
Retake Exam for Advanced Statistical Physics: NS-370B

Date: December 18th, 2023

Time for Regular Students: 18:30 - 21:30

Extra-Time Students Only: 18:30 – 22:00

This exam consists of **6** 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, NOT a new 4-PAGE SHEET**.

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:

  $Z(N,V,T) = \dfrac{1}{N!h^{3N}} \displaystyle\int d\mathbf{\Gamma} \exp[-\beta H(\mathbf{\Gamma})]$, 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:

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

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

  $B_2 = -\dfrac{1}{2}\displaystyle\int_V \mathrm{d}\boldsymbol{r}\ (\exp(-\beta\phi(r)) - 1)$.

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

  $\dbinom{m}{n} = \dfrac{m!}{(m-n)!n!}$.

- Stirling's approximation to order $O(N)$ is given by: $\log(N!) = N\log N - N$.

- Gaussian Integral:

  $\displaystyle\int_{-\infty}^{\infty} dx\ e^{-x^2} = \sqrt{\pi}$.

- The Taylor series of $f(x)$ around $x = a$ is given by:

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

- From the Taylor series we obtain:

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

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

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

  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: (16 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 $\mathrm{d}U$. Explain in a *few* words what must hold to use this expression.

(d) Make the transition to the μVT ensemble by deriving $\mathrm{d}\Omega = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu$. Provide the transformation **and** the intermediate steps.

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

(f) Show that $\Omega(\mu, V, T) = -p(\mu, T)V$ and explain in *few* words.

2. Gibbs and Boltzmann Entropy: (16 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.

Next, we will use $\sum_s p_s = 1$ and $\langle \epsilon_s \rangle = E$ as a constraint to maximize S.

(b) Define the Lagrangian $\mathcal{L}$ and show that $p_s \propto \exp(-c\epsilon_s)$, with c some constant.

(c) Use the definition of temperature $1/T = (\partial S/\partial U)_{N,V}$ to determine c. Under what conditions do we set $U = E$ typically? Explain in a *few* words.

3. Small Clusters: (21 points)

Consider a square-lattice model with A sites of which n are occupied by particles. If two particles are adjacent, they bond with bonding energy $-\epsilon$ (with $\epsilon > 0$). However, a particle that is already bonded cannot bond with any other, *i.e.*, the system consists of monomers and dimers. Here, we develop an approximate solution to the problem for low densities. Further assume that there is an average monomer density $\rho_1 = n_1/A$ and dimer density $\rho_2 = n_2/A$, with n_1 and n_2 the number of monomers and dimers, respectively. Also assume that the monomers and dimers do not interact, so both behave ideal gas like.

(a) Show that the canonical partition sum for the monomers $Q_1(n_1, A, T) = A^{n_1}/(n_1!)$, with T the temperature. Assume periodic boundary conditions and explain your answer using a *few* words.

(b) Use your answer in (a) to provide the canonical partition function for the dimers. Hint: Remember that the dimers can have two orientations.

(c) Calculate the (reduced) Helmholtz free energy

$$\beta F(\rho_1, \rho_2, A, T)/A = \rho_1(\log \rho_1 - 1) + \rho_2(\log \rho_2 - 1) - \rho_2(\log 2 + \beta\epsilon), \tag{1}$$

of the system, where $\beta = 1/(k_{\mathrm{B}}T)$ is the inverse thermal energy with k_{B} Boltzmann's constant. Hint: Use Stirling's approximation $\log n! = n \log n - n$.

(d) Show that in equilibrium the chemical potentials of monomers and dimers should obey: $2\mu_1 = \mu_2$.

(e) Demonstrate that $2\mu_1 = \mu_2$ imposes $\rho_2 = 2\rho_1^2 \exp(\beta\epsilon)$.

(f) Use the relation between n, n_1, and n_2 to arrive at

$$\rho_1 = \frac{\sqrt{1 + 16\rho e^{\beta\epsilon}} - 1}{8e^{\beta\epsilon}}. \tag{2}$$

(g) What happens to ρ_1 and ρ_2 in the limit where $\epsilon \to 0$ (assuming low density)? Hint: You can either perform the lengthy calculation or use your physical intuition. In either case explain your answer in a *few* words.

The exam continues on the next page ⇒

4. Percolation: (7 points)

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

5. Bose Gas at High Temperatures: (23 points)

At high temperatures T, a gas of conserved bosons in a volume V behaves similar to a classical ideal gas. In this problem, the goal is to determine the leading-order corrections to the classical ideal gas law $pV = Nk_\mathrm{B}T$, where p is the pressure, N the particle number, and k_B is the Boltzmann constant. We start from the grand-canonical partition function $\Xi(\mu, V, T) = \prod_i Z_i$ with $Z_i = \sum_{n_i=0}^{\infty} \exp(\beta n_i(\mu - \epsilon_i))$, where μ is the chemical potential and ϵ_i the energy of the i-th quantum level of a single particle.

(a) Use a general relation between $\langle N \rangle$ and Ξ to show that the particle number N is given by the integral representation

$$N = \int \mathrm{d}E\, g(E) f_\mathrm{BE}(E), \tag{3}$$

where $g(E)$ is the density of states and $f_\mathrm{BE}(E)$ adheres to Bose-Einstein statistics.

(b) Use the definition of the wave vector $\boldsymbol{k} = \pi\boldsymbol{n}/L$, with $\boldsymbol{n}$ the vector containing the quantum numbers n_x, n_y, and n_z, and the expression for the energy $E_{\boldsymbol{n}} = (\hbar^2 k^2)/(2m)$, with m the particle mass, $k = |\boldsymbol{k}|$, and $\hbar = h/(2\pi)$ the reduced Planck constant, to arrive at the density of states

$$g(E) = \frac{L^3}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}. \tag{4}$$

We will identify $L^3 = V$ for the remainder of this exercise.

(c) Input both $g(E)$ and $f_\mathrm{BE}(E)$ into the expression for N and rework it using a substitution to arrive at the following scaling of the particle density $\rho = N/V$ with the thermal wavelength Λ

$$\rho = \frac{1}{\Lambda^3}\frac{2}{\sqrt{\pi}}\int \mathrm{d}x \frac{\sqrt{x}}{z^{-1}e^x - 1}, \tag{5}$$

with $z = \exp(\beta\mu)$. Hint: You can find the expression for $f_\mathrm{BE}(E)$ on the cheat sheet if you could not solve part (a).

(d) Under what criterion involving Λ and ρ will the system show significant quantum effects? Explain using a *few* words.

(e) Argue using only a *few* words and the above expression for N that at high temperatures T the chemical potential μ becomes large but negative, such that $z = e^{\beta\mu} \ll 1$. In your answer you should reference the ensemble that you must choose to work in to make the comparison to the classical ideal-gas law.

(f) Turning to a **classical** ideal gas (in 3D), use equipartition to show that the pressure satisfies $pV = 2E/3$ with E the energy. Explain your answer in a *few* words.

Using your answer in (c) and an analogous expression for E it can be shown that the quantum correction to the classical ideal gas result is given to leading-order by

$$\beta p = \rho - \frac{\Lambda^3}{4\sqrt{2}}\rho^2. \tag{6}$$

(g) Does this result make sense? Explain in a *few* words whether you would expect to have a lower pressure for bosons than purely classical particles at the same density.

The exam continues on the next page ⇒

6. Landau Theory for Needle-like Objects: (17 points)

Here, we examine the phase behavior of anisotropic particles (long rods) using Landau theory for the isotropic-nematic (IN) phase transition without an external field.

(a) What are the isotropic and nematic phase for a (colloidal) liquid crystal? Illustrate using sketches and explain using a *few* words only.

(b) Provide an approximate expression for the second virial coefficient B_2 for thin, long rods of length L and diameter D, *i.e.*, $D \ll L$. Explain your expression using a *few* words. Hint: The expression for B_2 can be found on the equation cheat sheet; it should depend on the respective orientation of the rods ($\hat{\boldsymbol{\omega}}_1$ and $\hat{\boldsymbol{\omega}}_2$).

The nematic director is the average orientation of the rods in the liquid crystal. Let θ measure the angle between a rod-like colloid and this director. It is sensible to create an order parameter that depends on a series in terms of $\cos\theta$, which takes values in the range $[-1, 1]$.

(c) Show that $S = \left\langle (1/2)\left(3\cos^2\theta - 1\right)\right\rangle$ is a suitable order parameter for the disordered phase, using its properties and the requirements of Landau theory.

A physicist arrives at the following form for the IN Landau free energy

$$F_{\mathrm{IN}} = \left[a(T - T_c) - b^2/(4c)\right] S^2 + cS^2 \left[S - b/(2c)\right]^2 , \tag{7}$$

where a, b, and c are positive constants, T_c indicates the temperature for which the isotropic phase fully destabilizes, and T is the temperature of the system. This vanishes $S = 0$ and for $S = b/(2c)$, provided the temperature is suitably chosen.

(d) What is the order of the isotropic-nematic phase transition? Use arguments supported by the above Landau theory and only a *few* words. You may want to provide a sketch.

(e) 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!**

The exam ends here ☺!