Final Exam for Advanced Statistical Physics: NS-370B

Date: November 6th, 2023

Time for Regular Students: 13:30 - 16:30

Extra-Time Students Only: 13:30 − 17:00

This exam consists of **8** questions of varying length.

The total number of possible points is: 100.

This is a **closed-book** exam, no notes are allowed.

You will not require a calculator or any other electronic device and are consequently not permitted one.

Please **start every exercise on a new PAGE of paper**.

Write your name clearly on every four-page sheet of paper.

Please number your sheets (1/3, 2/3, ...) and indicate which questions are on it.

The exam can be written in English or Dutch.

Please write CLEARLY and using PEN!

Equation Cheat Sheet

A few formulas and information that may be useful for this exam:

- The canonical partition function of a classical thermodynamic system of N identical particles in a volume V a temperature T with Hamiltonian $H(\mathbf{\Gamma})$ — $\mathbf{\Gamma}$ is a point in phase space — is written:

$$Z(N, V, T) = \frac{1}{N! h^{3N}} \int d\mathbf{\Gamma} \exp[-\beta H(\mathbf{\Gamma})], \text{ where } \beta^{-1} = k_{\mathrm{B}} T.$$

- The grand partition function of identical particles is given by (pay attention to the N dependence of Z for each term in the sum):

$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \exp(\beta \mu N) Z(N, V, T)$,

and the grand-canonical distribution is given by:

$$f_g(\mathbf{\Gamma}, N) = \frac{\exp[\beta \mu N - \beta H(\mathbf{\Gamma})]}{N! h^{3N} \Xi(\mu, V, T)}, \text{ with } \mu \text{ the chemical potential.}$$

- The second virial coefficient B_2 for an isotropic pair potential $\phi(r)$ is given by:

$$B_2 = -\frac{1}{2} \int_V d\boldsymbol{r} \left(\exp(-\beta \phi(r)) - 1 \right).$$

- $k_{\mathrm{B}} = 1.13 \times 10^{-23}$ 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:

$$\binom{m}{n} = \frac{m!}{(m-n)! n!}.$$

- 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:

$$f(x) = f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f^{(3)}(a)}{3!}(x-a)^3 + \cdots.$$

- From the Taylor series we obtain:

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} \qquad \& \qquad \log(1-x) = -\sum_{n=1}^{\infty} \frac{x^n}{n}.$$

- Maxwell-Boltzmann ($s = 0$), Bose-Einstein ($s = -1$), and Fermi-Dirac ($s = 1$) statistics are:

$$f(\epsilon) = \frac{1}{\exp[\beta(\epsilon - \mu)] + s},$$

where ϵ is the energy (of a single-particle level) and μ the chemical potential.

- The quantum single-level 'grand'-canonical partition functions Z_i are given by:

$Z_i = \sum_{n_i=0}^{M} \exp(\beta n_i(\mu - \epsilon_i))$,

where ϵ_i is the energy associated with the i-th level and μ is the chemical potential. The value of M depends on the statistics; $M = 1$ for fermions and $M = \infty$ for bosons. These lead to the following grand canonical partition function

$\Xi(\mu, V, T) = \prod_i Z_i$,

for the system, where i runs over all available levels.

1. Thermodynamics: (20 points)

In this question, we consider several useful thermodynamic relations, identities, and transformations.

(a) Write down the mathematical expressions for the *first* and *second* law of thermodynamics. Write down what the symbols mean and explain the sign convention that you picked in a *few* words.

(b) Provide the two standard forms of work. Ensure agreement with your choice in part (a).

(c) Combine the laws and choices of work to obtain dU. Explain in a *few* words what must hold to use this expression.

(d) Make the transition to the NpT ensemble and provide an expression for $dG = -SdT + Vdp + \mu dN$. Provide the transformation **and** the intermediate steps.

(e) Derive expressions for μ, V, and S in terms of $G(N, p, T)$ based on your result from (d).

(f) Show that $G(N, p, T) = \mu(p, T)N$ and explain in *few* words.

2. Mixing on a Square Lattice: (22 points)

Consider a square lattice. Each site has four nearest neighbors and can be in one of three different states, which we will label A, B, and C. The interaction between lattice sites is such that the contribution to the energy is zero when nearest neighbor lattices are in different states, while it is $-J$ when they are in the same state. The Hamiltonian is given by

$$H = -\frac{J}{2} \sum_i {\sum_j}' \delta_{\sigma_i, \sigma_j}, \tag{1}$$

where ${\sum_j}'$ indicates a sum over nearest neighbors; σ_i represents the state site i, and can be either A, B, or C; and $\delta_{\sigma_i, \sigma_j}$ is the Kronecker delta function: $\delta_{\sigma_i, \sigma_j} = 0$ if $\sigma_i \neq \sigma_j$ and $\delta_{\sigma_i, \sigma_j} = 1$ if $\sigma_i = \sigma_j$.

If there is a phase transition in this system, the ordered phase will have one of the three states (A, B, or C) 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. Here, we want to use the random mixing approximation (a form of mean-field theory) to study the phase behavior of this system. 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 the probability that it is in state B, and p_C the probability that it 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, $p_B = p_C = (1 - p_A)/2$.

(b) What is the expected potential energy in the system for a given value of p_A? Express your result in terms of J, N, and p_A only.

(c) What is the entropy for given value of p_A? Express your result in terms of k_B, N, and p_A only.

Within the random mixing approximation, the free energy of the system can be written

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

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

(d) Use properties of the system to show that an appropriate order parameter is $m = \frac{3}{2}(p_A - 1/3)$. Explain your result in a *few* words.

The free energy can be rewritten in terms of m and expanded into the following form

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

(e) Using the above Landau free energy, determine the transition temperature for this system. Is the phase transition continuous or discontinuous? Explain in a *few* words. **Hint: Solve the general form $f = bm^2 - cm^3 + dm^4$, before reintroducing the prefactors.**

The exam continues on the next page $\Rightarrow$

3. Interpreting Equipartition: (9 points)

We consider a Hamiltonian of the form

$$\mathcal{H} = \sum_{i=1}^{M} a_i s_i^2 \tag{4}$$

with $a_i > 0$ some constant and s_i a generalized coordinate of the system. The canonical partition function for such a Hamiltonian leads to

$$\langle \mathcal{H} \rangle = \frac{M}{2} k_{\mathrm{B}} T. \tag{5}$$

(a) Consider dilute nitrogen gas N_2 in three dimensions (3D). What is the internal energy U around room temperature? Explain using a *few* words.

(b) What is U for temperatures close to ionization? Explain your results in a *few* words.

(c) Explain the difference in the two temperatures referencing the classical and quantum-mechanical features of the bond.

4. Percolation: (7 points)

Consider a square lattice. Assume that a 2×2 subset in this lattice 'spans' if **more** than half the superblock is filled. Show that $R(p) = 4p^3(1-p) + p^4$ and support your argumentation toward this result using sketches. Determine the fully reduced analytic expression for the non-trivial fixed point.

5. Gibbs and Boltzmann Entropy: (14 points)

The Gibbs definition of entropy S states that $S = -k_{\mathrm{B}} \sum_s p_s \log p_s$, where the sum is over all states labelled by s. The probability of being in that state is p_s and k_{B} is Boltzmann's constant.

(a) Show that the Gibbs definition leads to an extensive entropy.

(b) Use $\sum_s p_s = 1$ as a constraint to maximize S. Show that you obtain the microcanonical probability from this set of assumptions.

(c) Suppose we introduce energies ϵ_s associated with each microstate 's' and demand $\langle \epsilon_s \rangle = E$ with the brackets indicating averaging and E some constant total energy? Show that then $p_s \propto \exp(-c\epsilon_s)$, with c some constant, but do **not** attempt to determine c.

6. The Isotropic-Nematic Transition: (10 points)

A system of hard (lyotropic) rod-like particles consists of rectangular blocks of length L and thickness D, *i.e.* of the form $L \times D \times D$. These can have 3 possible orientations along the axes of a lab frame $\hat{\boldsymbol{x}}_\alpha$, $\alpha = 1, 2, 3$. In the second-virial approximation, the free energy F is given by

$$\frac{F}{V k_{\mathrm{B}} T} = \sum_{\alpha=1}^{3} \rho_\alpha \left(\log \rho_\alpha \mathcal{V} - 1 \right) + \sum_{\alpha=1}^{3} \sum_{\alpha'=1}^{3} B_{\alpha\alpha'} \rho_\alpha \rho_{\alpha'}, \tag{6}$$

with V the volume, T the temperature, k_{B} the Boltzmann constant, ρ_α the density of particles with orientation α, and $\mathcal{V}$ the (irrelevant) thermal volume.

(a) Argue that $B_{\alpha\alpha'}$ is a symmetric 3×3 matrix using a *few* words only.

(b) 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.

(c) Explain in a *few* words how the hard-rod F may be used to obtain the free energy for a system of rod-like particles with a small, short-ranged attraction. Assume that the attraction can be seen as a perturbation. Provide the expression that connects the source and target free energies. **Hint: No more than one equation is needed!**

7. Chemical Reactions: (8 points)

Let us start by considering a chemical reaction between M chemical species X_i, $i \in \{1, \ldots, M\}$, and M' chemical species X_j', $j \in \{1, \ldots, M'\}$. Then the reaction scheme becomes

$$\sum_{i=1}^{M} v_i X_i \rightleftharpoons \sum_{j=1}^{M'} v_j' X_j', \tag{7}$$

where v_i is the stoichiometric coefficient for species X_i and v_j' is the the ones for species X_j'.

(a) Use properties of the Gibbs free energy G to show that, when we isolate a single species N_r and change the system by dN_r, the change in G due to the dN_r chemical reactions is

$$v_r dG = \left(-\sum_{i=1}^{M} v_i \mu_i + \sum_{j=1}^{M'} v_j' \mu_j' \right) dN_r. \tag{8}$$

A general reference density ρ_0 can be introduced, so that the concentrations with respect to this density may be written as $[X_i] \equiv \rho_i/\rho_0$. Equation (8) then gives

$$\frac{\prod_{i=1}^{M} [X_i]^{v_i}}{\prod_{j=1}^{M'} [X_j']^{v_j'}} = \exp\left(-\beta \Delta\mu^{(0)} \right). \tag{9}$$

(b) Explain in a *few* words what $\Delta\mu^{(0)}$ represents **and** what therefore must happen, when we change one of the consentrations at constant temperature $[\beta = 1/(k_B T)]$.

8. Black-Body Radiation: (10 points)

Consider a cubic box with volume V in three dimensions. You may assume that the density of states is given by

$$g(\omega) = \frac{V\omega^2}{\pi^2 c^3}, \tag{10}$$

where ω is the frequency of light corresponding to an energy $E = \hbar\omega$ and c is the speed of light. Further assume that the photon system is in thermal equilibrium (with the walls of the box) at temperature T.

(a) Argue why the photon chemical potential must be zero using a *few* words.

(b) Starting from the factorized grand-canonical partition function

$$\Xi(\mu, V, T) = \prod_{i} \sum_{n_i}^{\infty} \exp[-\beta n_i(\epsilon_i - \mu)] = \prod_{i} Z_i, \tag{11}$$

determine Z_i based on the above information about photons.

(c) Using $E = -\partial \log \Xi / \partial \beta$, write the energy in form of a continuous frequency integral.

(d) Find the temperature dependence of the energy density $\epsilon = E/V$ by making the integral dimensionless; that is, by substituting $x = \beta \hbar \omega$.

The exam ends here ☺!