Final Exam for Advanced Statistical Physics: NS-370B

This exam consists of 5 questions. Total points possible: 75.
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: $e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$

1. (15 points) Consider a system consisting of a gas with N particles in a volume V at temperature T (note that the system is not on a lattice). Assume that the particles do not interact with each other.

   (a) What is the canonical partition function for the system?

   (b) What is the Helmholtz free energy?

   Now assume that each particle has a spin, which can rotate freely in three dimensions. Moreover, assume that the gas of particles is located in an external electric field $\mathbf{E} = E\hat{\mathbf{z}}$. The particles interact with the field via their spin, such that for each particle, the potential energy is given by:

   $$U_i = \epsilon \cos\theta_i, \tag{1}$$

   where θ_i is the angle between the spin of the particle and the z-axis. Note that the particles still do not interact with each other.

   (c) What is the partition function for this system?

   (d) What is the corresponding Helmholtz free energy?

   (e) What is the average alignment $\langle\cos\theta\rangle$ as a function of ϵ.

   (f) Is there a phase transition in this system? Explain.

2. (15 points) Consider a system of N argon atoms in a volume V at temperature T. The interaction potential for this system is well described by the Lennard Jones potential.

   (a) Write down an expression for the Lennard Jones potential. Make sure to clearly indicate what all the variables represent, and give a motivation for all terms.

   (b) Sketch the Lennard Jones potential. Make sure to clearly label the axes and any other important features.

   (c) Sketch the phase diagram for the Lennard Jones systems in the density (ρ) versus temperature (T) representation. Sketch the phase diagram in the temperature (T) versus pressure (p) representation. Make sure to clearly label the axes and all special points on the phase diagram. Clearly identify the phases and coexistence regions.

   Consider a different system which consists of N spherical colloids of diameter σ in a volume V at temperature T. A simple model that describes the behaviour of colloidal systems is the hard sphere potential.

   (d) Does the hard sphere potential undergo a gas-liquid phase transition? Explain why or why not?

   Now, assume that polymers at chemical potential μ_p have been added to the colloidal system. Assume that the polymer diameter is given by σ_p.

   (e) Sketch the "effective" interaction between the colloidal particles arising due to the polymers. Make sure to clearly label the axes and any other important features.

3. (15 points)

   (a) Consider nucleation of a liquid (with density ρ) from a gas. i) First, using classical nucleation theory, write down an expression for the free energy barrier for a spherical nucleus in terms of the chemical potential difference between the liquid and the gas $\Delta\mu$ and the gas-liquid surface tension γ_{gl}. ii) Next, write down an expression for a nucleation barrier for a hemispherical (half a sphere) droplet where the rounded part of the hemisphere is in contact with the gas (i.e. has a surface tension γ_{gl} while the flat part is in contact with a wall and has a surface tension γ_{lw}). The surface tension between the gas and the wall is γ_{gw}.

(b) In this problem we examine percolation on a triangular lattice. Let p be the probability that a site is occupied. i) What are the four spanning configurations for the smallest possible cell on a triangular lattice? (They should span both left-right and up-down). ii) Write down the recursion relation $p' = R(p)$. iii) Find any non-trivial fixed points. Explain what the presence of a non-trivial fixed point means.

4. (10 points)

(a) Consider a system of N particles in a volume V at temperature T. Assume that the interaction between the particles is well described by a square well with well depth ϵ. Note that the square well potential can simply be written as a perturbation on top of a hard sphere potential. We define an auxiliary Hamiltonian for this system as

$$H_\lambda(\gamma) = \sum_{i=1}^{N} \frac{\mathbf{p}_i}{2m} + \Phi_0\left(\mathbf{r}^N\right) + \lambda\Phi_1\left(\mathbf{r}^N\right) \tag{2}$$

where Φ_0 is the contribution from the hard-sphere potential, and Φ_1 the contribution to the potential from the pair-wise interaction given by

$$\phi_1(r) = \begin{cases} 0 & r < \sigma \\ -\epsilon & \sigma < r < \gamma\sigma \\ 0 & r > \gamma\sigma \end{cases}, \tag{3}$$

where γ is a measure for the range of the attractive well and must be greater than 1. Show that the free energy of the square well system can be written

$$F(N,V,T) = F_{HS}(N,V,T) + \int_0^1 d\lambda \left\langle \Phi_1 \right\rangle_\lambda \tag{4}$$

where F_{HS} is the free energy of the hard sphere system, and $\langle A \rangle_\lambda$ denotes the canonical ensemble average of A associated with the Hamiltonian H_λ.

(b) Consider a system consisting of N particles in a volume V at temperature T. Assume that the Hamiltonian for the system is given by

$$\mathcal{H}(\Gamma) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j}^{N} \phi(r_{ij}), \tag{5}$$

with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ the radial distance between particle i and j. Note that we have assumed that the interactions are radially symmetric. Define the partition function

$$Z(N,V,T) = Q(N,V,T)/N!\Lambda^{3N},$$

with

$$Q(N,V,T) = \int_V d\mathbf{r}^N \exp[-\sum_{i<j}^{N} \phi(r_{ij})/kT].$$

(i) Show that $\beta p = (\partial \ln Q/\partial V)_{N,T}$.

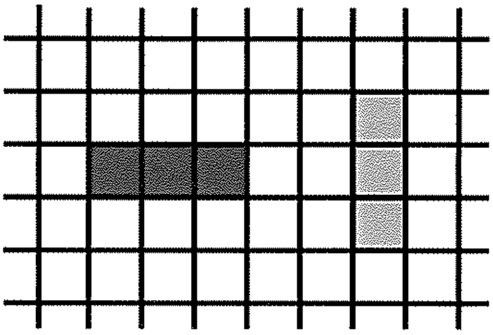

Figure 1: An A-particle (left) and a B-particle (right), with $L = 3$.

(ii) It can be shown that the volume derivative gives rise to

$$\beta p = N/V - \frac{1}{6kTV}\int_V d\mathbf{r}_1 d\mathbf{r}_2 r_{12}\phi'(r_{12})\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2),$$

where $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is the pair distribution function. Show that in the case where we have a homogeneous and isotropic system, this expression reduces to

$$p = \rho k_B T - \frac{\rho^2}{6}\int d\mathbf{r} r\phi'(r)g(r),$$

where $g(r)$ is the radial distribution function.

5. (20 points) In this problem, we consider a system of particles on a square lattice. Each particle covers L lattice sites, arranged in a line. There are two species of particles A and B, oriented horizontally and vertically, respectively (see Figure). Note that all A particles are identical and all B particles are identical. Whenever two particles overlap, they have an interaction energy of $\epsilon > 0$. Particles that do not overlap have an interaction energy of 0. Note that each particle can interact with multiple other particles, even at the same lattice site. Assume there are N_A particles of species A and N_B particles of species B, in a volume V at temperature T, so that the number density of the two species are $\rho_A = N_A/V$ and $\rho_B = N_B/V$. Additionally, assume periodic boundary conditions.

(a) (i) Assuming that all particles are homogeneously spread over the system (i.e. within a mean field approximation), argue that the average potential energy of an A particle due to its interaction with other A particles is given by

$$U_{AA} = (2L - 1)\rho_A\epsilon$$

(ii) Assuming that the B particles are also homogeneously spread over the system (i.e. within a mean field approximation), argue that the average potential energy of a B particle due to its interaction with other B particles is given by

$$U_{BB} = (2L - 1)\rho_B\epsilon$$

(iii) Within the mean field approximation, i.e. where we assume that the particles of both species are homogeneously spread over the system, argue that the average potential energy of an A particle due to its interaction with the B particles is given by

$$U_{AB} = L^2 \rho_B \epsilon$$

(b) Using your results from parts (a), show that the energy of this system within the mean field approximation is given by

$$U = \frac{1}{2} L^2 \epsilon \left(N_A \rho_B + N_B \rho_A \right) + L\epsilon \left(N_A \rho_A + N_B \rho_B \right) - \epsilon \frac{(N_A \rho_A + N_B \rho_B)}{2} \tag{6}$$

(c) Calculate the Helmholtz free energy $F(N_A, N_B, V, T)$ associated with the mean field theory outlined in a). Make the substitution that $x = N_A/N$ to obtain the free energy as a function of $F(x, N, V, T)$. Show that this free energy is given by

$$\begin{aligned} \frac{\beta F(x,N,V,T)}{N} &= \ln(\rho) - 1 + (1-x)\ln(1-x) + x \ln x \\ &\quad + \beta\rho\epsilon \left(L^2(1-x)x + L\left(2x^2 - 2x + 1\right) - x^2 + x - \frac{1}{2} \right) \end{aligned} \tag{7}$$

where $x = N_A/N$, and $\rho = N/V$, with $N = N_A + N_B$.

(d) Assume now that the particles can freely change identity between species A and B, at no additional free energy cost. Argue that in this case, in equilibrium

$$\frac{\partial F(x,N,V,T)}{\partial x} = 0. \tag{8}$$

Show that $x = 1/2$ is always an extremum of the free energy. What does the system look like when $x = 1/2$? Is this an ordered phase or a disordered phase? Explain.

(e) If we substitute $m = x - 1/2$ into the Helmholtz free energy, and expand around $m = 0$ we obtain a Landau free energy

$$\frac{\beta F}{N} = C + \left(-\beta\rho\epsilon - \beta L^2 \rho\epsilon + 2\beta L\rho\epsilon + 2 \right) m^2 + \frac{4m^4}{3} + \frac{32m^6}{15} + O\left(m^7\right) \tag{9}$$

where C is a constant. Using this Landau free energy, at what temperature does a phase transition occur in this system? What type of phase transition is it (continuous or discontinuous)? Explain. Describe what the "disordered" and "ordered" phases look like in this system.