Midterm Exam Soft Condensed Matter Theory, April 11, 2018, 13:30h-16:30. This exam consists of 18 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. Give arguments for your answers and write clearly -unreadable answers are no anwers. You may use that the viscosity of water is $\eta = 10^{-3}$ Pa s, the Bjerrum length of water at room temperature is 0.72nm, 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 $k_B = 1.38 \cdot 10^{-23}$ J/K the Boltzmann constant. The differential of the internal energy is $dU = TdS - pdV + \mu dN + \gamma dA + \psi dQ - fdL + \cdots$ with the usual meaning of symbols.

Problem 1

Consider a one-component system in a volume V at temperature T and chemical potential μ. The number of particles in this system, N, fluctuates according to the probability distribution $W(N) = \Xi^{-1}(\mu, V, T) \exp[(\mu N - F(N, V, T))/k_B T]$ where $F(N, V, T)$ is the Helmholtz free energy of the N-particle system and $\Xi(\mu, V, T)$ the grand-canonical partition function.

(a) Show that the average number of particles, $\langle N \rangle$, is equal to $k_B T (\partial \ln \Xi(\mu, V, T)/\partial \mu)_{V,T}$.

(b) Show first that $k_B T (\partial \langle N \rangle / \partial \mu)_{V,T} = \langle N^2 \rangle - \langle N \rangle^2$, and use then e.g. the Gibbs-Duhem equation to derive that $k_B T (\partial \rho / \partial p)_T = (\langle N^2 \rangle - \langle N \rangle^2)/\langle N \rangle$, with p the pressure.

Consider now the case of a homogeneous bulk fluid of colloidal hard spheres with a diameter σ at density ρ and temperature T, with the Carnahan-Starling excess (over ideal) free energy $F_{exc} = N k_B T (4\eta - 3\eta^2)/(1 - \eta)^2$ with η the packing fraction.

(c) Give an expression for η in terms of the given variables and calculate the hard-sphere pressure p within the Carnahan-Starling approximation.

(d) Calculate the second-virial coefficient $B_2(T)$ of hard spheres and check whether or not your result of (c) is consistent with $B_2(T)$.

(e) Sketch the radial distribution function $g(r)$ of these hard spheres for (i) $\eta = 0.01$ and (ii) $\eta = 0.49$. Think of units/scales on both axes and distinguish the two graphs clearly.

(f) Derive and/or explain how the hard-sphere free energy $F_{HS}(N, V, T)$ and the hard-sphere radial distribution function $g(r; \eta)$ can be used to accurately calculate the free energy of dense Lennard-Jones fluids.

(g) What happens to a colloidal hard-sphere system if $\eta > 0.5$? Briefly describe two experimental techniques with which this can be observed.

(h) An experimentalist tracks many trajectories of a single colloidal sphere in a dilute hard-sphere suspension, and finds the displacements in the cartesian x-direction after time t to be distributed as a Gaussian $\propto \exp(-\alpha x^2/t)$ with $\alpha = 10$ s/μm^2. Estimate the diameter of these hard spheres if the medium is water at room temperature.

Problem 2

The Helmholtz free energy $F(N, V, T)$ of N Argon atoms of mass $m = 6.6 \cdot 10^{-26}$ kg in a volume V (density $\rho = N/V$) at temperature T is assumed to be given by

$$F(N, V, T) = N k_B T \left(\log \frac{N\Lambda^3}{V - Nb} - 1 \right) - \frac{aN^2}{V}, \tag{1}$$

with constants $a > 0$ and $b > 0$, and Λ the thermal Debroglie wavelength. Here k_B is the Boltzmann constant.

(a) Give a physical interpretation of a and b, and give their dimensionality.

(b) Derive an expression for Λ and explain whether $b \gg \Lambda^3$ or $b \ll \Lambda^3$ at $T = 300\text{K}$.

(c) Schetch the free energy density F/V as a function of $\rho \in [0, 1/b]$ for (i) $T > T_c \equiv 8a/27bk_B$ and (ii) $T < T_c$, and graphically construct the coexisting gas- and liquid density ρ_g and ρ_l, respectively. Explain your construction briefly.

We now consider an interface between the coexisting bulk gas phase (with density ρ_g) and bulk liquid phase (with density ρ_l). The interface height at horizontal position (x, y) is denoted by the height $z = h(x, y)$, with a gravitational force mg acting on every Argon atom in the downward vertical z-direction. The interfacial tension is known and denoted by γ, and the average height can be set to zero without loss of generality.

(d) Present a derivation, or give and explain the ingredients, of the capillary wave Hamiltonian $H_{cw} = \frac{\gamma}{2} \int dx dy [(\partial h(x,y)/\partial x)^2 + (\partial h(x,y)/\partial y)^2 + \ell^{-2} h^2(x, y)]$ for this interface. Derive an expression for the capillary length ℓ.

(e) Estimate (with arguments), or calculate, for the case of a typical air-liquid or oil-water interface at room temperature, the order of magnitude of (i) the tension γ and (ii) the capillary length ℓ. Also give the order of magnitude of (iii) the interface thickness $\sqrt{\langle \overline{h^2} \rangle}$ with $\overline{h^2}$ the lateral average of h^2 and $\langle .. \rangle$ the thermal average.

Problem 3

Consider a 1:1 electrolyte (dielectric constant ϵ, temperature T, ion point charges $\pm e$) in the space between two parallel planar electrodes with equal surface potential ψ_s at separation H. The cartesian coordinate normal to the electrodes is $z \in [-H/2, H/2]$, i.e. $z = 0$ is the symmetry midplane of the system. The electrolyte is in osmotic equilibrium with a bulk 1:1 electrolyte with total ion concentration $2\rho_s$ at zero potential. We wish to calculate the electric potential $\psi(z)$ and the ionic concentration profiles $\rho_\pm(z)$ within (linearised) Poisson-Boltzmann theory, for $z \in [-H/2, H/2]$. In SI units the Poisson equation reads $\psi''(z) = -Q_e(z)/(\epsilon_0 \epsilon)$ with ϵ_0 the vacuum permittivity and $Q_e(z)$ the total charge density.

(a) For $z \in (-H/2, H/2)$, write the ion concentrations as Boltzmann distributions, express $Q_e(z)$ in terms of $\rho_\pm(z)$, and combine all this into the Poisson-Boltzmann equation for $\psi(z)$.

(b) Show for $z \in (-H/2, H/2)$ 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.

(c) Solve, using the boundary conditions, the equation of (b) for $\phi(z)$ and calculate the surface charge density of the electrodes.

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.

(d) Express $\Phi_{eff}(\{\mathbf{R}\}; \mu_s, T)$, with motivation, in terms of $\Phi(\{\mathbf{R}\}, \{\mathbf{r}\})$.

(e) Give *two* examples of medium-induced interactions between colloidal spheres.

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