Physics 112 - Intro to Statistical and Thermal Physics - Spring 2023
Problem Set 07

Due Friday, March 17 at 11:59 PM (PDT)
Last Update: March 10, 2023

Programming note: The midterm exam will be released on Wednesday, March 22 at 6:00pm, PDT. The exam will be distributed via e-mail so I will need confirmation of everyone's e-mail addresses. I will send out an e-mail along with the release of this problem set to confirm your e-mail addresses. ***If you have not received this confirmation e-mail by the evening of Friday, March 10 please contact me directly at ajh38@berkeley.edu or through the bCourses messaging system.***

As mentioned, the exam will be a 24-hour take-home exam and will be open-book/open-notes/open-internet-within-reason. You will not be allowed to collaborate with anyone, use any AI-assisted chat tools, use any "study aid" sites that allow you to submit questions, or copy any portion of the exam to a search engine.

The exam will cover through the end of the material covered on this week's problem set (dealing with the canonical ensemble). Solutions will be posted promptly at the late deadline so you have them available for study and to reference during the exam period.

The next problem set after this one - Problem Set 08 - will not be due until the end of the week we return from spring break.

- **Highlighted/Most Relevant Reading for the material on this week's problem set:**
    - Schroeder, Sections 6.1-6.7.
- **Reading for next week:**
    - Schroeder, 6.4-6.7; 7.1

Problem 7.1 - The Canonical Two-State Paramagnet

Alright, people, let's do this one last time!

Consider again a paramagnet system of N spins in a magnetic field B. We will use the symbol s to denote a microstate of this system, which ammounts to determining all N individual spins $\sigma_i = \pm 1$ $(i = 1, \cdots, N)$. The Hamiltonian/energy function for this system is a function of the N individual spins,

$$E(s) = \mathcal{H}(\{\sigma_i\}) = -\mu B \sum_{i=1}^{N} \sigma_i.$$

Let our paramagnet be a closed system in thermal contact with a large reservoir of constant temperature T.

(a) Use the Boltzmann factor to find the probability distribution of just the first spin. That is, find $P_1(\uparrow, T)$ and $P_1(\downarrow, T)$.

(b) Find the canonical partition function $Z(T, N)$ for the N-spin paramagnet.

(c) Using the canonical partition function, show that the expectation value of energy is $\langle E \rangle = -N\mu B \tanh\left(\frac{\mu B}{k_B T}\right)$. Then find the heat capacity C_V.

[*Supplementary Part (Not for Credit): Find the standard deviation of the energy $\sigma_E \equiv \sqrt{\langle E^2 \rangle - \langle E \rangle^2}$ for this system.*]

The **magnetization** M of a system is the magnetic moment density - that is, the magnetic moment per unit volume,[1]

$$M \equiv \frac{1}{V}\left(\mu \sum_{i=1}^{N} \sigma_i\right) = -\frac{\mathcal{H}}{BV}.$$

This means the expected value of magnetization is related to the expected value of energy via

$$\langle M \rangle = -\frac{\langle E \rangle}{BV}.$$

The **magnetic susceptibility** χ is defined as the measure of how much our paramagnet will "become magnetized" when exposed to an external magnetic field B,

$$\chi \equiv \left(\frac{\partial \langle M \rangle}{\partial B}\right)_V.$$

Suppose our system has a density of spins $n \equiv N/V$.

(d) **Extra Part** (*Not for Credit*) Show the following results for the magnetization $\langle M \rangle$ and susceptibility χ of our paramagnet as functions of temperature,

$$\langle M \rangle = n\mu \tanh\left(\frac{\mu B}{k_B T}\right), \qquad \chi = \frac{n\mu^2}{k_B T \cosh^2\left(\frac{\mu B}{k_B T}\right)}$$

(e) Consider some reference magnetic field scale B_0. First, demonstrate or argue that parameters $b \equiv B/B_0$, $\tau \equiv k_B T/\mu B_0$, $m \equiv \langle M \rangle/n\mu$, and $x \equiv \chi B_0/n\mu$ are non-dimensional and intensive (i.e. independent of the size of the system). Graph m-vs-τ and x-vs-τ at fixed $B = B_0$ and comment on what happens in the $T \to 0$ and $T \to \infty$ limits at fixed B? Then graph m-vs-b and x-vs-b at fixed $T = \mu B_0/k_B$ and comment on what happens in the $b \to 0$ and $b \to \pm\infty$ limits.

[*Note: Only a brief discussion of the graphs is expected but think about why it makes sense for the magnetization graphs to look the way they do and what high/low temperature and field mean for how the spins in the paramagnet behave.*]

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[1]Schroeder just uses the total magnetic moment, ignoring the volume V but this is the more accurate definition. To make the leap all we do is assume our paramagnet model takes up a fixed volume V.

(f) Use the partition function Z to determine the Helmholtz free energy F. How can we use our knowledge of F to determine the entropy, S? How do we expect F and S to relate to $\langle E \rangle$?
[*Supplementary Part (Not for Credit): Now do it! Solve for S and explicitly show that your relation between F, S, and $\langle E \rangle$ is satisfied.*]

Problem 7.2 - Canonizing the Ideal Gas

In Problems 5.2 and 6.2 we looked at an ideal gas as an isolated system and from the microcanonical standpoint. It was a lot and even then we were only looking at monoatomic gases. Now that we have our canonical ensemble we should have an easier time and we will also be able to study internal structure! In particular, even though we still have a gigantic phase space, we can easily break up our closed system into managable closed sub-systems.

Consider N particles of ideal gas in a box of volume V and in thermal contact with a reservoir of temperature T. We will let our ideal gas particles have some internal structure and dynamics, like rotational and vibrational modes.[2] Let $i = 1, \cdots N$ label the gas particles and let $E_{\text{int},i}$ be the ***internal energy*** of the i-th molecule (containing, for example, the rotational energy and vibrational kinetic and potential energies). Rather than studying the full gas let's focus our attention on a *single molecule*. Given a microstate $\jmath_1$, the energy is given by

$$E(\jmath) = \frac{|\vec{p}_1|^2}{2m} + E_{\text{int},1},$$

where our microstate is determined by its position $\vec{x}$ (which can be any position inside our volume), its momentum $\vec{p}$ (with no restrictions), and its internal state $\jmath_{\text{int}}$ (which may contain information like the rotational and vibrational quantum numbers). We will also make use of the following definitions:

$$Z_{\text{int},1} \equiv \sum_{\jmath_{\text{int}}} e^{-\beta E_{\text{int},1}(\jmath_{\text{int}})}, \qquad \lambda_{th} \equiv \frac{h}{\sqrt{2\pi m k_B T}}, \qquad n_Q \equiv \frac{1}{\lambda_{th}^3} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}.$$

Note that the "sum over microstates" for the phase space variables $(\vec{x}_1, \vec{p}_1)$ of our first particle becomes a phase space integral,

$$\text{``} \sum_{\jmath(\vec{x},\vec{p})} (\text{stuff}) \text{''} \quad \Longrightarrow \quad \iiint \iiint (\text{stuff}) \frac{d^3\vec{x}\, d^3\vec{p}}{h^3},$$

where the h^3 is our "unit of phase space volume."

(a) Determine the partition function Z_1 for a single particle of our ideal gas.
Hint (highlight to reveal): [The "sum over microstates" will become a 3D volume integral $\iiint d^3\vec{x}$ over positions, a 3D momentum integral $\iiint d^3\vec{p}$ over the momenta, and a discrete sum $\sum_{\jmath_{\text{int}}}$ over the internal microstates.]
Answer (highlight to reveal): [$Z_1 = V n_Q Z_{\text{int},1} = V Z_{\text{int},1}/\lambda_{th}^3$.]

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[2]To see some of the many possible vibrational modes and their energies for a polyatomic molecule, check out the dancing molecules at https://www.chem.purdue.edu/jmol/vibs/.

If our N gas particles were *distinguishable* we would be able to use our result from Problem Set 6 and simply declare that since each of the N particles has the same 1-particle partition function Z_1, the total partition function would be

$$Z = Z_1^N, \qquad \text{Distinguishable particles.} \tag{1}$$

On the other hand, if the particles are *indistinguishable*, we will need to divide by an "overcounting" factor $N!$ to get the proper partition function (just like we needed to do with Ω),

$$Z = \frac{Z_1^N}{N!}, \qquad \text{Indistinguishable particles.} \tag{2}$$

(b) Show that the Helmholtz free energy as determined by Eq. 1 is *not* extensive but that the Helmholtz free energy as determined by Eq. 2 *is* extensive. You may use Stirling's approximation for the second part (and may ignore the square root term).

(c) Find the Helmholtz free energy for our ideal gas using Eq. 2 and use this to find the chemical potential.
[*Note: You may define* $\mu_{int} = -k_B T \ln Z_{int,1}$.]

Now we can explore some internal structure! First, let's look at a vibrational mode. Consider a single internal vibrational mode of frequency[3] ω. This is just another harmonic oscillator so we can use our result from analyzing the Einstein solid last week and in the lecture notes to show

$$Z_{\text{int},1} = \left(2 \sinh \left(\frac{\hbar \omega}{2 k_B T} \right) \right)^{-1}.$$

(d) **Extra Part** (*Not for Credit*) Determine μ_{int} for this vibrational mode, non-dimensionalize, and plot the graph of non-dimensionalized chemical potential vs. non-dimensionalized temperature.

Are you ready for a cool application?[4] Let us gaze long the abyss of interstellar space and learn about the universe via what gazes back into us.[5] Cold interstellar gas clouds often contain the molecule **cyanogen** (CN), which we will treat as an ideal gas with internal *rotational* modes. The Hamiltonian for rotations of a diatomic molecule is

$$\mathcal{H} = \frac{|\vec{L}|^2}{2I},$$

where $\vec{L}$ is the angular momentum about the center of mass and I is the moment of inertia. According to quantum mechanics, the angular momentum states are given by two quantum numbers j and m_j, where j gives the magnitude of angular momentum,

$$\left| \vec{L} \right|^2 = \hbar^2 j(j+1), \qquad j \in \{0, 1, 2, \cdots\},$$

and m_j gives the z-component. What is important here is that, given a j, the quantum number m_j can take on $2j+1$ possible values ranging from $-j$ to $+j$. Therefore, the energy levels and energy multiplicities for a single diatomic molecule's rotations is given by

$$s_{\text{rotation}} = \{j, m_j\}, \qquad E(s_{\text{rotation}}) = \frac{\hbar^2 j(j+1)}{2I} = \varepsilon\, j(j+1), \qquad \varepsilon \equiv \frac{\hbar^2}{2I}.$$

For cyanogen, we measure that $\varepsilon = 2.4 \times 10^{-4}\,\text{eV}$.

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[3]For example, in hydrogen chloride there is a single vibrational mode which has $\omega \approx 5 \times 10^{14}\,\text{s}^{-1}$.

[4]Of course you are!

[5]This problem is adapted from Schroeder problem 6.12.

In 1941, studies of starlight passing through interstellar gas clouds showed that the relative probability of CN molecules being in excited $j = 1$ states as compared to the ground state is 0.29 (29%).

(e) Under the assumption that the CN cloud was in thermal equilibrium with some thermal reservoir at temperature T, what would T need to be to account for these observations? Comment on the result - what is this "thermal reservoir"?
[*Note: The temperature should be* near *a familiar temperature, though errors in the data were fairly large so it doesn't match the modern accepted value exactly.*]
Hint (highlight to reveal): [There are *three* different possible $j = 1$ states (corresponding to $m_j = -1, 0, +1$), so you wlil have to take this multiplicity into account.]

(f) Assuming the temperature you found in the previous part is accurate, what is the predicted relative proportion of molecules in $j = 2$ states as compared to the ground state?

(g) Extra Part (*Not for Credit*) Define non-dimensional temperature $x \equiv k_B T/\varepsilon$ and create a script (in Python or some other program) that will generate a data table for the probability distribution P_j for a given (non-dimensional) temperature input x. That is, P_j is the probability of being in an internal microstate with energy $E_j = \varepsilon j(j+1)$ when the temperature is $T = x\varepsilon/k_B$. Note that since there is no upper bound on the quantum number j you will need to impose a "reasonable" cutoff j_{max} for the sum, but it is up to you how to choose this cutoff. Plot your results as histograms for $x = 3$, $x = 30$, and finally for the temperature you found in part (e).
Hint (highlight to reveal): [The results are given in Figure 6.7 of Schroeder.]

Problem 7.3 - Probability Distributions

In lecture we will derive the ***Maxwell distribution of speeds*** from the canonical ensemble,

$$\rho(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 e^{-mv^2/k_B T}, \tag{3}$$

where $\rho(v)\, dv$ is defined as the probability of finding the speed of a particle within some infinitessimal range dv of the speed v. Note that this distribution is normalized, $\int_0^{\inf} \rho(v) dv = 1$. The first few sub-parts of this problem will be laying the groundwork for this result. We assume that we have a "kinetic-plus-potential" Hamiltonian,

$$\mathcal{H} = \sum_{i=1}^{N} \frac{|\vec{p}_i|^2}{2m} + V(\{\vec{x}_i\}).$$

(a) Extra Part (*Not for Credit*) Argue that the probability distribution for the first momentum vector $\vec{p}_1$ must have the form

$$\rho_p(\vec{p}_1) \propto e^{-|\vec{p}_1|^2/2mk_B T}$$

With this result, normalize to show

$$\rho_p(\vec{p}_1) = \frac{e^{-|\vec{p}_1^2|/2mk_B T}}{(2\pi mk_B T)^{3/2}}.$$

A very useful skill for Part III of this course will be to change variables in probability distributions or densities. The main rule is that the density *times the differential* in one set of variables should equal the density *times the differential* in the other set of variables. If we want to convert between momentum and velocity, for example, we want to satisfy

$$\rho_p(\vec{p}_1)d^3\vec{p}_1 = \rho_v(\vec{v})d^3\vec{v}.$$

We can also define the velocity vector $\vec{v}$ by its magnitude v and the spherical angles θ and φ so $d^3\vec{v} = v^2\, dv\, d\cos\theta\, d\varphi$.

(b) Starting with the result from (a), show that these manipulations do indeed reproduce the Maxwell speed distribution given in Eq. 3.
Hint (highlight to reveal): [An intermediate result should be $\rho_v(\vec{v}_1) = m^3 \rho_p(m\vec{v}_1)$.]

(c) Show that the rms-speed $v_{rms} \equiv \sqrt{\langle v^2 \rangle}$ for this distribution matches what we expect from equipartition.
[Supplementary Part (Not for Credit): Also find the expected speed $\langle v \rangle$ and the speed that occurs with maximum probability $v_{\max}$. These three measures should be near each other but different.]
[Supplementary Part (Not for Credit): Graph the distribution and identify v_{rms}, $\langle v \rangle$, and $v_{\max}$.]

Consider a quadratic term in the Hamiltonian in some variable q, $\mathcal{H}_{q\text{-term}}(q) = C(q - q_0)^2$, where C and q_0 are some constants. Following a similar logic to part (a), we can argue that the probability distribution in q is given by

$$\rho(q) \propto e^{-\beta C(q-q_0)^2}.$$

(d) Find $\langle q \rangle$, σ_q, and $\langle \mathcal{H}_{q\text{-term}} \rangle$.

Commentary: Holy blap! It's equipartition!!

Finally, suppose we have an ideal gas with particles of mass m in a very tall box (so we can approximate the height as effectively infinite) of cross-sectional area A and subjected to gravity. This adds a gravitational potential energy term to the Hamiltonian,

$$\mathcal{H}_{gpe} = \sum_{i=1}^{N} mgz_i,$$

where z_i is the height of the i-th particle and $z = 0$ at the base of the box. Assume no other part of the Hamiltonian depends on the particle heights z_i. Let the box be in thermal equilibrium with a reservoir of temperature T.

(e) Find the normalized probability distribution $\rho(z_1)$ and the expectation value of height $\langle z_1 \rangle$ for one particle. At what height is the probability of finding a particle a factor of 2 smaller than the probability of finding it at ground level?

Commentary: This has been yet another derivation of the law of atmospheres.

Not for Credit - Problem X.1 - The Entropy of Mixing

Note: *If you missed more than one problem set prior to this or if you have already used up the excused late penalties, you may submit this problem to recover points lost from a late penalty or as a partial (25%) assignment. There will be a separate submission bin on Gradescope - do not submit this problem with the rest of Problem Set 7.*

Consider the mixing of two gases. We have a box of total volume $2V$ divided by a non-insulating wall evenly into two chambers each with volume V. The chambers are in thermal contact with each other and the whole box is in thermal contact with a reservoir at temperature T. The left chamber contains N_A particles of an ideal gas of species A and the right chamber contains an equal number N_B particles of an ideal gas of a different species B. At some point we remove the wall dividing the two chambers.

(a) Find the partition function for this system both before and after the wall is removed. Then determine the change in entropy between the two configurations (having the wall vs. not having the wall).
[*Note: You will need to use Stirling's approximation. You do not need to keep track of the factors of $\sqrt{2\pi N}$ for this part but you* will *need it for the next part.*]
Hint (highlight to reveal): [Don't overthink the first part! You will use Eq. 1 and the result from Problem 7.2(a).]
Hint (highlight to reveal): [The most important feature here is that $Z_1 \propto V$]
Hint (highlight to reveal): [To get the entropy first find the Helmholtz free energy.]

(b) Repeat the previous part but now assume that both sides of the box contain the *same* species of particle.
Hint (highlight to reveal): [You will need to use the factor of $\sqrt{2\pi N}$ in Stirling's approximation to get a non-zero result.]
Hint (highlight to reveal): [After removal, all $2N$ particles are now indistinguishable.]
[*Supplementary Part (Not for Credit): Try to explain the physical origin and implications of this (tiny) increase in entropy.*]

Commentary: The additional entropy generated in the above two parts is called the ***entropy of mixing***.

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