^{-23}\text{J/K}$ the Boltzmann constant. The differential of the internal energy is $dU = TdS - pdV + \mu dN + \gamma dA + \psi dQ - fdL + \dots$ with the usual meaning of symbols.

Problem 1 Consider a bulk fluid of N identical particles at temperature T and pressure p .

- (a) Show that the combination $G(N, p, T) = U - TS + pV$ is the appropriate thermodynamic potential, and combine the differential of G with extensivity arguments to derive the Gibbs-Duhem equation.

Another one-component fluid, at chemical potential μ and temperature T in a volume V , is in contact with a planar solid substrate of area A . The equilibrium density profile is denoted by $\rho(z)$ with $z > 0$ the distance from the substrate at $z = 0$, with $\rho_b \equiv \rho(z \rightarrow \infty)$ the bulk density. The interfacial tension between the fluid and the substrate is denoted by $\gamma(\mu, T)$, such that the grand potential of the system reads $\Omega(\mu, V, T, A) = -p(\mu, T)V + \gamma(\mu, T)A$.

- (b) Show that $\left(\frac{\partial\gamma}{\partial\mu}\right)_T = -\int_0^\infty dz(\rho(z) - \rho_b)$.

Problem 2 We now consider an aqueous 1:2 electrolyte in the half space $z > 0$ in contact with a solid electrode in the plane $z = 0$ at known potential $\psi_0 > 0$. The solvent is viewed as a dielectric continuum with relative dielectric constant ϵ at room temperature T , such that the Bjerrum length is $\lambda_B = e^2 / (4\pi\epsilon_0\epsilon k_B T)$ with e the elementary charge. The system also contains dissolved monovalent pointlike cations (charge $+e$, density profile $\rho_+(z)$) and divalent pointlike anions (charge $-2e$, density profile $\rho_-(z)$). For $z > 0$ the electrostatic potential $\psi(z)$ satisfies the Poisson equation $e\psi''(z)/k_B T = -4\pi\lambda_B q(z)$ with $eq(z)$ the charge density. Far from the electrode we set the potential to zero and $\rho_+(\infty) = \rho_s$ and $\rho_-(\infty) = \rho_s/2$ with a known concentration ρ_s .

- (a) Write $q(z)$ in terms of $\rho_\pm(z)$, assume $\rho_\pm(z)$ to be given by a Boltzmann distribution, and construct the nonlinear Poisson-Boltzmann (PB) equation for $\psi(z)$. Give appropriate boundary conditions.
- (b) Consider small potentials $0 < \psi_0 \ll 10$ mV, argue that the PB equation can be linearised as $\psi''(z) = \kappa^2\psi(z)$, and give an expression for the Debye length κ^{-1} .
- (c) Solve the (linearised) PB equation using the boundary conditions, and calculate the surface charge density $e\sigma$ of the electrode assuming that $\psi(z \leq 0) = \psi_0$.
- (d) Sketch $\rho_+(z)$ and $\rho_-(z)$ for $0 < z < 4\kappa^{-1}$ for $\psi_0 = 10\text{mV}$ in a single graph that includes a scale on both axes, and give an interpretation of the plot in a few words.
- (e) Give numerical estimates for (i) λ_B , (ii) κ^{-1} , and (iii) the volume (in nm^3) per ion in the bulk, all for the case that $\rho_s = 1$ mM.

Problem 3 Consider a homogeneous and isotropic macroscopic 3D bulk fluid of N identical classical particles (mass m , positions \mathbf{r}_i , momenta \mathbf{p}_i) in a volume V at temperature T . The hamiltonian reads $H = K + \Phi$ with kinetic energy $K = \sum_{i=1}^N \mathbf{p}_i^2/2m$ and potential energy $\Phi = \sum_{i<j}^N \phi(|\mathbf{r}_i - \mathbf{r}_j|)$ with a radially symmetric pair potential $\phi(r)$. The two-body correlation function is defined as $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \langle \sum_{i=1}^N \sum_{j \neq i}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \rangle$ with the angular brackets denoting a thermal average in the canonical ensemble.

- (a) For the case that $\phi(r) \equiv 0$, calculate the canonical partition function, the internal energy $\langle H \rangle$, the pressure, the chemical potential, and the entropy.
- (b) Give arguments why we can write $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho^2 g(|\mathbf{r} - \mathbf{r}'|)$ with $\rho = N/V$ the homogeneous density, and show for arbitrary $\phi(r)$ that $\langle \Phi \rangle = 2\pi V \rho^2 \int_0^\infty r^2 g(r) \phi(r) dr$.
- (c) For the case of a hard-sphere fluid with particle diameter σ and packing fraction $\eta = (\pi/6)\rho\sigma^3$, sketch $g(r)$ for $0 < r < 5\sigma$ for (i) $\eta = 0.01$ and (ii) $\eta = 0.49$, of course with units on both axes. Calculate $\langle \Phi \rangle$ for both cases.

We now assume that the fluid is a square-well fluid with $\phi(r) = \infty$ for $0 < r \leq \sigma$, $\phi(r) = -\epsilon < 0$ for $\sigma < r \leq 2\sigma$, and $\phi(r) = 0$ for $r > 2\sigma$. The Helmholtz free energy of this fluid is denoted by $F(N, V, T)$.

- (d) Calculate the second virial coefficient $B_2(T)$ of this square-well fluid.
- (e) Show that $F(N, V, T) = F_{HS}(N, V, T) + \Delta F(N, V, T)$ with F_{HS} the hard-sphere free energy and $\Delta F = -2\pi\epsilon V \rho^2 \int_\sigma^{2\sigma} dr r^2 \int_0^1 d\lambda g_\lambda(r)$ with $g_\lambda(r)$ the radial distribution function in a square-well system with well-depth $-\lambda\epsilon$.
- (f) Show within first-order perturbation theory that $F/V = F_{HS}/V - a\rho^2$, give an expression for a , and argue on this basis whether or not you expect the homogeneous fluid phase at a density $\rho = 0.4\sigma^{-3}$ to be stable at all T . Give arguments for your answer.

Problem 4 The radius of gyration R_g of a single polymer of $N \gg 1$ beads and contour length Nb in a good solvent satisfies to a good approximation $R_g = bN^{3/5}$. The (osmotic) pressure Π of a solution of M of these polymers in a volume V , so with monomer volume fraction $\phi = MNb^3/V$, can be written as $b^3\Pi/k_B T = (\phi/N)f(\phi/\phi^*)$ with $f(x)$ to be determined.

- (a) Explain in a few words (i) how R_g compares to that of a single ideal polymer and (ii) how R_g gives rise to the monomer overlap volume fraction $\phi^* = N^{-4/5}$.
- (b) Show that $f(x) = 1 + cx$ (with c an order-unity number) in the dilute regime ($x \ll 1$), and give a DeGennes-type scaling argument why $f(x) = x^m$ for $x \gg 1$ in the semi-dilute regime ($\phi^* \ll \phi \ll 1$); determine m and the scaling of Π with ϕ in the latter regime.

Dispersions of colloidal spheres of radius a exhibit Brownian motion.

- (c) Show that the typical time t_D for a colloid to diffuse over a distance of the order of its own size scales, in a dilute dispersion, as $t_D \propto a^3$. Briefly describe two experimental techniques to study this Brownian motion for $a = 1\mu\text{m}$.
- (d) Briefly describe the three ingredients of the DLVO-potential between a pair of colloidal particles in an aqueous NaCl solution, and sketch this potential for a salt concentration of (i) 1 mM and (ii) 1 M.

THE END