PHSX 671: Homework #4

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Problem 1

4.1: A system consists of N identical, non-interacting, and distinguishable particles. There are two energy states accessible to each particle, ϵ_1 and ϵ_2 with $\epsilon_2 > \epsilon_1$.

(a) What is the partition function for a single particle of this system?

Solution:

The partition function is

$$Z = \sum_{i=1}^{N} e^{-\beta\epsilon_n}$$

Where we have two states, so it is then

$$Z = e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}$$

(b) What is the partition function for the entire system of N particles?

Solution:

We found in class that for a system of N particles the partition function Z is exponentiated by the number of particles:

$$Z = \left(e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}\right)^N$$

(c) What is the mean energy of this system?

Solution:

$$\begin{aligned}
\bar{\epsilon} &= \frac{\sum_{n=1}^{N} p_n \epsilon_i}{\sum_{n=1}^{N} p_n} \\
&= \frac{\sum \frac{g_n \epsilon_n e^{-\beta e_n}}{Z}}{\sum \frac{g_n e^{-\beta e_n}}{Z}} \\
&= \frac{\sum g_n \epsilon_n e^{-\beta e_n}}{\sum g_n e^{-\beta e_n}} \\
&= -\frac{1}{Z}\frac{\partial}{\partial \beta}\sum e^{-\beta \epsilon_i} \\
&= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\
&= -\frac{\partial \ln Z}{\partial \beta}
\end{aligned}$$

In our case we then have:

$$\begin{aligned}
\bar{\epsilon} &= -\frac{\partial}{\partial \beta}\left[\ln\left\{\left(e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}\right)^N\right\}\right] \\
&= -N\frac{\partial}{\partial \beta}\ln\left(e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}\right) \\
&= -N\frac{1}{-e^{-\beta\epsilon_1} - e^{-\beta\epsilon_2}}\left(-\epsilon_1 e^{-\beta\epsilon_1} - \epsilon_2 e^{-\beta\epsilon_2}\right) \\
&= N\frac{\epsilon_1 e^{-\beta\epsilon_1} + \epsilon_2 e^{-\beta\epsilon_2}}{e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}}
\end{aligned}$$

(d) What is the entropy of this system?

Solution:

The definition of entropy most easily applied here is equation (4.3)

$$\begin{aligned}
\mathcal{S} &= \ln(Z) + \beta\bar{\epsilon} \qquad (4.3) \\
&= (-\beta\epsilon_1 - \beta\epsilon_2) + \beta N\frac{\epsilon_1 e^{-\beta\epsilon_1} + \epsilon_2 e^{-\beta\epsilon_2}}{e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}} \\
&= -N\frac{\beta e^{-\beta\epsilon_2}\epsilon_1 + \beta e^{-\beta\epsilon_1}\epsilon_2}{e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}}
\end{aligned}$$

Problem 2

4.2: Now add an energy baseline or offset term, ϵ_0, to each of the accessible energy states in Question 4.1. Thus, the new energy states are $\epsilon_1 + \epsilon_0$ and $\epsilon_2 + \epsilon_0$.

(a) What is the partition function for a single particle of this system?

Solution:

$$\begin{aligned} Z' &= e^{-\beta\epsilon_1+\epsilon_0} + e^{-\beta\epsilon_2+\epsilon_0} \\ &= e^{\epsilon_0} Z \end{aligned}$$

(b) What is the partition function for the entire system of N particles?

Solution:

$$\begin{aligned} Z' &= \left(e^{-\beta\epsilon_1+\epsilon_0} + e^{-\beta\epsilon_2+\epsilon_0}\right)^N \\ &= e^{N\epsilon_0} Z \end{aligned}$$

(c) What is the mean energy of this system?

Solution:

$$\begin{aligned} \bar{\epsilon} &= -\frac{N}{e^{-\beta\epsilon_1+\epsilon_0} + e^{-\beta\epsilon_2+\epsilon_0}} \left\{-\epsilon_1 e^{-\beta\epsilon_1+\epsilon_0} - \epsilon_2 e^{-\beta\epsilon_2+\epsilon_0}\right\} \\ &= N\frac{\epsilon_1 e^{-\beta\epsilon_1} + \epsilon_2 e^{-\beta\epsilon_2}}{e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}}\epsilon_0 \end{aligned}$$

(the extra term factors out nicely!)

(d) What is the entropy of this system?

Solution:

$$\begin{aligned} \mathcal{S} &= \ln(Z') + \beta\bar{\epsilon} \\ &= \ln(Z') + \beta\left(N\frac{\epsilon_1 e^{-\beta\epsilon_1} + \epsilon_2 e^{-\beta\epsilon_2}}{e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}}\epsilon_0\right) \\ &= \epsilon_0 \ln(Z) + \beta\left(N\frac{\epsilon_1 e^{-\beta\epsilon_1} + \epsilon_2 e^{-\beta\epsilon_2}}{e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}}\epsilon_0\right) \\ &= -N\beta\frac{\beta e^{-\beta\epsilon_2}\epsilon_1 + \beta e^{-\beta\epsilon_1}\epsilon_2}{e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}} \end{aligned}$$

(e) What properties of the system were affected by this energy offset? What properties were not affected? What conceptual arguments can you give for this?

Solution: The mean energy increases, but the entropy does not. This is because the energy does go up on average but the distribution of energies is not changed.

Problem 3

4.3: A system possesses three energy levels, $E_1 = \epsilon$, $E_2 = 2\epsilon$ and $E_3 = 3\epsilon$, with degeneracies $g(E_1) = g(E_3) = 1$, $g(E_2) = 2$. Determine the mean energy of this system.

Solution:
The partition function with degeneracy is

$$\begin{aligned} Z &= \sum_{i=1}^{N} g_i e^{-\beta\epsilon_i} \\ &= e^{-\beta\epsilon} + 2e^{-\beta 2\epsilon} + e^{-\beta 3\epsilon} \end{aligned}$$

$$\begin{aligned} \bar{\epsilon} &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\ &= \left(e^{-\beta\epsilon} + 2e^{-\beta 2\epsilon} + e^{-\beta 3\epsilon}\right)^{-1}\left(-\epsilon e^{-\beta\epsilon} - 4\epsilon e^{-\beta 2\epsilon} - 3\epsilon e^{-\beta 3\epsilon}\right) \\ &= \frac{\epsilon e^{-\beta\epsilon} + 4\epsilon e^{-\beta 2\epsilon} + 3\epsilon e^{-\beta 3\epsilon}}{e^{-\beta\epsilon} + 2e^{-\beta 2\epsilon} + e^{-\beta 3\epsilon}} \end{aligned}$$

Problem 4

4.4: A system consists of N non-interacting particles at a temperature T sufficiently high so that we are in a classical limit. Each particle has mass m and is free to perform one dimensional oscillations about its equilibrium position. Calculate the heat capacity of this system of particles at this temperature when

(a) The restoring force for the oscillations is proportional to the displacement of the particle from its equilibrium position.

Solution:

$$C = \frac{\partial S}{\partial T}$$

The force and energy is given by

$$F = -kx; \quad \rightarrow \quad U = -\int_0^x -kx\ dx$$
$$E = \sum_i^N \frac{p_i^2}{2m} + \frac{1}{2}kx_i^2$$

Chapter 4 gives us the equipartition theorem, each quadratic term contributes $\frac{1}{2\beta}$ average energy to the system, where $\frac{1}{\beta} = k_BT$:

$$\frac{\bar{E}}{N} = \frac{1}{2}k_BT + \frac{1}{2}k_BT = k_BT$$

Which for N particles is just

$$\bar{E} = Nk_BT$$

Consequently heat capacity C is

$$C = Nk_B$$

(b) The restoring force for the oscillations is proportional to the cube of the displacement of the particle from its equilibrium position.

Solution:

$$F = -kx^3; \quad \rightarrow \quad U = -\int_0^{x^3} -kx\ dx$$
$$E = \sum_i^N \frac{p_i^2}{2m} + \frac{1}{4}kx_i^4$$

$$Z = \prod_i^N \int_{-\infty}^{\infty} e^{-\beta p_i^2/(2m)}\, dp_i \int_{-\infty}^{\infty} e^{-\beta kx^4/4}\, dx_i$$
$$= \left(\frac{\pi(2m)}{\beta}\right)^{N/2} \prod_i^N \int_{-\infty}^{\infty} e^{-\beta kx^4/4}\, dx_i$$

Since mean energy is given by $-\frac{\partial \ln Z}{\partial \beta}$, we can actually just try separating out β, because even if we don't know the full solution to the second integral, as long as it does not depend on β it will go to

Problem 4 continued on next page...

zero. I will make a u-substitution:

$$u_i = \beta^{1/4} x_i, \quad du_i = \beta^{1/4} dx_i$$

$$= \left(\frac{\pi(2m)}{\beta}\right)^{N/2} \prod_i^N \int_{-\infty}^{\infty} \beta^{-1/4} e^{ku^4/4}\, du_i$$

$$= \beta^{-3N/4} (2\pi m)^{N/2} \prod_i^N \int_{-\infty}^{\infty} e^{ku^4/4}\, du_i$$

$$\ln Z = \ln\left(\beta^{-3N/4}\right) + \ln(2\pi m)^{N/2} + \ln\left(\prod_i^N \int_{-\infty}^{\infty} e^{ku^4/4}\, du_i\right)$$

Only the first term now depends on β, so the mean energy is then:

$$\bar{E} = \frac{3N}{4\beta} = \frac{3}{4} N k_B T$$

$$C = \frac{3}{4} N k_B$$

Problem 5

4.5: A very sensitive spring balance consists of a quartz spring suspended from a fixed support; the mass of the object is determined by the displacement of the spring from its equilibrium position. The spring constant is α and the balance is at temperature T in a location where the acceleration due to gravity is g.

(a) If a very small object of mass m is suspended from the spring, what is the magnitude of the thermal fluctuations of the object about its equilibrium position?

Solution:

The mean displacement is what we want to find here. By the equipartition theorem we have every quadratic in the hamiltonian contributing $\frac{1}{2}k_B T$ in the mean energy.

$$\begin{aligned}\frac{1}{2}kx^2 &= \frac{1}{2}k_B T\\ x^2 &= \frac{k_B T}{k}\\ x &= \sqrt{\frac{k_B T}{k}}\end{aligned}$$

I equated energy to mean energy, so I will argue that this is then the mean displacement.

$$\bar{x} = \sqrt{\frac{k_B T}{k}}$$

(b) What is the minimum mass that can be measured accurately with this balance? (Hint: the thermal fluctuations of the movement of the mass will cause uncertainty in the measurement).

Solution:

Equating the force due to a hanging mass to the spring force, then setting $x \to \bar{x}$:

$$\begin{aligned}mg &= kx\\ m &= \frac{k}{g}\sqrt{\frac{k_B T}{k}}\end{aligned}$$

Problem 6

4.6: 2 moles of nitrogen gas (N_2) and 6 moles of hydrogen gas (H_2) are inside a container and separated from each other by a valve. The entire container is thermally and mechanically isolated from the outside. The gases are initially at the same temperature, T_i. If the valve is opened, the gases interact to form ammonia (NH_3) What is the final temperature of the system if 1 mole of ammonia is formed? You can treat the gasses as ideal with associated molar heat capacities of $\frac{5}{2}R$ for N_2 and H_2 and $3R$ for NH_3.

Solution:
We have remaining moles

$$(2-0.5)N_2 + (6-1.5)H_2 \to NH_3$$

$$1.5N_2 + 4.5H_2 \to NH_3$$

$$\begin{aligned}
\overline{\Delta E} &= nC_V T = 0 \\
&= (2)\left(\frac{5}{2}R\right)T_i + (6)\left(\frac{5}{2}R\right)T_i \\
&\quad -(0.5)\left(\frac{5}{2}R\right)T_f + (1.5)\left(\frac{5}{2}\right)T_f + (1)\,(3R)\,T_f \\
0 &= 20RT_i - 18RT_f \\
T_f &= \frac{20}{18}T_f
\end{aligned}$$

Problem 7

4.7: According to quantum mechanics, rotational kinetic energy is described by the following equation:

$$\epsilon_R = \frac{\hbar^2}{2I} r(r+1) \quad r = 0, 1, 2, \ldots$$

In this equation, I is the moment of inertia for the rotation and each energy level has a degeneracy of $(2r+1)$. The partition function can therefore be calculated as

$$Z_{rot} = \sum_0^{\infty} (2r+1) e^{-\beta \frac{\hbar^2}{2I} r(r+1)}$$

What is the mean rotational kinetic energy at high temperatures? Assume that T is so large that the spacing between the energy levels is small enough to allow for integration of the Boltzmann factors.

Solution:

$$u = \beta \frac{\hbar^2}{2I} r(r+1) \quad \rightarrow \quad du = \beta \frac{\hbar^2}{2I} 2r+1 \; dr$$

$$Z \approx \int_0^{\infty} (2r+1) e^{-\beta \frac{\hbar^2}{2I} r(r+1)} \; dr$$

$$Z \approx \left(\beta \frac{\hbar^2}{2I} \right)^{-1} \int_0^{\infty} \frac{\cancel{2r+1}}{\cancel{2r+1}} e^{-u} \; du$$

Applying the same trick as in problem 4, we can completely ignore the integral and just focus on the part with β.

$$\begin{aligned} \bar{E} = -\frac{\partial \ln Z}{\partial \beta} &= \frac{\partial}{\partial T} \ln \left(\frac{2I}{\hbar^2 \beta} \right) + \cancelto{0}{\ln \ldots} \\ &= -\frac{1}{\beta} \\ &= k_B T \end{aligned}$$