Final Exam for Advanced Statistical Physics: NS-370B

Date: November 6, 2018

Time : 13:30 - 16:30

This exam consists of 5 questions. Total points possible: 65.
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 must be written in pen.
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.
- $k_B = 1.13 \times 10^{-23}\mathrm{J/K}$, $e = 1.6 \times 10^{-19}\mathrm{C}$, and $R = 8.31\mathrm{J/K/mol}$.
- 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. (16 points)
Consider a system of N Argon atoms in a volume V at temperature T. Now, assume we bring this gas into into contact with a two dimensional surface. Assume that on this surface there are M lattice sites, arranged on a triangular lattice, which can adsorb molecules from the gas with a binding energy $-\epsilon$.

   If we focus on the behaviour of the surface, we can treat the Argon gas as a reservoir of particles for the surface. Assume that the chemical potential of this reservoir is μ.

   (a) Assume that the particles on the surface do not interact at all, i.e. multiple particles can share a lattice site at no cost.

   i) What is the canonical partition function for this surface assuming that exactly N_a particles are adsorbed onto the surface?

   ii) Show that the corresponding Helmholtz free energy is given by:

$$F(N_a, M, T) = k_B T N_a (\log \rho_a - \beta\epsilon - 1)\,, \tag{1}$$

   where $\rho_a = N_a/M$.

   iii) What is the grand canonical partition function for the 2d surface?

   iv) What is the free energy associated with this grand canonical partition function?

   v) Determine $\langle N_a \rangle / M$.

   (b) Now let us model the repulsion between the molecules on the surface using a very simple approximation. Specifically, assume that two particles cannot be on the same lattice site, but that particles on different lattice sites do not interact at all. Hence, each lattice site can be either occupied by a particle or not occupied by a particle.

   i) What is the canonical partition function for the surface assuming that exactly N_a particles are adsorbed onto the surface?

   ii) Show that the corresponding Helmholtz free energy is given by:

$$F(N_a, M, T) = k_B T M\left(\rho_a \log \rho_a + (1-\rho_a)\log(1-\rho_a) - \beta\rho_a\epsilon\right), \tag{2}$$

   where $\rho_a = N_a/M$.

2. (12 points)
Consider a triangular lattice consisting of N particles that can each be in one of 4 states: A, B, C, and D. Note that on a triangular lattice, each lattice site has six nearest neighbours. Assume that the interaction between lattice sites is such that the contribution to the energy is zero when nearest neighbour lattices are in different states, while it is $-J$ when they are in the same state, in other words, the Hamiltonian for this system is given by

$$H = -\frac{J}{2}\sum_i \sum_j{}' \delta_{\sigma_i,\sigma_j} \tag{3}$$

   where $\delta_{\sigma_i,\sigma_j}$ is the Kronecker delta function defined by

$$\delta_{\sigma_i,\sigma_j} = \begin{cases} 0 & \text{if } \sigma_i \neq \sigma_j \\ 1 & \text{if } \sigma_i = \sigma_j \end{cases}, \tag{4}$$

   where $\sum_j{}'$ indicates a sum over nearest neighbours, and σ_i indicates the state of the lattice site, i.e. it can be either A, B, C or D.

For this system, the **disordered** phase consists of and equal number of lattice sites in each of the four states A, B, C, and D, while the **ordered** phase will be in one of the states more often than all the others. For simplicity, we will assume that the ordered state consists of more A lattice sites than either B, C or D.

Here we will use a form of mean field theory, namely the random mixing approximation, to explore the phase behaviour of this system. Recall that within the random mixing approximation, *the states of all lattice sites are uncorrelated.* Define p_A to be the probability that a particular lattice site is in state A, p_B to be the probability a particular lattice site is in state B, p_C to be the probability a particular lattice site is in state C, and p_D to be the probability a particular lattice site is in state D. Note that in the disordered state, $p_A = p_B = p_C = p_D$.

(a) Argue why, in both the ordered and disordered phases,

$$p_B = p_C = p_D = \frac{1 - p_A}{3}$$

.

(b) What is the expected potential energy in the system for a given value of p_A?

(c) Show that, within the random mixing approximation, the free energy of the system can be written

$$\frac{\beta F}{N} = -A\left(p_A^2 + \frac{1}{3}(1-p_A)^2\right) + p_A \log(p_A) + (1-p_A)\log\left(\frac{1-p_A}{3}\right), \qquad (5)$$

where A is a constant that can be written in terms of J and β, and N is the number of lattice sites.

(d) In the disordered phase, $p_A = 1/4$. Now, we define an order parameter m such that $m = \frac{3}{2}(p_A - 1/4)$. Note that is it 0 in the disordered phase and non-zero in the ordered phase. The Landau expansion for the free energy can then be written

$$\frac{\beta F}{N} = -\log(4) - \frac{A}{4} + \left(\frac{3}{2} - \frac{3}{4}A\right)m^2 - m^3 + \frac{7m^4}{4} + O(m^5). \qquad (6)$$

Using this Landau free energy, determine whether this system has a first or second order phase transition.

(e) Sketch the Landau free energy i) above the phase transition temperature, ii) below the phase transition temperature, and iii) at the phase transition temperature. Make sure to clearly label all axes and any important points on the graphs.

(f) Sketch the order parameter m as a function of the temperature. Make sure to clearly label all axes and any important points on the graphs.

3. (9 points)
Consider a dispersion of anisotropic Brownian particles which are in the shape of a cylindrical disk ("a CD") of diameter D and thickness $L \lll D$. Assume that these disks interact via a hard-core repulsion. If $\mathbf{u}_i$ is the unit vector pointing along the cylindrical axis of one such disk, then the excluded volume of a pair of such disks is given by $E(\mathbf{u}_1, \mathbf{u}_2) = 2D^3|\sin\gamma_{12}|$, with γ_{12} the angle between $\mathbf{u}_1$ and $\mathbf{u}_2$.

(a) At low densities, one expects this system to exhibit an isotropic phase. Sketch an isotropic phase and explain the important characteristics of such a phase.

(b) As the density increases, one expects this system to exhibit a phase transition. i) What phase do you expect at (slightly) higher densities? ii) Sketch the phase and explain the important characteristics of such a phase.

(c) Recall that the second virial coefficient for isotropic particles is given by $B_2(T) = (1/2)\int d\mathbf{r}[1-\exp(-\beta\phi(r))]$ for pair potential $\phi(r)$. Generalize this description to the case of a cylindrical disk and calculate the second virial coefficient $B_2(T)$ for the low-density isotropic fluid phase of cylindrical disks.

(d) Does $B_2(T)$ depend on the temperature for the hard cylindrical disks? Explain.

4. (Points: 14)
Consider a system of N identical particles in a volume V at temperature T. Assume that the particles interact via a so-called square shoulder potential, that is to say that the pairwise interaction between the particles is given by

$$U(r) = \begin{cases} \infty & r < \sigma \\ \epsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}, \qquad (7)$$

where σ denotes the hard-core diameter, where $\lambda > 1$ is a measure for the range of the repulsive shoulder and ϵ is a measure of the strength of the repulsion. Note that in this case $\epsilon > 0$. The density is denoted by $\rho = N/V$.

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

(b) Show that for such a system the pair correlation function $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ can be written:

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') = \frac{N(N-1)}{Q_N}\int d\mathbf{r}_3\cdots\mathbf{r}_N \exp[-\beta\Phi(\mathbf{r},\mathbf{r}',\mathbf{r}_3,\cdots,\mathbf{r}_N)], \qquad (8)$$

where

$$Q_N = \int d\mathbf{r}^N \exp[-\beta\Phi(\mathbf{r}^N)], \qquad (9)$$

with $\Phi(\mathbf{r}^N)$ the total energy of the system.

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.

(c) 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. **Hint:** Recall that the $g(|\mathbf{r}-\mathbf{r}'|) = \rho^{(2)}(\mathbf{r},\mathbf{r}')/\rho^2$.

(d) Sketch the $g(r)$ and $S(q)$ for the case of very low density ($\rho\sigma^3 = 0.01$) and high temperature ($k_BT \gg \epsilon$). Remember to label the axes and identify all important points.

One option for determining the thermodynamic behaviour of this system is to use thermodynamic perturbation theory, using hard spheres as the so-called "reference state". 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 H_0 and a perturbation Φ_1. Specifically,

$$H_\lambda(\Gamma) = H_0(\Gamma) + \lambda\Phi_1(\mathbf{r}^N), \qquad (10)$$

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 $\lambda = 1$.

(e) In the case of the square shoulder particles, where hard spheres are the reference system, write down expressions for $H_0(\Gamma)$ and $\Phi_1(\mathbf{r}^N)$.

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

$$F(N,V,T) = F_0(N,V,T) + \int_0^1 d\lambda \langle \Phi_1 \rangle_\lambda, \tag{11}$$

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

5. (14 points)
The Hamiltonian for the zero field Ising model in $d = 1$ is given by

$$\mathcal{H} = -J \sum_{i=1}^{N-1} S_i S_{i+1}. \tag{12}$$

where J is the strength of the coupling between the spins. Assume we are only interested in ferromagnetic ordering (e.g. $J > 0$) and assume open boundary conditions.

(a) Determine the canonical partition function. What is the associated Helmholtz free energy?

(b) Does this system exhibit a phase transition? Explain using the free energy you calculated in part (a).

(c) Show that

$$\langle S_k S_{k+1} \rangle = \tanh(\beta J)$$

and

$$\langle S_k S_{k+p} \rangle = \tanh^p(\beta J)$$

(d) What is the correlation length for this system?

(e) Sketch a renormalization group flow diagram for this system. (Do not try to calculate it analytically - just sketch it)

(f) Now consider an Ising model on a square lattice with $d = 2$. The 2d Ising system undergoes a 2nd order phase transition at $T_c = 2.27J/k_B$. Sketch the renormalization group flow diagram for the 2d Ising model. Describe the behaviour of the correlation length as T approaches T_c.