
Midterm Exam for Advanced Statistical Physics: NS-370B

Date: October 8th, 2024

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

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

This exam consists of **6** questions of varying length.

The total number of possible points is 100 (+ 10 bonus).

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

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

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:

  $B_2 = -\dfrac{1}{2}\displaystyle\int_V \mathrm{d}\boldsymbol{r}\ \left(\exp(-\beta\phi(r)) - 1\right).$
- $k_{\mathrm{B}} = 1.13 \times 10^{-23}$ 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:

  $\dbinom{m}{n} = \dfrac{m!}{(m-n)!n!}.$
- 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: (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 $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$. Explain in a *few* words what must hold to use this expression to obtain the difference in U between state-space points.

(d) Make the transition to the NpT ensemble. Provide the transformation from $U(S, V, N)$ to $G(N, p, T)$, name the ensemble and the transformation, **and** give the intermediate steps.

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

(f) Show that $G(N, p, T) = \mu(T, p)N$ and explain how you arrived at this result in *few* words.

(g) Use the expression in (f) to derive the Gibbs-Duhem relation $V\mathrm{d}p = N\mathrm{d}\mu + S\mathrm{d}T$.

2. Gibbs and Boltzmann Entropy: (20 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, by considering two systems with respective entropies S_1 and S_2 and bringing these into contact.

Next, we will maximize the entropy S under constraint.

(b) Write down the Lagrangian $\mathcal{L}$ for the constraint $\langle \epsilon_s \rangle = E$ **and** use this to show that $p_s \propto \exp(-c\epsilon_s)$, with c some constant.

A researcher now applies this formalism to some well-characterized system and pushes the calculation a bit further. They arrive at an expression for the entropy that reads

$$\frac{S}{k_\mathrm{B}N} = \log\left(2\cosh\left(\beta J\right)\right) - \beta J \tanh\left(\beta J\right), \tag{1}$$

where $\beta = 1/(k_\mathrm{B}T)$ and $J > 0$ a positive coupling constant, with T the temperature.

(c) Does this system undergo a phase transition at finite temperature? Explain your answer using only a *few* words, referencing properties of the entropy S.

3. Gas Adsorption: (20 points)

Consider a simple model for a surface which consists of M adsorption sites which are arranged on a square lattice. Assume that the molecules of a gas are indistinguishable and can be adsorbed onto one of the lattice sites, but that each lattice site can only adsorb a single molecule. Further assume that an occupied site has binding energy ϵ and that the adsorbed gas is in thermal equilibrium at temperature T. Note that for a two-dimensional system (such as an adsorbed layer) the area A and surface pressure Π play the same role as the volume V and pressure P in a 3D system.

(a) If there are N molecules adsorbed onto the surface, what do the microstates for this system look like? Draw a few (more than 1 less than 10, please).

(b) Argue from the definition that the canonical partition function is given by $Z = \binom{M}{N}\exp(-\beta\epsilon N)$ where $\beta = 1/(k_\mathrm{B}T)$ with k_B Boltzmann's constant.

(c) Show that the grand canonical partition function is given by $\Xi = \left(1 + \exp\left(\beta\left(\mu - \epsilon\right)\right)\right)^M$.

(d) Express Π as a function of z, A, and T, where $z = e^{\beta\mu}$ is the fugacity.

(e) Calculate $\langle N \rangle$ and interpret your results physically in terms of the *statistics* that appears in your expression (is your result expected?). Use only a *few* words.

(f) Without performing involved calculations, provide the limiting behavior of the equation of state $\Pi(N/A, T)$ at low dilution. Explain in a *few* words how you arrive at this result.

The exam continues on the next page ⇒

4. Light from a Hot Metal Bar: (20 points)

Consider a cubic box with volume V in three dimensions. Photons are non-conserved spin-1 bosons with energy $E = \hbar\omega$; ω is the angular frequency and $\hbar$ the reduced Planck constant, we will also denote the speed of light by c. Assuming that the photon system is in thermal equilibrium (with the walls of the box) at temperature T. You may use for the photon density of states $g(\omega) = V\omega^2/(\pi^2 c^3)$.

(a) Starting from (i-th level occupation) factorized grand-canonical partition function

$$\Xi(\mu, V, T) = \prod_i \sum_{n_i}^{\infty} \exp[-\beta n_i(\epsilon_i - \mu)] = \prod_i Z_i, \tag{2}$$

determine Z_i based on the above information about photons. Here, μ denotes the chemical potential and $\beta = 1/(k_\mathrm{B}T)$ with T the temperature and k_B Boltzmann's constant.

(b) Show that for non-conserved particles we can write $E = -\partial \log \Xi/\partial\beta$. Explain in a *few* words why this is not the case for conserved bosons.

(c) Use the expression in (b) to derive an expression for the energy in form of a continuous frequency integral. Hint: If you could not solve (a) use $Z_i = 1/(A - Be^{-\beta\hbar\omega})$ instead.

(d) Find the temperature dependence of the energy density $\epsilon = E/V$ by making the integral dimensionless; that is, by substituting $x = \beta\hbar\omega$. Explain in a *few* words why the integral converges to some (largely irrelevant) positive number.

(e) Provide a physical argument why we should expect the scaling $\epsilon \propto T^4$. Hint: note that your problem depends on k_B, c, $\hbar$, and T; V has been divided out. Identify a relevant energy and time scale, which *via* c gives you access to a length. Explain your reasoning using only a *few* words.

5. Phase Coexistence: (20 points)

Consider a closed system of N identical particles in a volume V and with energy U. Assume that this system has two competing phases labeled 1 and 2, with associated free energies. Suppose phase 1 consists of N_1 particles in a volume V_1 and phase 2 consists of N_2 particles in a volume V_2. The total energy of phase 1 is U_1 while the total energy of phase 2 is U_2. Since the total number of particles is N, we can immediate write that $N = N_2 + N_1$. Similarly, we have $V = V_2 + V_1$ and $U = U_2 + U_1$.

(a) Sketch the situation.

(b) Use the second law of thermodynamics and properties of equilibrium to argue in a *few* words that

$$\left(\frac{\partial S}{\partial U_1}\right)_{V_1, V_2, N_1, N_2, U} = 0. \tag{3}$$

(c) Using the first and second law, rewrite the expression in Eq. (3) to show that in coexistence and in equilibrium the temperatures must be equal. Hint: use problem Q1c if you need $\mathrm{d}U$.

It turns out that when the material is in phase 1, the equation of state is given by

$$\beta p = a(\beta) + b(\beta)\beta\mu \tag{4}$$

where $\beta = 1/(k_\mathrm{B}T)$, with T the temperature and k_B Boltzmann's constant, and $a(\beta)$ and $b(\beta)$ are positive functions of β and μ is the chemical potential. In phase 2, the equation of state is given by

$$\beta p = c(\beta) + d(\beta)\,(\beta\mu)^2\,, \tag{5}$$

where $c(\beta)$ and $d(\beta)$ are positive functions of β and $d > b$ and $c < a$.

(d) Determine the density change $(\rho_2 - \rho_1)$ that occurs when the material undergoes a phase transition from phase 1 to phase 2; assume that the density ρ_1 is smaller than ρ_2 at coexistence.

(e) Also determine the pressure at which the transition occurs.

The final answer for both questions (d) and (e) should be an expression of a, b, c, d, and β only. Hint: The Gibbs-Duhem equation might be useful (see problem Q1g).

The exam continues on the next page ⇒

6. Particles in a Well: (10 *bonus* points)

Assume we have a system of N non-interacting — for part (a) you may presume these to be point-like — particles in a three-dimensional volume V. The particles are attracted to a well and experience a potential given by

$$\beta U(r) = \begin{cases} \lambda\left(\left|\frac{\boldsymbol{r}_i}{r_c}\right| - 1\right) & \text{if} \quad |\boldsymbol{r}_i| < r_c \\ 0 & \text{if} \quad r \geq r_c \end{cases} \tag{6}$$

where $\boldsymbol{r}_i$ is the position of the i-th particle and r_c is the range of the interaction between the particles and the well.

(a) Write $V_0 = (4/3)\pi r_c^3$ and use this to show that the free energy is given by

$$\beta F/N = \log\left(\rho\Lambda^3\right) - 1 - \log\left(1 - \frac{V_0}{V} + 3\frac{V_0}{V}\int_0^1 \mathrm{d}x\, x^2 e^{-\lambda(x-1)}\right), \tag{7}$$

where Λ is the de Broglie wavelength. Hint: Assume that the total volume V is spherical, with radius R, and start by writing down the Hamiltonian of the system and appropriate expression for the partition function.

A scientist now performs diligent calorimetric measurements on the gas particles and finds the following curve for the ratio γ of the isobaric and isochoric heat capacities, see Fig. 1.

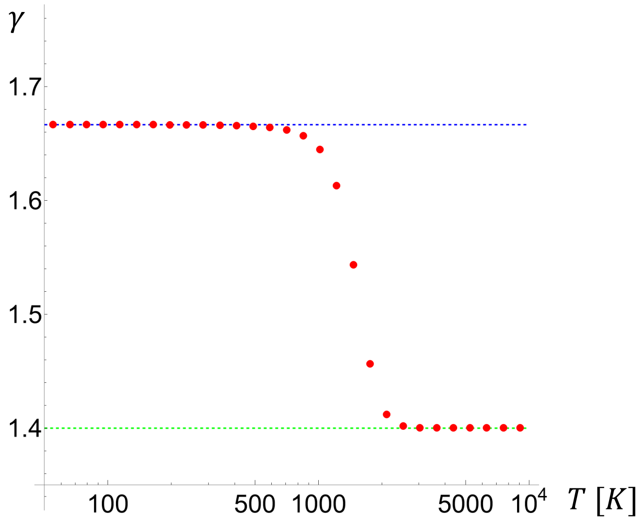

Figure 1: The heat-capacity ratio γ as a function of the temperature T.

(b) Use your knowledge of equipartition to argue how many degrees of freedom this gas has at low and high temperature. Use a *few* words to explain your answer.

The exam ends here ☺!