Final Exam for Advanced Statistical Physics: NS-370B 07-11-17

This exam consists of 4 questions. Total points possible: 87.
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.
Exam can be written in either English or Dutch. Please write clearly!

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.
- $k_B = 1.13 \times 10^{-23}$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 objects can be chosen from m objects) is given by $\left(\frac{m!}{(m-n)!n!}\right)$.
- Stirling's approximation to order $O(N)$ is given by $\log(N!) = N\log N - N$.
- Gaussian Integral: $\int_{-\infty}^{\infty} dx\, e^{-x^2} = \sqrt{\pi}$
- 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 second virial coefficient for a system of spherically symmetric particles is given by $B_2(T) = -\frac{1}{2}\int d\mathbf{r} f(r)$, where $f(r) = \exp[-\beta\phi(r)] - 1$ is the so-called Mayer function.
- 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*

1. (Points: 26)
Consider a gas of N Argon atoms, in a volume V. Assume that the volume V is fully closed so that this system cannot exchange energy with its environment, and hence is at energy U.

   (a) Write down the first law of thermodynamics. Make sure to identify which differentials involved are exact and which are inexact. Explain the difference between an exact and an inexact differential.

   (b) Write down the second law of thermodynamics.

   (c) Assuming that the only types of work that can act on the system are mechanical and chemical work, write down an expression for dU that follows from the first and second laws. Make sure to list any assumptions that are required in writing down this expression.

   If we now connect this system to heat and particle baths, such that the energy and number of particles are no longer constant, we arrive at a system with constant chemical potential μ, volume V, and temperature T.

   → (d) One important relation in this ensemble is that $\Omega(\mu, T, V) = -p(\mu, T)V$, where p is the pressure. Derive this important result. Fugacity ?

   (e) Assume that the system is at an extremely low density such that we can accurately approximate its behaviour by that of an ideal gas. i) Determine the grand canonical partition function for this system (i.e. of an ideal gas). ii) Determine the associated grand potential. iii) Calculate the average density in terms of the chemical potential and temperature.

   Consider a system of blocks on a square lattice. Assume that each block is occupied with a probability p and that there are no interactions between the blocks. Here we will use renormalization group theory to predict the percolation threshold. Consider subblocks of size 3x3. Consider a mapping where the system percolates only when a majority of the subblocks are filled (i.e. 5 of the 9).

   (f) Determine the renormalization transformation $R(p)$. Describe how one would use $R(p)$ to determine the percolation threshold.

2. (Points: 25)
Consider a spin system on a square lattice (consisting of N spins), where each site in the system can either be in state +1 or -1. Assume that there are both nearest neighbour and next nearest neighbour interactions in the system. Let the nearest neighbour coupling be J_1 and the next nearest neighbour coupling be J_2, and assume $J_1 > 0$ and $J_2 > 0$. The Hamiltonian for this system is given by

$$\mathcal{H} = -\frac{J_1}{2}\sum_i \sum_j{}' S_i S_j - \frac{J_2}{2}\sum_i \sum_j{}'' S_i S_j \tag{1}$$

   where $\sum_j{}'$ indicates a sum over nearest neighbours, and $\sum_j{}''$ a sum over next nearest neighbours.

   → (a) Determine the Hamiltonian up to linear order in the fluctuations (i.e. develop a mean field Hamiltonian by ignoring correlations between fluctuations).

(b) Using this mean field Hamiltonian, one can determine a self-consistent expression for the magnetization that has the form:

$$m = \tanh(\alpha m),$$

where $\alpha = 4\beta(J_1 + J_2)$. **Do not try and derive this expression.** i) Use a graphical method to show how you could determine values of m that satisfy this expression. (Note that you do not need an exact solution for m.) Describe the
7 dependence of the solutions on α. ii) For some choices of α, one finds multiple solutions. Describe how can one could determine which value of α corresponds to the "equilibrium" phase?

(c) The Landau free energy (to order m^4) for this system has the form

$$F(m,T) = b(T)m^2 + dm^4 \tag{2}$$

7 where d is a positive constant. i) What type of phase transition does this free energy correspond to? Explain. ii) Sketch the equilibrium value of m as a function of T. Make sure to clearly label the axes.

(d) When an external field is added, the Landau free energy can be written

$$F(m,t) = -hm + b(t)m^2 + dm^4. \tag{3}$$

where we have defined $t = \frac{T - T_C}{T_C}$. For simplicity we make the further approximation that $b(t) = b't$. Determine the critical exponents β, γ and δ associated with this Landau free energy.

(e) What happens to the correlation length as one approaches the critical temperature?

3. (Points: 18)
Liquid crystalline phases appear when we start to consider particles that are not spherically symmetry, but rather significantly flattened or elongated in a direction. Consider a dispersion of rectangular, rod-shaped particles of dimensions $L \times D \times D$. Assume that the rods interact via a hard-core repulsion. Make the further approximation that the number of possible orientations of each rod is three, such that the main axes of the rods can only point in the direction of a laboratory frame $\hat{x}_\alpha$, $\alpha = 1, 2, 3$. A particle with orientation α has its long axis along $\hat{x}_\alpha$. The Helmholtz free energy F of $N = \rho V$ of such rods in a volume V at temperature T is given, within the second virial approximation, by

$$\frac{F}{VkT} = \sum_{\alpha=1}^{3} \rho_\alpha \left(\ln \rho_\alpha \mathcal{V} - 1 \right) + \sum_{\alpha=1}^{3} \sum_{\alpha'=1}^{3} B_{\alpha\alpha'} \rho_\alpha \rho_{\alpha'},$$

with ρ_α the density of particles with orientation α, and $\mathcal{V}$ the (irrelevant) thermal volume.

(a) At very low densities, this systems forms a so-called "isotropic" phase. Sketch an isotropic phase (within the above approximation) and explain the important characteristics of such a phase.

(b) As the density increases, one expects this system to exhibit a first order phase transition from the isotropic phase to a nematic phase. (You do not have to calculate this transition.) Define the two densities associated with this first order phase transition to be ρ_1 and ρ_2, with $\rho_1 < \rho_2$. The stable phase for densities just higher than ρ_2 is the nematic phase. Sketch this phase and explain the important characteristics of such a phase.

(c) Argue that $B_{\alpha\alpha'}$ is a symmetric 3×3 matrix.

(d) Calculate the second virial coefficients $B_{11} = B_{22} = B_{33} \equiv B_{\parallel}$ and $B_{12} = B_{13} = B_{23} \equiv B_{\perp}$ for pairs of parallel and perpendicular rods, respectively.

Now consider adding polymers to this system. Assume that the polymer-polymer interaction is ideal (i.e. $\Phi_{pp} = 0$), and that the colloid-polymer interaction is hard, where the polymers have a diameter σ_p.

(e) Do the polymers induce an effective attraction or a repulsion between two rods? Explain.

(f) Is this effect stronger or weaker at increasing polymer density? Explain.

(g) Do you expect the interaction strength to depend on the orientation of the particles? Explain.

4. (Points: 18)
Consider a system of N identical hard spheres (diameter σ) with positions $\mathbf{r}_i$ in a volume V at temperature T.

? (a) Can this system undergo a gas-liquid phase transition? Explain why or why not.

Now, assume that this system is in an isotropic and homogeneous fluid phase. The structure factor of this fluid is defined as $S(q) = \langle N^{-1} \sum_{i,j}^{N} \exp[i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \rangle$ with $\mathbf{q}$ the scattering vector and $q = |\mathbf{q}|$ the wavenumber. The density is denoted by $\rho = N/V$ and the packing fraction by $\eta = (\pi/6)\rho\sigma^3$.

(b) Show that $S(q) = 1 + \rho \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} g(r)$ with $g(r)$ the radial distribution function.

? → (c) For $\sigma = 500$nm, sketch $g(r)$ (ensure that the axes are labeled and appropriately scaled) for (i) $\eta = 0.01$ and (ii) $\eta = 0.49$. Briefly motivate your sketches.

Hard spheres are a useful reference system for thermodynamic perturbation theories. As a first step in developing a thermodynamic perturbation theory, one generally defines a so-called "auxiliary" Hamiltonian, where the interaction part of the "real" Hamiltonian is decomposed into a reference part Φ_0 and a perturbation Φ_1. Specifically,

$$H_\lambda(\Gamma) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \Phi_0(\mathbf{r}^N) + \lambda\Phi_1(\mathbf{r}^N) \equiv H_0(\Gamma) + \lambda\Phi_1(\mathbf{r}^N), \tag{4}$$

where H_0 is the *reference Hamiltonian*, and $\lambda \in [0,1]$ a *coupling constant* that switches H_λ from the reference Hamiltonian at $\lambda = 0$ to the Hamiltonian of interest at $\lambda = 1$.

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(d) Show that the Helmholtz free energy of the "real" system can be written

$$F(N,V,T) = F_0(N,V,T) + \int_0^1 d\lambda \langle \Phi_1 \rangle_\lambda, \tag{5}$$

with F_0 the free energy of the reference system. (Note that this expressions is exact - there are no approximations here).

(e) Thermodynamic perturbation theory is based on a λ-expansion of the integrand of Eq.(5) around $\lambda = 0$. Show that

$$\langle \Phi_1 \rangle_\lambda = \frac{\langle \Phi_1 \rangle_0 - \lambda\beta \langle \Phi_1^2 \rangle_0 + \frac{1}{2}\lambda^2\beta^2 \langle \Phi_1^3 \rangle_0 + \cdots}{1 - \lambda\beta \langle \Phi_1 \rangle_0 + \frac{1}{2}\lambda^2\beta^2 \langle \Phi_1^2 \rangle_0 + \cdots} \tag{6}$$

where $\langle \cdot \rangle_0$ is a canonical average over the ensemble of the reference system.

END OF EXAM