PHYS301
Homework 6 solutions

Spring 2026

Due: March 15th

Contents

Problem 1 [10 points]

This problem explores the connection between the canonical (standard) partition function Z and its cousin the grand partition function $\mathcal{Z}$ (also called the Gibbs sum). Let Z_N be the canonical partition function for N particles.

a) Show that the **grand partition function** $\mathcal{Z}$ can be written as

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} \lambda^N Z_N(V, T) \tag{1}$$

where $\lambda = e^{\beta\mu}$ is referred to as the *fugacity*. Here, μ is the chemical potential and $\beta = 1/(k_B T)$. We therefore see that the grand partition function can be written as a sum over the standard partition function of systems with different number of particles, each weighted by a different power of λ.

b) The fugacity allows us to write simple expressions for the average particle number $\langle N \rangle$ and its variance $(\Delta N)^2$. Show that

$$\begin{aligned} \langle N \rangle &= \lambda \frac{\partial}{\partial \lambda} \ln \mathcal{Z} \\ (\Delta N)^2 = \langle N^2 \rangle - \langle N \rangle^2 &= \left(\lambda \frac{\partial}{\partial \lambda} \right)^2 \ln \mathcal{Z} \end{aligned} \tag{2}$$

c) If $Z_N = Z_1^N / N!$ (where Z_1 is the partition function for one particle), show that

$$\mathcal{Z}(\mu, V, T) = e^{\lambda Z_1(V,T)} \tag{3}$$

d) In this case, show that the particle number N in the system is very sharply peaked around $\langle N \rangle$ when N is large, that is,

$$\frac{\Delta N}{\langle N \rangle} = \frac{1}{\langle N \rangle^{1/2}} \tag{4}$$

a) Recall that the canonical (standard) partition function Z was defined as

$$Z = \sum_n e^{-\beta E_n} \tag{5}$$

To make things clear, it is relevant to write the grand partition function as a double sum

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{\text{states } i} e^{-\beta(E_{i,N} - \mu N)} \tag{6}$$

That is, N labels how many particles we have in a given microstate, while the index i labels the configuration for those N particles. With both sums explicitly, we see that

$$\begin{aligned}\mathcal{Z} &= \sum_{N=0}^{\infty} \sum_{\text{states } i} e^{-\beta E_{i,N}} e^{\beta\mu N} \\ &= \sum_{N=0}^{\infty} \left(\sum_{\text{states } i} e^{-\beta E_{i,N}} \right) (e^{\beta\mu})^N \\ &= \sum_{N=0}^{\infty} Z_N(V,T)\lambda^N\end{aligned} \tag{7}$$

as expected.

b) By definition, $\langle N \rangle$ is

$$\langle N \rangle = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} N\lambda^N Z_N \tag{8}$$

By direct computation, we see that the proposed formula matches the above:

$$\begin{aligned}\lambda \frac{\partial}{\partial\lambda} \ln \mathcal{Z} &= \frac{\lambda}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \lambda} \quad \text{(chain rule)} \\ &= \frac{\lambda}{\mathcal{Z}} \sum_{N=0}^{\infty} N\lambda^{N-1} Z_N \\ &= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} N\lambda^N Z_N \\ &= \langle N \rangle\end{aligned} \tag{9}$$

To show the result for variance, first note that

$$\langle N^2 \rangle = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} N^2 \lambda^N Z_N \tag{10}$$

Then by direction computation, we see that

$$\begin{aligned}\left(\lambda \frac{\partial}{\partial\lambda}\right)^2 \ln \mathcal{Z} &= \left(\lambda \frac{\partial}{\partial\lambda}\right) \lambda \frac{\partial}{\partial\lambda} \ln \mathcal{Z} \\ &= \lambda \frac{\partial}{\partial\lambda} \left(\frac{\lambda}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial\lambda} \right) \\ &= \frac{1}{\mathcal{Z}} \lambda \left(\frac{\partial \mathcal{Z}}{\partial\lambda} - \frac{\lambda}{\mathcal{Z}} \left(\frac{\partial \mathcal{Z}}{\partial\lambda} \right)^2 + \lambda \frac{\partial^2 \mathcal{Z}}{\partial\lambda^2} \right) \\ &= \langle N \rangle - \langle N \rangle^2 + \frac{\lambda^2}{\mathcal{Z}} \sum_{N=0}^{\infty} N(N-1)\lambda^{N-2} Z_N \\ &= \langle N \rangle - \langle N \rangle^2 + \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} N(N-1)\lambda^N Z_N \\ &= \langle N \rangle - \langle N \rangle^2 + \langle N^2 \rangle - \langle N \rangle \\ &= \langle N^2 \rangle - \langle N \rangle^2\end{aligned} \tag{11}$$

c) Given

$$Z_N = \frac{Z_1^N}{N!} \tag{12}$$

It follows that

$$\begin{aligned}
\mathcal{Z} &= \sum_{N=0}^{\infty} \lambda^N Z_N \quad \text{(as in part (a))} \\
&= \sum_{N=0}^{\infty} \lambda^N \frac{Z_1^N}{N!} \\
&= \sum_{N=0}^{\infty} \frac{(\lambda Z_1)^N}{N!} \\
&= e^{\lambda Z_1}
\end{aligned} \tag{13}$$

Where the last line follows from the series expansion of the exponential function:

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} \tag{14}$$

d) Using the results from part (b), it follows that

$$\begin{aligned}
(\Delta N)^2 &= \left(\lambda \frac{\partial}{\partial \lambda}\right)\left(\lambda \frac{\partial}{\partial \lambda}\right) \ln e^{\lambda Z_1} \\
&= \left(\lambda \frac{\partial}{\partial \lambda}\right)\left(\lambda \frac{\partial}{\partial \lambda}\right) \lambda Z_1 \\
&= \left(\lambda \frac{\partial}{\partial \lambda}\right) \lambda Z_1 \\
&= \lambda Z_1
\end{aligned} \tag{15}$$

And

$$\begin{aligned}
\langle N \rangle &= \lambda \frac{\partial}{\partial \lambda} \ln e^{\lambda Z_1} \\
&= \lambda \frac{\partial}{\partial \lambda} \lambda Z_1 \\
&= \lambda Z_1
\end{aligned} \tag{16}$$

It follows that

$$\Delta N = \sqrt{\lambda Z_1} = \langle N \rangle^{1/2} \tag{17}$$

Hence

$$\frac{\Delta N}{\langle N \rangle} = \frac{1}{\langle N \rangle^{1/2}} \tag{18}$$

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Problem 2 [4 points]

Live cells from plants and animals are generally not in chemical equilibrium with their surrounding. For instance, the number density $n = N/V$ of potassium K^+ ions in the internal sap of a plant cell (for example, a fresh water alga) may exceed by a factor of 10^4 the number density of K^+ ions in the pond water in which the cell is growing. The chemical potential of the K^+ ions is thus much higher inside the cell than in its surrounding. Estimate the difference in chemical potential between the cell's interior and the pond water surrounding it at $T = 300$ Kelvin, and show that it is equivalent to a voltage of 0.24 volts across the cell wall. You can approximate the chemical potential μ as that of an ideal gas.

Recall that the entropy for an ideal gas with thermal wavelength λ is (Sackur-Tetrode)

$$\begin{aligned} S &= k_B N \left(\ln\left(\frac{V}{N\lambda^3} \right) + \frac{5}{2} \right) \\ (C = h/\sqrt{2\pi m k_B}) \qquad &= k_B N \left(\ln\left(\frac{V}{NC^3 T^{-3/2}} \right) + \frac{5}{2} \right) \\ (\text{since } E = \frac{3}{2}k_B N T) \qquad &= k_B N \left(\ln\left(\frac{V}{NC^3} \left(\frac{2}{3}\frac{E}{k_B N} \right)^{3/2} \right) + \frac{5}{2} \right) \\ &= k_B N \left(\ln\left(\frac{V}{NC^3} \right) + \frac{3}{2}\ln\left(\frac{2E}{3k_B N} \right) + \frac{5}{2} \right) \end{aligned} \tag{19}$$

So we can compute the chemical potential directly, paying special attention to implicit N-dependence[1].

$$\begin{aligned} \mu &= -T\left(\frac{\partial S}{\partial N} \right)_{E,V} \\ &= -T\left(k_B \ln\left(\frac{V}{c^3 N} \right) + \frac{3}{2}k_B \ln\left(\frac{2E}{3k_B N} \right) \right) \\ &= -Tk_B \ln\left(\frac{V}{c^3 N} \right) - Tk_B \ln(T^{3/2}) \\ &= -Tk_B \ln\left(\frac{V}{N}\frac{1}{\lambda} \right) \\ &= -Tk_B \ln(1/n\lambda^3) \\ &= k_B T \ln(n\lambda^3) \end{aligned} \tag{20}$$

Then the difference in chemical potentials is

$$\Delta\mu \equiv \mu_{\text{in}} - \mu_{\text{out}} = k_B T \ln\left(\frac{n_{\text{in}}}{n_{\text{out}}} \right) \tag{21}$$

[1] The thermal wavelength is given by $\lambda = CT^{-1/2}$, where C is a constant with value $C = h/\sqrt{2\pi m k_B}$, and T itself depends on energy as $E = \frac{3}{2}Nk_BT$. This means that if we vary N while keeping E constant (which we do when we compute μ), then T must vary as well.

With the formal expression out of the way, let's plug the numbers $\frac{n_{\text{in}}}{n_{\text{out}}} = 10^4$ and $T = 300$ Kelvin:

$$\begin{aligned}\Delta\mu &= (8.6173 \times 10^{-5}\ \text{eV} \cdot \text{K}^{-1})(300\ \text{K}) \ln\left(10^4\right) \\ &= 0.238105\ \text{eV} \\ &\simeq 0.24\ \text{eV}\end{aligned} \tag{22}$$

Where I conviniently used Boltzmann's constant in[2] eV per Kelvin (rather than Joules per Kelvin), which allows us to directly see that there is a voltage of **0.24 volts** across the cell wall. ■

[2]Recall that an electronvolt is the energy gained by moving a charge e (electron's charge) across 1 volt of potential difference.

Problem 3 [8 points]

Consider a system of five particles, inside a container where the allowed energy levels are nondegenerate and evenly spaced (that is, the energy levels are 0, ϵ, 2ϵ, 3ϵ, 4ϵ, etc.) In this problem you will consider the allowed states for this system, depending on whether the particles are identical fermions, identical bosons, or distinguishable particles.

a) Describe the ground state of this system, for each of these three cases.

b) Suppose that the system's total energy is ϵ. Describe the allowed states of the system, for each of the three cases. How many possible system states are there in each case?

c) Repeat part (b) when the total energy of the system is 2ϵ.

d) Suppose that the temperature of this system is low, so that the total energy is low (through not necessarily zero). In what way will the behavior of the bosonic system differ from that of the system of distinguishable particles? Discuss

a) The ground state if

- Fermions: Each level can be held by at most one fermion, so the lowest energy state consists of one electron in each of the 5 lowest levels, so

$$E = 0 + \epsilon + 2\epsilon + 3\epsilon + 4\epsilon = 10\epsilon \tag{23}$$

- Bosons: Bosons can occupy the same energy level, even if it is already occupied. As such, the lowest state has all 5 particles in the lowest level, yielding a total energy of

$$E = 0 + 0 + 0 + 0 + 0 = 0 \tag{24}$$

- Distinguishable particles: Same as bosons, so $E = 0$.

b) Let $E = \epsilon$.

- Fermions: There are no possible states. We can put one of the fermions in the $E = 0$ level, the next in the $E = \epsilon$ level, and we already ran out of energy budget to allocate. This, again, follows from the fact that fermions can't share a level with other fermions.
- Bosons: We can't distinguish them, so only *relative* positions matter. The only way to have total energy $E = \epsilon$ is to have four of them in the lowest energy state ($E = 0$) and one of them in the first excited energy level $E = \epsilon$. This satisfies the budget: $0+0+0+0+\epsilon = \epsilon$, and it is the only possible state.
- Distinguishable particles: Then the bosonic example above can be written in 5 different ways, each corresponding to having one of the five particles in the ϵ level while the other four are in the 0 level.

c) Let $E = 2\epsilon$.

- Fermions: Same as in (b), no states.

- Bosons: We can have one of them in the 2ϵ level and the rest in the 0 level, or two of them in the ϵ level while the other three are in the 0 level. These two are the only states with total $E = 2\epsilon$.
- Distinguishable particles: Following on the two states described for bosons, the case where one of them is in the 2ϵ level can be achieved in 5 different ways, while the case where we pick two from 5 of them to be in the ϵ level can be achieved in $\binom{5}{2} = 10$ ways. There are a total of $5 + 10 = 15$ states with $E = 2\epsilon$.

d) As we observed from parts (b) and (c), the bosonic system and the distinguishable-particles system *share* configurations (such as "one particle in ϵ state while the rest are in the 0 state"), with the distinguishable-particles system always having more states per configuration. As such, at a given temperature, we can expect the entropy of the distinguishable system to be larger than the entropy of the bosonic system. Conceptually, the distinguishable system has more *disorder*.

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