PHYS301
Homework 4 solutions

Spring 2026

Due: February 22nd

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Problem 1 [4 points]

For a system of 1 particle that has nearly continuous microstates in 1 dimension, the partition function can be written as

$$Z_1 = \frac{1}{h}\int dxdp\, e^{-\beta H(x,p)} \tag{1}$$

where $H(x,p)$ is the Hamiltonian of the system as a function of position x and momentum p.

a) If the Hamiltonian is

$$H(x,p) = \frac{p^2}{2m} + \lambda x^4 \tag{2}$$

show that the heat capacity for a gas of N independent such particles is $C_V = 3Nk_B/4$.

b) Explain why the heat capacity is the same regardless of whether the particles are distinguishable or indistinguishable.

a) Recall that heat capacity is defined as

$$C_V = \left(\frac{\partial \langle E\rangle}{\partial T}\right)_V , \tag{3}$$

and that the average energy $\langle E\rangle$ of a system with partition function Z is $\langle E\rangle = -\frac{\partial \ln Z}{\partial \beta}$. Combining this two equations yields an expression for C_V in terms of the partition function:

$$C_V = k_B\beta^2\frac{\partial^2 \ln Z}{\partial \beta^2} \tag{4}$$

Where chain rule was used ($\frac{d\beta}{dT} = -1/k_BT^2$). The partition function for a single particle is:

$$\begin{aligned}
Z_1 &= \frac{1}{h}\int_{p=-\infty}^{\infty}\int_{x=-\infty}^{\infty} e^{-\beta H(x,p)}\, dxdp \\
&= \frac{1}{h}\int_{p=-\infty}^{\infty}\int_{x=-\infty}^{\infty} e^{-\beta p^2/2m}e^{-\beta\lambda x^4}\, dxdp \\
&= \frac{1}{h}\left(\int_{-\infty}^{\infty} e^{-\beta p^2/2m}dp\right)\left(\int_{-\infty}^{\infty} e^{-\beta\lambda x^4}dx\right) \\
&= \frac{1}{h}\sqrt{\frac{2\pi m}{\beta}}\,\frac{2\Gamma(5/4)}{(\beta\lambda)^{1/4}} \\
&= \frac{\sqrt{8\pi m}\Gamma(5/4)}{h\lambda^{1/4}}\beta^{-3/4}
\end{aligned} \tag{5}$$

The partition function for N independent particles is

$$Z = (Z_1)^N \tag{6}$$

The heat capacity follows:

$$\begin{aligned}
C_V &= k_B\beta^2 \frac{\partial}{\partial\beta}\frac{\partial \ln Z}{\partial\beta} \\
&= k_B\beta^2 \frac{\partial}{\partial\beta}\left(\frac{\partial}{\partial\beta}\ln(Z_1^N)\right) \\
&= k_B\beta^2 \frac{\partial}{\partial\beta}\left(\frac{\partial}{\partial\beta}N\ln(Z_1)\right) \\
&= Nk_B\beta^2 \frac{\partial}{\partial\beta}\left(\frac{\partial}{\partial\beta}\ln\left(\frac{\sqrt{8\pi m}\Gamma(5/4)}{h\lambda^{1/4}}\beta^{-3/4}\right)\right) \\
&= Nk_B\beta^2 \frac{\partial}{\partial\beta}\left(\frac{\partial}{\partial\beta}\left(\ln\left[\frac{\sqrt{8\pi m}\Gamma(5/4)}{h\lambda^{1/4}}\right] - \frac{3}{4}\ln(\beta)\right)\right) \\
&= -\frac{3}{4}Nk_B\beta^2 \frac{\partial}{\partial\beta}\left(\frac{\partial}{\partial\beta}\ln(\beta)\right) \\
&= -\frac{3}{4}Nk_B\beta^2 \frac{\partial}{\partial\beta}\left(\frac{1}{\beta}\right) \\
&= -\frac{3}{4}Nk_B\beta^2 \frac{(-1)}{\beta^2} \\
&= \frac{3}{4}Nk_B
\end{aligned} \tag{7}$$

b) The difference between them being distinguishable or indistinguishable comes in the shape of a constant *counting* factor for Z that depends on N and not on β. As we say in part a, while working equation 7 we effectively removed any constant factors from the partition function, since log properties allow us to split the log as a sum and under differentiation with respect to β, such a term vanishes.

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Problem 2 [3 points]

Cold interstellar molecular clouds often contain the molecule cyanogen (CN), whose first rotational excited states have an energy of 4.7×10^{-4} eV (above the ground state). There are actually three such excited states, all with the same energy. Suppose that a study of the absorption spectrum of starlight that passes through one of these molecular clouds showed that for every ten CN molecules that are in the ground state, approximately three others are in the three first excited states (that is, an average of one in each of these states). Use this information to determine the temperature of the cloud. You may find it useful to express the Boltzmann constant in units of eV/K:

$$k_B = 8.62 \times 10^{-5} \,\frac{\text{eV}}{K} \tag{8}$$

Recall that the Boltzmann distribution tells us that the probability for a system to occupy the microstate n (with energy E_n) at some temperature given by β, is

$$p(n) = \frac{e^{-\beta E_n}}{Z} \tag{9}$$

Where Z is the partition function of the system. We are told that the relative probability of the system occupying the ground state and the first excited state is

$$\frac{p(n=2)}{p(n=1)} \equiv \frac{p(\text{first excited state})}{p(\text{ground state})} = \frac{3}{10} \tag{10}$$

In terms of the Boltzmann distribution, we have

$$\frac{p(n=2)}{p(n=1)} = \frac{3e^{-\beta E_2}}{e^{-\beta E_1}} \tag{11}$$

Where the triple degeneracy (3) of the first excited state was taken into account. Combining Eqs. 10 and 11, we see that

$$\begin{aligned} \frac{3}{10} &= \frac{3e^{-\beta E_2}}{e^{-\beta E_1}} \\ \frac{3}{30} &= e^{\beta(E_1 - E_2)} \\ \ln\frac{1}{10} &= \beta(E_1 - E_2) \\ \frac{-\ln(10)}{E_1 - E_2} &= \beta \end{aligned} \tag{12}$$

From which we can find the temperature of the cloud:

$$\begin{aligned} T &= \frac{1}{k_B \beta} \\ &= \frac{E_1 - E_2}{-k_B \ln(10)} \\ &= \frac{4.7 \times 10^{-4} \text{ eV}}{\left(8.62 \times 10^{-5} \,\frac{\text{eV}}{K}\right) \ln(10)} \\ &= 2.36796 \text{ Kelvin} \end{aligned} \tag{13}$$

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Problem 3 [3 points]

For a system at fixed T (i.e., obeying the Boltzmann distribution), we discussed that the system has a well-defined average energy $\langle E \rangle$. The actual energy of the system can of course fluctuate about this average value. Show that these fluctuations in energy

$$\begin{aligned}\langle \Delta E^2 \rangle &= \langle (E - \langle E \rangle)^2 \rangle \\ &= \langle E^2 \rangle - \langle E \rangle^2\end{aligned} \tag{14}$$

are always proportional to the heat capacity C_V. This means that the energy fluctuations in a system are related to its capacity to absorb (or dissipate) energy. This is known as the *fluctuation-dissipation theorem.*

Using the definition of expectation value (average) $\langle \cdot \rangle$,

$$\begin{aligned}\langle \Delta E^2 \rangle &= \langle E^2 \rangle - \langle E \rangle^2 \\ &= \frac{\sum_n E_n^2 e^{-\beta E_n}}{Z} - \left(\frac{\sum_n E_n e^{-\beta E_n}}{Z} \right)^2 \\ &= \frac{\frac{\partial^2}{\partial \beta^2} \sum_n e^{-\beta E_n}}{Z} - \frac{\left(-\frac{\partial}{\partial \beta} \sum_n e^{-\beta E_n} \right)^2}{Z^2} \\ &= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left(-\frac{\partial Z}{\partial \beta} \right)^2 \\ &= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 \\ &= \frac{\partial^2 \ln Z}{\partial \beta^2}\end{aligned} \tag{15}$$

But average energy is given by $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$, so

$$\langle \Delta E^2 \rangle = -\frac{\partial \langle E \rangle \beta}{\partial} \tag{16}$$

Using chain rule to write this in terms of T-derivatives, we see that

$$\begin{aligned}\langle \Delta E^2 \rangle &= -\frac{\partial T}{\partial \beta} \frac{\partial \langle E \rangle}{\partial T} \\ &= -\left(-\frac{1}{k_B \beta^2} \right) C_V \\ &= \frac{1}{k_B \left(\frac{1}{k_B T} \right)^2} C_V \\ &= k_B T^2 C_V\end{aligned} \tag{17}$$

Where we used the fact that $C_V = \frac{\partial \langle E \rangle}{\partial T}$. ■