

**Midterm Exam for Advanced Statistical Physics: NS-370B**

**Date: October 10st, 2017**

**Time : 13:15 - 15:15**

This exam consists of 3 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 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  $V$  at 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  $\mu$  the chemical potential.
- $k_B = 1.38 \times 10^{-23} \text{J/K}$ ,  $e = 1.6 \times 10^{-19} \text{C}$ , and  $R = 8.31 \text{J/K/mol}$ .
- 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  $\binom{m}{n} = \frac{m!}{(m-n)!n!}$ .
- 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  $f(x) = f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f^{(3)}(a)}{3!}(x-a)^3 + \dots$ .
- From the Taylor series we get:  $e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$

1. (30 points) An interesting extension of the Ising model, is the so-called three state “clock” model. The Hamiltonian for this system is given by

$$\mathcal{H} = -\frac{J}{2} \sum_i \sum_j' \mathbf{n}_i \cdot \mathbf{n}_j \quad (1)$$

where  $J > 0$  is a coupling constant, and each unit vector  $\mathbf{n}_i$  can take on one of three possible values:

$$\mathbf{n}_i = \hat{\mathbf{x}} \quad \mathbf{n}_i = -\frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}} \quad \mathbf{n}_i = -\frac{1}{2}\hat{\mathbf{x}} - \frac{\sqrt{3}}{2}\hat{\mathbf{y}} \quad (2)$$

Recall that  $\sum_j'$  is used to indicate a sum over nearest neighbours.

Consider this clock model on a square lattice (i.e. each particle has 4 nearest neighbours). Assume that we have  $N$  lattice sites, and that the system is at temperature  $T$ . Similar to the Ising model, this system undergoes a phase transition as a function of temperature, from a phase where all three directions occur in approximately equal amounts (i.e. disordered) to a phase where the particles on average point in one direction. Without loss of generality, we can assume that this preferential direction is the  $\hat{\mathbf{x}}$  direction. Hence, we expect  $\langle \mathbf{n}_i \rangle = m\hat{\mathbf{x}}$ , where  $m$  is the order parameter (i.e. in the disordered phase  $m = 0$  while  $m \neq 0$  in the ordered phase).

- (a) Show that by expanding the Hamiltonian to linear order in the fluctuations (i.e. developing a mean field Hamiltonian by ignoring correlations between fluctuations), that the Hamiltonian becomes

$$\mathcal{H} = 2NJ \langle \mathbf{n}_i \rangle^2 - 4J \langle \mathbf{n}_i \rangle \cdot \sum_i \mathbf{n}_i \quad (3)$$

- (b) Using  $\langle \mathbf{n}_i \rangle = m\hat{\mathbf{x}}$ , rewrite the Hamiltonian in terms of the order parameter  $m$ .  
(c) Calculate the canonical partition function for this mean field Hamiltonian as a function of  $m$ .  
(d) Calculate the associated mean field free energy as a function of  $m$ .  
(e) One can use the resulting free energy in order to determine the transition temperature. Specifically, the Landau free energy for this system is given by

$$\frac{\beta F(m, T)}{N} = -\log(3) + 2\beta J (1 - 2\beta J) m^2 - \frac{8}{3}\beta^3 J^3 m^3 + 4\beta^4 J^4 m^4 + \mathcal{O}(m^5). \quad (4)$$

**Do not try and derive this Landau expansion.** Sketch this Landau free energy for this system for  $T < T_c$ ,  $T = T_c$  and  $T > T_c$ , where  $T_c$  is the temperature associated with the phase transition. Clearly label the axes and identify all important features. Is this a continuous or discontinuous phase transition?

- (f) Now, assume that instead of a 2d square lattice, instead we had examined a 1d string of particles (where each particle has two neighbours).  
(i) Based on our studies of the Ising model, do you think that there is a phase transition in a one dimensional version of this system? Explain.  
(ii) Would mean field theory predict a phase transition in this case? If yes, would it be continuous or discontinuous? Explain both answers.

- (g) Now, assume that instead of a 2d square lattice, we had a 3d cubic lattice (where each particle has 6 neighbours).
- (i) Based on our studies of the Ising model, do you think that there is a phase transition in the three dimensional version of this system? Explain.
  - (ii) Would mean field theory predict a phase transition in this case? If yes, would it be continuous or discontinuous? Explain both answers.
- (h) Of the three cases (1d, 2d and 3d), in which dimension do you expect mean field to work the best? Explain.
2. (20 points) Assume we have a system of  $N$  spheres in a volume  $V$  at temperature  $T$  that interact via a square shoulder potential, given by

$$\phi_{SW}(r) = \begin{cases} \infty & r < \sigma \\ \epsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}, \quad (5)$$

where  $\sigma$  denotes the hard-core diameter, and where  $\lambda > 1$  is a measure for the range of the repulsive shoulder. Note that as we are assuming that this potential is a repulsive potential,  $\epsilon > 0$ .

- (a) Assume that the density is sufficiently low that that the behaviour of the system is well approximated as an ideal gas.
    - (i) Determine the canonical partition function for this system.
    - (ii) Determine the corresponding Helmholtz free energy.
    - (iii) Calculate the pressure as a function of density for this system.
  - (b) As the density increases, the ideal gas approximation becomes less accurate. One improvement on this is the virial expansion for the pressure. Write down the virial expansion for the pressure in terms of the virial coefficients. You do not need to provide expressions for the virial coefficients.
  - (c) The second virial coefficient 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.
    - (i) Sketch the Mayer function for this system (of square shoulder particles). Clearly label the axes and identify all important features.
    - (ii) Calculate the second virial coefficient  $B_2(T)$ . Does  $B_2(T)$  depend on  $T$  for this system?
    - (iii) Recall that  $B_2$  for hard spheres is given by  $B_2 = \frac{2\pi\sigma^3}{3}$ . In the limit that  $\epsilon$  goes to zero, the square shoulder potential becomes a hard sphere potential. Show that  $B_2$  becomes the hard sphere  $B_2$  in this limit.
    - (iv) Sketch the ideal gas equation of state. Then sketch the second-order virial equation of state for the system of square shoulder particles in the same plot. Clearly label the axes and identify all important features.
3. (15 points) The van der Waals equation of state is one of the simplest equations of state that we can use to describe a “real” liquid. Recall that the van der Waals equation of state is given by

$$p = \frac{\rho k_B T}{1 - \rho b} - a\rho^2, \quad (6)$$

where  $\rho = N/V$  is the density and  $a$  and  $b$  are phenomenological parameters.

- (a) Sketch a simple phase diagram for this system in the density temperature ( $\rho - T$ ) representation. Clearly indicate the gas, liquid, fluid, and co-existence regions. Clearly indicate the critical point.
- (b) Sketch the equation of state for this system for i) a temperature just above  $T_c$ , ii) a temperature at  $T_c$  and iii) a temperature just below  $T_c$ .
- (c) Based on your observations associated with the equations of state, write down two equations that allow you to determine the critical point from the equation of state. Do not solve these equations.

Another attempt to improve the equation of state for simple liquids was proposed in 1899 by Dieterici. The equation of state he proposed is given by

$$\beta P = \frac{e^{-\beta a \rho}}{1/\rho - b} \quad (7)$$

Similar to the van der Waals system, this equation of state exhibits a gas-liquid phase transition below a critical temperature  $T_c$ .

- (d) Calculate the critical temperature and critical density.