Final Exam Advanced Statistical Physics: NS-370B, Nov. 4, 2014, 13:30-16.30. The exam consists of 4 exercises, each worth 25 points. This is a closed-book exam, i.e. notes and electronic devices are not allowed. Please start every exercise on a new sheet of paper, with your name clearly written on every page. The exam can be written in either English or Dutch, but unreadable work will not be graded!

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

- The canonical partition function of a classical thermodynamic system of N identical particles in a volume V a temperature T with Hamiltonian $H(\Gamma)$ is written as $Z(N,V,T) = 1/(N!h^{3N}) \int d\Gamma \exp[-\beta H(\Gamma)]$, where $\beta^{-1} = k_B T$.
- The grand partition function of identical particles is $\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \exp(\beta\mu N) Z(N,V,T)$, and the grand-canonical distribution is $f_g(\Gamma, N) = \exp[\beta\mu N - \beta H(\Gamma)]/[N!h^{3N}\Xi(\mu,V,T)]$, with μ the chemical potential.
- The second virial coefficient is $B_2(T) = (1/2)\int d\mathbf{r}[1-\exp(-\beta\phi(r))]$ for pair potential $\phi(r)$.
- The two-body distribution function reads
$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{Q_N(V,T)} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \exp[-\beta\Phi(\mathbf{r}_1, \cdots, \mathbf{r}_N)] \tag{1}$$
with $Q_N(V,T) = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp[-\beta\Phi(\mathbf{r}_1, \cdots, \mathbf{r}_N)]$ the configurational integral.
- $k_B = 1.13 \times 10^{-23}$J/K, $e = 1.6 \times 10^{-19}$C, and $R = 8.31$J/K/mol.
- The binomial coefficient (i.e. m choose n, which is the number of ways n object can be choosen from m objects) is given by $\left(\frac{m!}{(m-n)!n!}\right)$.
- Stirling's approximation to order $O(N)$ is given by $\log(N!) = N\log N - N$.
- The Taylor series of $f(x)$ around $x = a$ is given by $f(x) = f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f^{(3)}(a)}{3!}(x-a)^3 + \cdots$.
- From the Taylor series we get: $e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$
- The following critical exponents for the Ising model:
  - β is associated with the *spontaneous magnetization.*
  - α is associated with the *specific heat* when the external field is zero
  - γ is associated with the *zero field susceptibility*
  - δ is associated with the *magnetization at the critical temperature*
- In a dielectric medium with relative dielectric constant ϵ the electrostatic potential $\psi(\mathbf{r})$ and the charge density $eQ(\mathbf{r})$ are related by the Poisson equation
$$\nabla^2\psi(\mathbf{r}) = -\frac{4\pi e Q(\mathbf{r})}{(4\pi\epsilon_0)\epsilon}, \tag{2}$$
where ϵ_0 is the vacuum permittivity (in SI units).

1. We consider a classical binary mixture of N_1 particles of species 1 and N_2 particles of species 2 in a volume V at temperature T. The particles are point particles with mass m_1 and m_2, respectively, and they interact with each other through pairwise potentials $\phi_{11}(r)$, $\phi_{12}(r)$, and $\phi_{22}(r)$, where r is the center-to-center seperation between a 1-1-pair, a 1-2 pair, and a 2-2 pair, respectively. The densities are denoted by $\rho_i = N_i/V$ for species $i = 1, 2$.

   (a) Give, as explicitly as possible, an expression for the canonical partition function $Z(N_1, N_2, V, T)$.

   (b) Calculate the Helmholtz free energy $F(N_1, N_2, V, T)$ and the pressure $p(\rho_1, \rho_2, T)$ for the ideal-gas case $\phi_{ij}(r) \equiv 0$.

   (c) If the particles are hard spheres with diameters σ_1 and σ_2, calculate the pressure p within the second-virial approximation.

   A computer simulator calculates the Gibbs free energy G of this mixture for many compositions $x = N_1/(N_1 + N_2)$ and for many pressures p at one fixed T. He/she finds that $G(N_1, N_2, p, T) = (N_1+N_2)k_BT\left(x\ln x + (1-x)\ln(1-x) - \frac{1}{2}cx^2\right)$, where c is independent of x but depends on p as $c(p) = (-1 + p/p_0)$ with $p_0 = 1$ atm.

   (d) Calculate the critical pressure p_c and the critical composition x_c, and sketch the spinodal and the binodal of the phase diagram in the composition-pressure (x-p) representation with $x \in [0, 1]$ and $p \in [0, 10]$ atm.

   (e) Give the functional form of the binodal $p(x)$ in the vicinity of the critical point in terms of p_c, x_c and a suitable critical exponent, and briefly describe the equilibrium state of the system for $x = x_c$ at (i) $p < 0.9p_c$ and (ii) $p > 1.1p_c$.

2. We consider a homogeneous fluid of $N = \rho V$ identical particles at positions $\mathbf{r}_i$ in a volume V at temperature T. The potential energy $\Phi(\mathbf{r}^N) = \sum_{i<j}^{N}\phi(|\mathbf{r}_i - \mathbf{r}_j|)$ is pairwise. Because of translational invariance the two-body distribution can be written as $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g(|\mathbf{r}_1 - \mathbf{r}_2|)$.

   (a) Show that the thermal avarage of the potential energy can be written as $\langle\Phi\rangle = 2\pi\rho^2 V\int_0^\infty dr r^2 g(r)\phi(r)$.

   (b) Show that the structure factor, defined as $S(q) = \overset{1/N}{\vee}\langle\sum_{i,j}^{N}\exp[i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_j)]\rangle$ with $\mathbf{q}$ the scattering vector and $q = |\mathbf{q}|$ its wavenumber, can be written as $S(q) = 1 + \rho\int d\mathbf{r}(g(r) - 1)\exp(i\mathbf{q}\cdot\mathbf{r}) + (2\pi)^3\rho\delta(\mathbf{q})$.

   (c) Define the total correlation function $h(r) = g(r) - 1$. Use the Ornstein-Zernike equation $h(r_{12}) = c(r_{12}) + \rho\int d\mathbf{r}_3 c(r_{13})h(r_{32})$ to show that $S(q) = (1 - \rho\hat{c}(q))^{-1}$ for $q \neq 0$.

   (d) For the case of a Lennard-Jones fluid (diameter σ, well-depth ϵ), sketch in five separate plots (i) the phase diagram in the ρ-T representation, (ii) the $g(r)$ in the dilute limit $\rho \to 0$ at the critical temperature, (iii) the $g(r)$ at packing fraction 0.49 in the high-T limit, (iv) the $S(q)$ close to the critical point, and (v) the $S(q)$ at the triple-point liquid. Label the sketches carefully (i)-(v), and put (estimated) scales on the axes of all five sketches.

   (e) If the Helmholtz free energy per unit volume is given by $f(\rho, T) = \rho k_B T(-1 + \ln\frac{\rho b}{1-b\rho}) - a\rho^2$, with positive constants a and b, calculate the pressure $p(\rho, T)$.

3. Consider a simple model for a surface of area $A = Ma^2$ which consists of M adsorption sites which are arranged on a square lattice with spacing a. Assume that the surface is in contact with a gas reservoir at temperature T and chemical potential μ. The molecules of the gas are indistinguishable and can be adsorbed onto one of the lattice sites, but each lattice site can only adsorb a single molecule at most. Further assume that an occupied site has binding energy ϵ. Note that for a two-dimensional system (such as an adsorbed layer) the area A and surface pressure Π play the same role as the volume V and pressure P in a three-dimensional system.

   (a) Assume that there are exactly N molecules adsorbed onto the surface and calculate the canonical partition function of the adsorbed gas.

   (b) Compute the grand partition function $\Xi(\mu, A, T)$ of the adsorbed gas and express Π as a function of μ, A, T.

   (c) Calculate $\langle N \rangle$ and determine the average fraction of sites f that are occupied.

   (d) Use the quantities you just derived to calculate the equation of state $\Pi(f, T)$. What is the surface pressure in the limit of low coverage. Is this what you would expect? Explain.

4. Consider a homogeneous surface in the plane $z = 0$ in contact with the halfspace $z > 0$ filled with a liquid electrolyte of relative dielectric constant ϵ at temperature T containing pointlike *divalent* salt ions (with charges $+2e$ and $-2e$); the Bjerrum length is $\lambda_B = e^2[(4\pi\epsilon_0)\epsilon k_B T]^{-1}$. Far from the wall ($z \to \infty$), where the electric potential is set to zero, the ion concentration is ρ_s for both the cations and the anions. The local concentration $\rho_+(z)$ of the cations and $\rho_-(z)$ of the anions are related to the electric potential $k_B T\phi(z)/e$ by the Poisson equation $\phi''(z) = -4\pi\lambda_B(\rho_+(z) - \rho_-(z) + \sigma\delta(z))$, where $e\sigma$ is the surface charge density on the wall and where a prime denotes a z-derivative.

   (a) Assume properly scaled Boltzmann distributions for $\rho_\pm(z)$ and derive a (non-linear) differential equation for $\phi(z)$ and boundary conditions $\phi(\infty) = 0$ and $\phi'(0^+) = -4\pi\lambda_B\sigma$.

   (b) Show that $\phi''(z) = \kappa^2\phi(z)$ for low potentials and derive an expression for κ^2.

   (c) Solve the equation of (b) with the boundary conditions mentioned in (a), and interpret the result in a few words.

   We consider N needle-shaped particles of length L and diameter $D \ll L$ that perform Brownian motion in a liquid of volume V. Initially at time $t = 0$ the volume V is so large that $V \gg NL^2D$, but due to an evoporation process the volume V very slowly shrinks to become of the order NL^2D at time $t = \tau_1$ and of order NLD^2 at an even later time τ_2, while T, N, L and D stay fixed.

   (d) Give or calculate the order of magnitude of the excluded volume $E_\parallel$ of a parallel pair of these rods and $E_\perp$ of a perpendicular pair.

   (e) Briefly describe the state of this suspension at times $t = 0$, $t = \tau_1$, and $t = \tau_2$. Provide arguments.

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