

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

**Date: 05-11-2013**

**Time : 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.

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  $T$  is written as  
 $Z(N, V, T) = 1/(N!h^{3N}) \int d\Gamma \exp[-\beta H(\Gamma)]$ , with Hamiltonian  $H(\Gamma) = \sum_{i=1}^N \mathbf{p}_i^2/2m + \sum_{i<j}^N \phi(r_{ij})$ , where  $\mathbf{p}_i$  is the momentum of particle  $i$ , and  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$  the distance between the positions of particle  $i$  and  $j$ , and with  $\phi(r)$  the pair potential and  $\beta^{-1} = k_B T$ .

- 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.

- 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

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{Q_N(V, T)} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \exp[-\beta\Phi(\mathbf{r}_1, \cdots, \mathbf{r}_N)] \quad (1)$$

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.

- $k_B = 1.38 \times 10^{-23} \text{J/K}$ ,  $e = 1.6 \times 10^{-19} \text{C}$ , and  $R = 8.31 \text{J/K/mol}$ .
- The OZ equation reads  $h(r_{12}) = c(r_{12}) + \rho \int d\mathbf{r}_3 c(r_{13}) h(r_{32})$ .
- 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  $\binom{m}{n} = \frac{m!}{n!(m-n)!}$ .
- 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  $f(x) = f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f^{(3)}(a)}{3!}(x-a)^3 + \cdots$ .
- The following critical exponents for the Ising model:
  - $\beta$  is associated with the *spontaneous magnetization*.
  - $\alpha$  is associated with the *specific heat* when the external field is zero
  - $\gamma$  is associated with the *zero field susceptibility*
  - $\delta$  is associated with the *magnetization at the critical temperature*
- The Poisson equation  $\nabla^2 \psi(\mathbf{r}) = -\frac{4\pi}{(4\pi\epsilon_0)\epsilon} Q(\mathbf{r})$  relates the electrostatic potential  $\psi(\mathbf{r})$  to the charge density  $\epsilon Q(\mathbf{r})$  in a medium of relative dielectric constant  $\epsilon$ . The factor  $4\pi\epsilon_0$  can be ignored in Gaussian units, and must be retained in SI units.

1. Consider a square lattice. On a square lattice, each lattice site has four nearest neighbours. Assume that each lattice site can be in one of three different states, which we will label  $A$ ,  $B$  and  $C$ . 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. The Hamiltonian for this system can be written

$$H = -\frac{J}{2} \sum_i \sum_j' \delta_{\sigma_i, \sigma_j} \quad (2)$$

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

$$\delta_{\sigma_i, \sigma_j} = \begin{cases} 0 & \text{if } \sigma_i \neq \sigma_j \\ 1 & \text{if } \sigma_i = \sigma_j \end{cases}, \quad (3)$$

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

Note that if there is a phase transition in this system it will be between a phase where the system consists of an equal number of lattice sites in states  $A$ ,  $B$ , and  $C$ , while in the ordered phase, one of the three will be more likely. For simplicity, in this problem we will assume that the ordered state consists of more  $A$  lattice sites than either  $B$  or  $C$ . In this problem we want to use the random mixing approximation (a form of mean field theory) to study 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  $B$ , and  $p_C$  to be the probability a particular lattice site is in state  $C$ . Note that in the disordered state,  $p_A = p_B = p_C$ .

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

$$p_B = p_C = \frac{1 - p_A}{2}$$

- (b) What is the expected potential energy in the system for a given value of  $p_A$ ?  
 (c) What is the entropy for given value of  $p_A$ ?  
 (d) Show that, within the random mixing approximation, the free energy of the system for a given value of  $p_A$  can be written

$$\frac{\beta F}{N} = -A \left( p_A^2 + \frac{1}{2}(1 - p_A)^2 \right) + p_A \log(p_A) + (1 - p_A) \log\left(\frac{1 - p_A}{2}\right), \quad (4)$$

where  $A = 2\beta J$ , and  $N$  is the number of lattice sites.

- (e) In the disordered phase,  $p_A = 1/3$ . Define an order parameter  $m$  such that  $m = \frac{3}{2}(p_A - 1/3)$ . Note that it is 0 in the disordered phase and non-zero in the ordered phase. Rewrite the free energy in terms of  $m$ . Show that the Landau expansion for the free energy can then be written

$$\frac{\beta F}{N} = -\log(3) - \frac{A}{3} + \left(1 - \frac{2}{3}A\right) m^2 - \frac{m^3}{3} + \frac{m^4}{2} + O(m^5). \quad (5)$$

- (f) Using the Landau free energy, determine whether this system has a first or second order phase transition, and determine the transition temperature.
2. (a) A simulator is studying a new particle, a gyrobifastigium (see Figure 1). To study the system, he performs simulations in the canonical ensemble. Once the system stops changing (the system equilibrates), he takes a picture of the simulation box. An image of what he observes is shown in Figure 1. Can he determine from this picture if the phase transition between the isotropic phase and crystal phase is first order or second order? And if he can, which one is it? Explain.
- (b) Consider a system with a Landau free energy given by

$$f(t, m) = -hm + r(t)m^2 + um^6. \quad (6)$$

with  $u$  a positive constant and  $t = \frac{T - T_C}{T_C}$ . Approach the critical point ( $T_C$ ) along the  $r$ -axis, setting  $r(t) = r't$ . Find the critical exponents  $\beta$ ,  $\gamma$  and  $\delta$ .

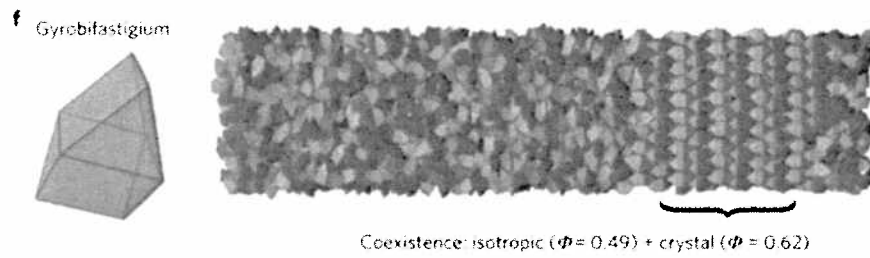


Figure 1: For question 2, part a)

- (c) Assume that we have a single-component system which can phase separate into two phases, labeled  $\alpha$  and  $\gamma$  at sufficiently low temperature.
- What are the conditions for equilibrium for this system?
  - A theorist develops an approximate theory to calculate the free energy of the system. The free energy she finds, is shown in Figure 2 for four different temperatures. Note that here she has plotted  $F/V$  as a function of the density  $\rho = N/V$ . Use the four plots to sketch a phase diagram of the system.
  - Explain why or show why we can ignore the contributions from the interface between phases  $\alpha$  and  $\gamma$  when we are deriving the equilibrium conditions for coexistence between the two phases.
  - Write down the classical nucleation theory expression for the free energy barrier associated with a spherical nucleus. Explain why it is essential to include contributions from the surface to the free energy in this case.

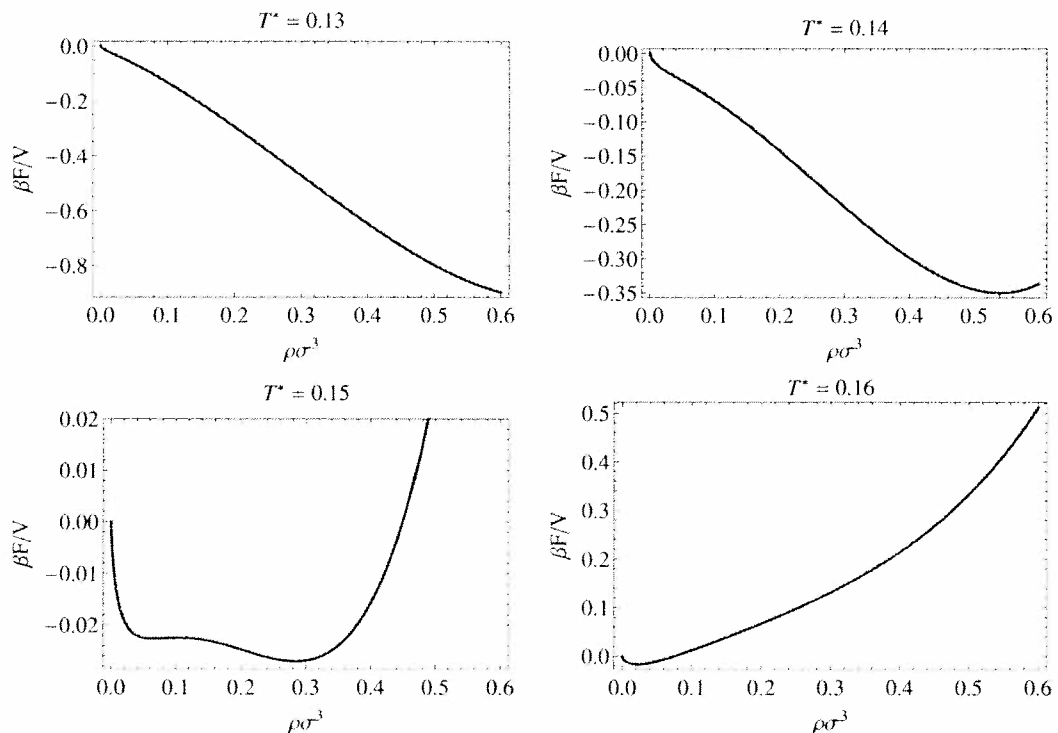


Figure 2: For question 2, part c).

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3. (a) Calculate the grand partition function  $\Xi(\mu_1, \mu_2, V, T)$  and the grand potential  $\Omega(\mu_1, \mu_2, V, T)$  of a classical two-component ideal-gas mixture of point particles of mass  $m_1$  and  $m_2$  in a volume  $V$  at chemical potentials  $\mu_1$  and  $\mu_2$  at temperature  $T$ .
  - (b) Consider a family of  $N$ -particle Hamiltonians  $H_\lambda(\Gamma) = H_0(\Gamma) + \lambda\Phi(\Gamma)$  with switching parameter  $\lambda \in [0, 1]$ , with  $\Gamma$  the phase-space point of the  $N$  particles in a volume  $V$ . Denoting the Helmholtz free energy of the system at temperature  $T$  at a particular value of  $\lambda$  by  $F_\lambda(N, V, T)$ , show that  $F_1(N, V, T) = F_0(N, V, T) + \int_0^1 d\lambda \langle \Phi \rangle_\lambda$  with the brackets  $\langle \dots \rangle_\lambda$  denoting the canonical ensemble average with Hamiltonian  $H_\lambda$ .
  - (c) Calculate the second virial coefficient  $B_2(T)$  of *two-dimensional* disks of hard-core diameter  $\sigma$  that interact with a square-well potential of depth  $-\epsilon < 0$  for  $\sigma < r < 2\sigma$ , with  $r$  the center-to-center distance between two disks. Sketch the temperature dependence of  $B_2(T)$  with appropriate units on the axes.
  - (d) The structure factor of a homogeneous and isotropic bulk fluid of  $N$  identical particles is defined by  $S(q) = \langle \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N \exp(i\mathbf{q} \cdot \mathbf{r}_{ij}) \rangle$ . Show that  $S(q) = 1 + \rho \int d\mathbf{r} \exp(i\mathbf{q} \cdot \mathbf{r})(g(r) - 1)$  for  $q \neq 0$  and  $\rho = N/V$ .
  - (e) Sketch in a single graph the radial distribution function  $g(r)$  of Brownian hard spheres with a diameter of 100 nm at a packing fraction (i)  $\eta = 0.01$  and (ii)  $\eta = 0.49$ . Label the curves clearly, and give a scale to both axes of the plot.
4. Consider a solid electrode at potential  $\psi_0$  with a homogeneous surface in the plane  $z = 0$ . The electrode is in contact with a liquid electrolyte in the halfspace  $z > 0$ . The electrolyte is at temperature  $T$  and has relative dielectric constant  $\epsilon$ , and it contains monovalent point ions of charge  $\pm e$  at a concentration  $c_+ = c_- \equiv c$  far from the electrode at  $z \rightarrow \infty$ . We wish to calculate the electric potential  $\psi(z)$  and the ion concentrations  $c_+(z)$  and  $c_-(z)$  for  $z > 0$ , where we choose  $\psi(z \rightarrow \infty) = 0$ . Note that the (average) energy of an ion of charge  $\pm e$  at position  $z$  equals  $\pm e\psi(z)$ .
    - (a) Assume Boltzmann distributions for  $c_+(z)$  and  $c_-(z)$ , and use this to *derive* the Poisson-Boltzmann equation  $d^2\phi(z)/dz^2 = \kappa^2 \sinh \phi(z)$  for  $z > 0$  for a properly defined dimensionless electrostatic potential  $\phi(z)$  and screening parameter  $\kappa$ . Define  $\kappa$  and give its dimension.
    - (b) Impose appropriate boundary conditions and solve the PB equation of (a) within the weak-potential limit where  $\sinh \phi(z) \simeq \phi(z)$ .
    - (c) Calculate the surface charge density  $e\sigma$  on the surface of the electrode, and estimate the order of magnitude of  $\kappa^{-1}$  and  $\sigma$  in the case of an electrolyte composed of water with  $c = 10^{-3}\text{M}$  at room temperature for  $\psi_0 = 10\text{mV}$ .

The excluded volume of a pair of hard needle-shaped colloidal particles with length  $L$  and diameter  $D \ll L$  at a relative angle  $\gamma$  is given by  $E(\gamma) = 2L^2D|\sin \gamma|$ .

- (d) Calculate the (osmotic) pressure of an isotropic suspension of  $N$  of these needles in a volume  $V$  at temperature  $T$ .
- (e) The needles show isotropic-nematic (I-N) phase coexistence at packing fractions  $\eta_I = 0.004$  and  $\eta_N = 0.005$ . Estimate the aspect ratio  $L/D$  of the rods, and sketch a 'snapshot' of about 10 rods in each of the two coexisting states, representing the rods by a line segment parallel to their long axis.

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