

Physics 112 - Intro to Statistical and Thermal Physics - Spring 2023

Problem Set 06

Due Friday, March 10 at 11:59 PM (PST)

Last Update: March 8, 2023

- **Highlighted/Most Relevant Reading for the material on this week's problem set:**

- Schroeder, Sections 2.6, 3.1-3.6.

- **Reading for next week:**

- Schroeder, Sections 3.4-3.6, 6.1-6.3

Problem 6.1 - Return of the Paramagnet

Let's return to our paramagnet system! Consider a two-state paramagnet (our usual setup) with N spins and consider the macrostate with N_{\uparrow} of the N spins aligned with the magnetic field B (and therefore we have $N_{\downarrow} = N - N_{\uparrow}$ spins anti-aligned with the magnetic field). The energy and number of spin orientations were related by

$$U = -\mu B(N_{\uparrow} - N_{\downarrow}); \quad N_{\uparrow} = \frac{N}{2} - \frac{U}{2\mu B}; \quad N_{\downarrow} = \frac{N}{2} + \frac{U}{2\mu B}.$$

For the multiplicity you found something equivalent to the following form (which will be a useful form for us),

$$\Omega(U) \approx \left(\frac{N_{\uparrow}}{N}\right)^{-N_{\uparrow}} \left(\frac{N_{\downarrow}}{N}\right)^{-N_{\downarrow}}.$$

If we have the energy U (and thus the number of up-spins N_{\uparrow}) fixed then the fundamental assumption of statistical mechanics says the microstate probability distribution is

$$P(\sigma_1, \sigma_2, \dots, \sigma_N) = \frac{1}{\Omega(U)},$$

where $\sigma_i = \pm 1$ gives the spin-state of the N_i -th spin (with +1 for aligned, -1 for anti-aligned). In Problem Set 5 we also found the relationship between energy and temperature for this system,

$$U(T) = -N\mu B \tanh\left(\frac{\mu B}{k_B T}\right).$$

Suppose we know that our system has N spins with N_{\uparrow} spins being aligned with the magnetic field (spin-up). Let's see what we can learn about the value of the *first* spin σ_1 (or equivalently any particular one of the N spins).

(a) How many microstates in the microcanonical ensemble associated with N_{\uparrow} have the first spin as spin-up? Given your answer and the fundamental assumption of statistical mechanics, what is the probability $P_1(\uparrow, U)$ of finding the first spin in a spin-up state? You may answer in terms of N and N_{\uparrow} .

Hint (highlight to reveal): [It's not just half of them! Think about the combinatorics. If we know we have N_{\uparrow} total up-spins and we know the first spin is one of the up-spins, what does that leave us?]

(b) Given your answer to (a), the relationship between N_{\uparrow} and energy, and the relationship between energy and temperature, show that

$$P_1(\uparrow, T) = \frac{e^{+\mu B/k_B T}}{2 \cosh\left(\frac{\mu B}{k_B T}\right)}$$

(c) **Extra Part** (*Not for Credit*) Follow similar steps to find $P_1(\downarrow, T)$ and show that our results are normalized as we should expect, $P_1(\uparrow, T) + P_1(\downarrow, T)$.

(d) What is the expectation value $\langle \sigma_1 \rangle(T)$ for the first spin?

Hint (highlight to reveal): [Recall that given a probability distribution $P(X)$ for an observable X , we have $\langle X \rangle = \sum_X X P(X)$]

(e) What happens to $U(T)$, $P_1(\uparrow, T)$, and $\langle \sigma_1 \rangle(T)$ in the two limits $T \rightarrow 0$ and $T \rightarrow \infty$? Plot the non-dimensionalized energy-per-spin $u \equiv U/N\mu B$, $P_1(\uparrow)$, and $\langle \sigma_1 \rangle$ as functions of the non-dimensionalized temperature $\tau \equiv k_B T/\mu B$.

Problem 6.2 - Exploring the Microcanonical Ideal Gas

Last week we found a formula for the entropy of an N -particle monoatomic ideal gas of total energy U in a box of volume V ,

$$S(U, V, N) = Nk_B \left[\frac{5}{2} + \ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right) \right]. \quad (1)$$

We also found that

$$T(U, V, N) = \frac{U}{\frac{3}{2} N k_B}, \quad (2)$$

which agrees with Equipartition.

(a) Show that Eq. 1 is extensive. That is, show that if we scale our system by a factor α ($N \rightarrow \alpha N$, $V \rightarrow \alpha V$, $U \rightarrow \alpha U$) then the entropy also scales by a factor α ($S \rightarrow \alpha S$). Argue or show that this would *not* be the case (that is, our formula would not be extensive) if we had neglected to include the “overcounting” factor of $1/N!$ in our microstate counting formula for $\Omega(U, V, N)$.

(b) Use Eq. 1 to derive the pressure $P(U, V, N)$ and chemical potential $\mu(U, V, N)$.

Hint (highlight to reveal): [Remember the thermodynamic identity for the entropy dS in terms of dU , dV , and dN]

You should have found that the chemical potential is of the form

$$\mu = +k_B T \ln \left(\frac{n}{n_Q} \right).$$

where $n = N/V$ is the concentration. The quantity n_Q has dimensions of concentration $((\text{length})^{-3})$ and is called the **quantum concentration** - the concentration at which we can't ignore quantum effects in our ideal gas. We can also define the **thermal de Broglie wavelength** λ_{th} such that

$$n_Q = \lambda_{th}^{-3}.$$

(c) **Extra Part** (*Not for Credit*) Use your result from part (b) to show that

$$n_Q = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}; \quad \lambda_{th} \equiv \frac{h}{\sqrt{2\pi m k_B T}}.$$

[Note: You can see from this expression that λ_{th} is the de Broglie wavelength associated with the typical momentum scale for our ideal gas particles.]

Suppose we are considering a gas of argon with a fixed number of particles N at room temperature.

(d) Estimate the thermal de Broglie wavelength λ_{th} and quantum concentration n_Q for this gas. Assuming room temperature and to within an order of magnitude, at what pressure would the ideal gas approach the quantum concentration? Alternatively, assuming standard pressure and to within an order of magnitude, at what temperature would the ideal gas approach the quantum concentration?

We claimed in class that the entropy function was very sharply peaked around its equilibrium value. Let's visualize that here. Suppose we break up our isolated system into two subsystems A and B . We let the total volume of the isolated system be V and the volume of sub-system A be $V_A = fV$, where $0 \leq f \leq 1$ is the fraction of the volume occupied by sub-system A . This leaves sub-system B with volume $V_B = V - V_A = (1 - f)V$. Let the total number of particles again be N and the total internal energy be U . Suppose we know that our two subsystems are already in thermal equilibrium at temperature T , which fixes their energies according to Eq. 2. This means we are only considering exchanges of particles. Our maximum entropy state here will correspond to *diffusive* equilibrium.

(e) **Extra Part** (*Not for Credit*) Show that if we use Eq. 2 in Eq. 1 we can write the entropy of our monoatomic ideal gas system (or sub-system) as

$$S(T, V, N) = N k_B \left[\frac{5}{2} + \ln \left(\frac{V n_Q}{N} \right) \right]. \quad (3)$$

Consider the total entropy of our isolated system given the additional piece of information that sub-system A contains $N_A = xN$ particles (leaving sub-system B with $N_B = N - N_A = (1 - x)N$ particles),

$$S_{tot}(T, V, N, x) = S_A(T, V_A, N_A) + S_B(T, V_B, N_B).$$

We expect diffusive equilibrium to occur when $x = f$.¹ Let $S_{max} \equiv S_{tot}(T, V, N, f)$, our entropy at diffusive equilibrium. We also introduce non-dimensionalized parameters $\sigma \equiv S/k_B$ and $v \equiv V n_Q$.

¹Try to convince yourself why this should be the case intuitively/without fancymath before moving on.

(f) Let $f = 0.75$, $v = 100$, and $N = 100$ and graph S_A , S_B , and S_{tot} -vs- x . Does the maximum of S_{tot} occur at $x = 0.75$ as claimed?

[Supplementary Part (Not for Credit): Prove that our maximum entropy does indeed occur when $x = f$ in general.] [Note: These graphs demonstrate that maximizing the total entropy does not necessarily maximize the entropy of the individual subsystems. You can try $N = 600$ as well.]

(g) What is the *relative* probability of finding sub-system A with a fraction x of the particles as compared to the diffusive equilibrium state where sub-system A has a fraction $x = f$ of the particles?

Hint (highlight to reveal): [As an intermediate step you should find

$$P_A(x) = e^{\sigma(x) - \sigma(f)}.$$

You will be able to cancel a lot of things out and at the end of the day your formula should only depend on the parameters x , f , and N . That is, the v s should disappear.]

(h) Graph $P_A(x)$ -vs- x when $f = 0.75$ (sub-system A is three-quarters of the box) for $N = 10^\eta$ for $\eta = \{1, 2, 3, 4\}$. What happens to the peak? What do you expect this graph to look like when we have a mole of gas?

(i) Suppose we had a gas of just $N = 10^6$ particles.² Use your previous results to estimate the probability of half the volume (sub-system A has volume $V/2$) containing only 49% of the particles.

Hint (highlight to reveal): [The answer is absurdly small.]

Problem 6.3 - Introducing Z into the Canon

The microcanonical ensemble is most useful when we have an *isolated* system. By definition, our isolated system has a fixed, conserved amount of total energy U . When we have a *closed* system, however, we can exchange energy with the environment and our closed system is better described by a fixed *temperature*.

Suppose we have a closed system in thermal contact with a large reservoir of temperature T (which fixes the temperature of our closed system to also be T). The **Boltzmann factor** for a given microstate of our closed system is given by

$$\text{Boltzmann factor for a microstate } s: \quad e^{-U(s)/k_B T},$$

where $U(s)$ is the internal energy of the microstate s . The Boltzmann factors represent an *unnormalized* probability distribution (the relative probability between two states is the ratio of their Boltzmann factors). We can normalize the probability distribution by introducing the **canonical partition function** Z ,

$$Z \equiv \sum_{\text{microstates } s} e^{-U(s)/k_B T} \implies P(s) = \frac{e^{-U(s)/k_B T}}{Z}.$$

Consider a system composed of N *non-interacting* subsystems i so that the total internal energy is $U = \sum_i E_i$, where E_i is the energy of the i -th subsystem. We can also define a canonical partition function for each subsystem,

$$Z_i \equiv \sum_{\text{subsystem microstates } s_i} e^{-E_i(s_i)/k_B T}.$$

²This is of course an extremely small number of particles in practice!

(a) Show that for the full system we have

$$Z = \prod_{i=1}^N Z_i.$$

(b) How does adding a *constant* E_0 to the internal energy U (i.e. the same amount of energy is added to *each* microstate in the system) change the Boltzmann factor for a microstate? How does it change the partition function? How does it change the microstate probability distribution $P(s)$?

(c) **Extra Part** (*Not for Credit*) Show that the expectation value of the energy can be found via

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}, \quad \beta \equiv \frac{1}{k_B T}.$$

Now consider an N -oscillator Einstein solid with frequency ω in thermal contact with a reservoir at temperature T . Recall that for a single oscillator the energy levels are $E_n = \hbar\omega(n + \frac{1}{2})$.

(d) What is the relative probability of finding the first oscillator in the n -th excited state as compared to the ground state ($n = 0$)?

(e) Find Z_1 , the partition function for a subsystem consisting of a single oscillator in the solid. Then use part (a) to find the full partition function Z .

Hint (highlight to reveal): [Remember your geometric series! $\sum_{k=0}^{\infty} r^k = 1/(1-r)$.]

(f) Find $\langle E \rangle(T)$ for the Einstein solid and graph $\langle E \rangle$ -vs- T . You will have to do appropriate non-dimensionalizations.

