

PHYS3020 Module 2 Problem Set

Thursday, 25 August 2022 8:37 AM

Q2

a. The partition function for the first particle is

$$Z_1 = \sum_s e^{-E(s)/kT}$$

$$= e^{-E_{11}/kT} + e^{-E_{12}/kT}$$

Similarly for the second particle,

$$Z_2 = e^{-E_{21}/kT} + e^{-E_{22}/kT}$$

However, the partition function of the whole system is

$$Z = e^{-(E_{11}+E_{21})/kT} + e^{-(E_{11}+E_{22})/kT} + e^{-(E_{12}+E_{21})/kT}$$

$$+ e^{-(E_{12}+E_{22})/kT}$$

Taking the natural logarithm of this gives

$$\ln(Z) = -\frac{[(E_{11}+E_{21}) + (E_{11}+E_{22}) + (E_{12}+E_{21}) + (E_{12}+E_{22})]}{kT}$$

$$= -\frac{2(E_{11}+E_{12}+E_{21}+E_{22})}{kT}$$

Now, the product of the two partition functions

$$Z_1 Z_2 = (e^{-E_{11}/kT} + e^{-E_{12}/kT})(e^{-E_{21}/kT} + e^{-E_{22}/kT})$$

$$= e^{-E_{11}/kT} + e^{-E_{21}/kT} + e^{-E_{12}/kT} + e^{-E_{22}/kT}$$

Taking the natural logarithm gives

$$\ln(Z_1 Z_2) = -\frac{(E_{11}+E_{21}) + (E_{11}+E_{22}) + (E_{12}+E_{21}) + (E_{12}+E_{22})}{kT}$$

$$= -\frac{2(E_{11}+E_{12}+E_{21}+E_{22})}{kT}$$

Clearly $\ln(Z) = \ln(Z_1 Z_2)$

$$\Rightarrow Z = Z_1 Z_2$$

b. As before, the partition function for a system of one particle is

$$Z_1 = e^{-E_{11}/kT} + e^{-E_{12}/kT} + \dots + e^{-E_{1n}/kT}$$

hence,

$$\ln Z_1 = -\frac{\left(\sum_{i=1}^n E_{1i}\right)}{kT}$$

Similarly, for a particle of species 2

$$\ln Z_2 = -\frac{\left(\sum_{i=1}^m E_{2i}\right)}{kT}$$

For a system composed of both particles, the partition function would be

$$Z = e^{-E_{11}+E_{21}} + e^{-E_{11}+E_{22}} + \dots + e^{-E_{1n}+E_{2m}}$$

$$= (F_1 + F_2) \dots F_m$$

$$Z = e^{-\frac{(E_{11}+E_{21})}{kT}} + e^{-\frac{(E_{12}+E_{22})}{kT}} + \dots + e^{-\frac{(E_{1n_1}+E_{2n_2})}{kT}}$$

And so,

$$\ln Z = -\frac{(E_{11}+E_{21}+E_{12}+E_{22}+\dots+E_{1n_1}+E_{2n_2})}{kT}$$

$$= -n_1 \sum_{i=1}^{n_1} E_{1i} - n_2 \sum_{i=1}^{n_2} E_{2i}$$

For the expression $Z_1 Z_2$,

$$Z_1 Z_2 = \left(\sum_{i=1}^{n_1} e^{-\frac{E_{1i}}{kT}} \right) \left(\sum_{i=1}^{n_2} e^{-\frac{E_{2i}}{kT}} \right)$$

$$= e^{-\frac{(E_{11}+E_{21})}{kT}} + e^{-\frac{(E_{12}+E_{22})}{kT}} + \dots + e^{-\frac{(E_{1n_1}+E_{2n_2})}{kT}}$$

$$+ \dots + e^{-\frac{(E_{1n_1}+E_{2n_2})}{kT}}$$

$$\Rightarrow \ln(Z_1 Z_2) = -\frac{(E_{11}+E_{21}+E_{12}+E_{22}+\dots+E_{1n_1}+E_{2n_2})}{kT}$$

$$= -n_1 \sum_{i=1}^{n_1} E_{1i} - n_2 \sum_{i=1}^{n_2} E_{2i}$$

$$= \ln(Z)$$

$$\Rightarrow Z = Z_1 Z_2$$

Where the partition functions Z_1 and Z_2 can be for any number of states (independent of each other), where n_i is the number of possible states for the particle 1, and similarly for n_2 .

$$\text{Q3 } E_s = s\hbar\omega, s \in \{0, \mathbb{Z}^+\}$$

$$\begin{aligned} a. \quad Z &= \sum_{s=0}^{\infty} e^{-\frac{E_s}{kT}} \\ &= \sum_{s=0}^{\infty} e^{-s\hbar\omega/kT} \\ &= \sum_{s=0}^{\infty} (e^{-\hbar\omega/kT})^s \end{aligned}$$

which is of the form of the geometric series with

$$\text{since } -1 < r < 1, \text{ the solution is}$$

$$Z = \frac{1}{1 - e^{-\hbar\omega/kT}} = \frac{e^{\hbar\omega/kT}}{e^{\hbar\omega/kT} - 1}$$

b. The thermal average energy is given by

$$\langle E \rangle = \frac{1}{Z} \sum E_s e^{-E_s/kT}$$

$$\Rightarrow \langle E \rangle = \frac{e^{\hbar\omega/kT} - 1}{e^{\hbar\omega/kT}} \cdot \sum_{s=0}^{\infty} s \hbar\omega e^{-s\hbar\omega/kT}$$

Let's look at the summation term first:

$$\sum_{s=0}^{\infty} s \hbar\omega e^{-s\hbar\omega/kT} = \sum_{s=1}^{\infty} s \hbar\omega e^{-s\hbar\omega/kT} = \hbar\omega \sum_{s=1}^{\infty} s (e^{-\hbar\omega/kT})^s$$

(since the first term has $s=0 \Rightarrow$ the whole term is 0)

The right hand side has the form of the -1 polylogarithm,

$$\sum_{k=1}^{\infty} k z^k = \frac{z}{(1-z)^2}$$

And so

$$\begin{aligned} \sum_{s=0}^{\infty} s \text{tew} e^{-s \text{tew}/kT} &= \frac{\text{tew} e^{-\text{tew}/kT}}{(1 - e^{-\text{tew}/kT})^2} \\ &= \frac{\text{tew} e^{\text{tew}/kT}}{(e^{\text{tew}/kT} - 1)^2} \end{aligned}$$

And so

$$\begin{aligned} U &= \frac{(e^{\text{tew}/kT} - 1)}{e^{\text{tew}/kT}} \cdot \frac{\text{tew} e^{\text{tew}/kT}}{(e^{\text{tew}/kT} - 1)^2} \\ &= \frac{\text{tew}}{e^{\text{tew}/kT} - 1} \end{aligned}$$

- c. As was found in question 2, $Z_{1+2} = Z_1 Z_2$
Since both harmonic oscillators have the same potential energy scales and frequency,

$$\begin{aligned} Z &= Z_1 Z_2 \\ &= \left(\frac{e^{\text{tew}/kT}}{e^{\text{tew}/kT} - 1} \right)^2 = \frac{e^{2\text{tew}/kT}}{(e^{\text{tew}/kT} - 1)^2} \end{aligned}$$

However, since the two harmonic oscillators are assumed indistinguishable (and are independent), a $1/2!$ term must be introduced due to overcounting, so

$$\begin{aligned} Z &= \frac{1}{2!} \frac{e^{2\text{tew}/kT}}{(e^{\text{tew}/kT} - 1)^2} \\ &= \frac{1}{2} \frac{e^{2\text{tew}/kT}}{(e^{\text{tew}/kT} - 1)^2} \end{aligned}$$

Since average thermal energies are additive, the thermal average energy of the system is

$$\begin{aligned} U_{\text{sys}} &= 2 \cdot U_1 \\ &= \frac{2 \text{tew}}{e^{\text{tew}/kT} - 1} \end{aligned}$$

- d. As above for the partition function, we have to introduce a factor of $1/N!$ to correct for the overcounting of N harmonic oscillators. Hence,

$$\begin{aligned} Z_{\text{sys}} &= \frac{1}{N!} Z_1^N \\ &= \frac{1}{N!} \frac{e^{N\text{tew}/kT}}{(e^{\text{tew}/kT} - 1)^N} \end{aligned}$$

And since the thermal average energy is additive,

$$\begin{aligned} U_{\text{sys}} &= N \cdot U_1 \\ &= \frac{N \text{tew}}{e^{\text{tew}/kT} - 1} \end{aligned}$$

Q4

- a. $E_0 = 0$ with degeneracy g_0
 $E_1 = E$ with degeneracy g_1

$$\begin{aligned} Z &= \sum_{S=0}^N g_S e^{-E_S/kT} \\ &= g_0 e^{-E_0/kT} + g_1 e^{-E_1/kT} \\ &= g_0 e^0 + g_1 e^{-E/kT} \\ &= g_0 + g_1 e^{-E/kT} \end{aligned}$$

I claimed without proof that $\sum_{S=0}^N e^{-E_S/kT} = \sum_S g_S e^{-E_S/kT}$ where N is the number of particles in the system.

The probabilities of the system being in a state of energy $E_0 = 0$ is

$$\begin{aligned} P(E_0=0) &= \frac{1}{Z} e^{-E_0/kT} \\ &= \frac{e^0}{g_0 + g_1 e^{-E/kT}} \end{aligned}$$

And the probability of the system being in the state $E_1 = E$ is

$$\begin{aligned} P(E_1=E) &= \frac{1}{Z} e^{-E_1/kT} \\ &= \frac{e^{-E/kT}}{g_0 + g_1 e^{-E/kT}} \end{aligned}$$

b. The thermal average energy of the system will be

$$\begin{aligned} U &= \langle E \rangle = \frac{1}{Z} \sum_S E_S g_S e^{-E_S/kT} \\ &= \frac{1}{Z} (0 + E g_1 e^{-E/kT}) \\ &= \frac{E g_1 e^{-E/kT}}{g_0 + g_1 e^{-E/kT}} \end{aligned}$$

To make this easier to differentiate, multiply by $1 = \frac{e^{E/kT}}{e^{E/kT}}$

$$\Rightarrow U = \frac{E}{g_0 e^{E/kT} + g_1}$$

We know that the heat capacity is given by

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T} \right) \\ &= \frac{\partial}{\partial T} \left[E \left(g_0 e^{E/kT} + g_1 \right)^{-1} \right] \\ &= E \cdot \frac{\partial E}{kT^2} e^{E/kT} \cdot -1 \left(g_0 e^{E/kT} + g_1 \right)^{-2} \\ &= -\frac{g_0 E^2 e^{E/kT}}{kT^2 (g_0 e^{E/kT} + g_1)^2} \\ &= \frac{E^2 e^{E/kT}}{g_0 kT^2 (e^{E/kT} + g_1)^2} \end{aligned}$$

In the high temperature limit, we'd expect $\frac{E}{kT} \rightarrow 0 \Rightarrow e^{E/kT} \rightarrow 1$

$$\Rightarrow U \xrightarrow{T \rightarrow \infty} \frac{E}{g_0 + g_1}$$

$$\Rightarrow C_V \xrightarrow{T \rightarrow \infty} \frac{E^2}{g_0 + g_1} \rightarrow 0$$

$$\Rightarrow U \rightarrow \frac{E}{g_0 + g_1}$$

$$\Rightarrow C_V \xrightarrow{T \rightarrow \infty} \frac{E^2}{g_0 k T^2 (e^{E/kT} + r)^2} \rightarrow 0$$

So, for high temperatures, the thermal average energy goes to a constant and the heat capacity goes to 0.

In the low temperature limit, $\frac{E}{kT} \rightarrow \infty \Rightarrow e^{-E/kT} \rightarrow 0$

$$\Rightarrow U = \frac{E}{r e^{E/kT} + g_0} \xrightarrow{T \rightarrow 0} 0$$

$$C_V = \frac{E^2 e^{-E/kT}}{g_0 k T^2 (e^{E/kT} + r)^2}$$

$$\approx \frac{E^2 e^{-E/kT}}{g_0 k T^2 e^{-2E/kT}}$$

$$= \frac{E^2}{g_0 k T^2 e^{-E/kT}}$$

Since $e^{-E/kT}$ changes faster than T^2 , $C_V \xrightarrow{T \rightarrow 0} 0$

In the high temperature limit, we had

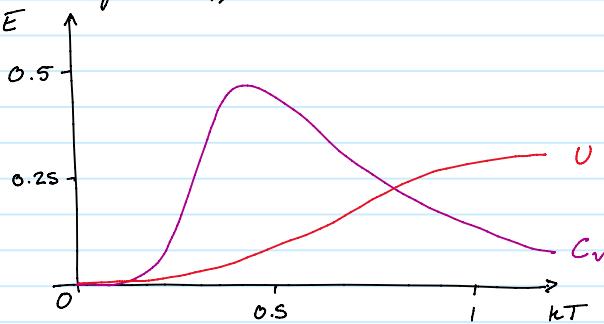
$$U \xrightarrow{T \rightarrow \infty} \frac{E}{g_0 + g_1} = \frac{E g_0}{1 + \frac{g_1}{g_0}} = \frac{E g_0}{1 + r}$$

$$\text{where } r = \frac{g_1}{g_0}$$

In the lower limit $r \rightarrow 0$, $U \rightarrow \frac{E g_0}{1} = E g_0$.

upper limit $r \rightarrow \infty$, $U \rightarrow \frac{E g_0}{\infty} = 0$

A sketch of the behaviour of U and C_V is shown below (for $r=1$)



The equations plotted are

$$U = \frac{E g_0}{e^{E/kT} + r} \quad \text{and}$$

$$C_V = \frac{E^2 e^{-E/kT}}{g_0 k T^2 (e^{E/kT} + r)^2}$$

We'd expect that, as r increases, U will decrease as will C_V , and the peak of C_V will move towards a lower value of T . The opposite will happen for an increase in r .

Q7

$$S(T, N, V) = k_B N \left(\ln \left(\frac{V_{\text{na}}}{N} \right) + \frac{S}{2} \right)$$

$$= k_B N \ln \left(\frac{V_{\text{na}}}{N} \right) + k_B N \cdot \frac{S}{2}$$

The change in entropy (of one particle) expanding to twice its volume when the wall is lifted is

$$\begin{aligned}
 \Delta S_A &= S_{Af} - S_{Ai} \\
 &= \left[k_B N \ln\left(\frac{2V_{Na}}{N}\right) + k_B N \cdot \frac{S}{2} \right] - \left[k_B N \ln\left(\frac{V_{Na}}{N}\right) + k_B N \cdot \frac{S}{2} \right] \\
 &= k_B N \left[\ln\left(\frac{2V_{Na}}{N}\right) - \ln\left(\frac{V_{Na}}{N}\right) \right] \\
 &= k_B N \ln\left(\frac{2V_{Na} \cdot N}{N \cdot V_{Na}}\right) \\
 &= k_B N \ln(2)
 \end{aligned}$$

Since both particles have the same mass, temperature, and pressure, $\Delta S_A = \Delta S_B$, and the total change in entropy is

$$\begin{aligned}
 \Delta S &= \Delta S_A + \Delta S_B = 2 \Delta S_A \\
 &= 2 k_B N \ln(2)
 \end{aligned}$$

which is exactly the entropy of mixing.

Q8

a. As per question 3, the partition function for one harmonic oscillator is

$$Z = \frac{1}{1 - e^{-\hbar\omega/kT}}$$

b. The free energy of a system is given by

$$F = -k_B T \ln Z$$

So, for the harmonic oscillator,

$$\begin{aligned}
 F &= -k_B T \ln\left(\frac{1}{1 - e^{-\hbar\omega/kT}}\right) \\
 &= -k_B T \left[\ln(1) - \ln(1 - e^{-\hbar\omega/kT}) \right] \\
 &= k_B T \ln(1 - e^{-\hbar\omega/kT})
 \end{aligned}$$

as required.

c. The entropy is given by

$$\begin{aligned}
 S &= -\left(\frac{\partial F}{\partial T}\right)_{V, N} \\
 \Rightarrow \frac{S}{k_B} &= -\frac{\partial}{\partial T} \left(T \ln(1 - e^{-\hbar\omega/kT}) \right) \\
 &= -\left(\ln(1 - e^{-\hbar\omega/kT}) \right. \\
 &\quad \left. + T \cdot \frac{1}{1 - e^{-\hbar\omega/kT}} \cdot -\frac{\hbar\omega}{kT^2} \cdot -e^{-\hbar\omega/kT} \right) \\
 &= \frac{\hbar\omega e^{-\hbar\omega/kT}}{kT (1 - e^{-\hbar\omega/kT})} - \ln(1 - e^{-\hbar\omega/kT}) \\
 &= \frac{(\hbar\omega/kT)}{(e^{\hbar\omega/kT} - 1)} - \ln(1 - e^{-\hbar\omega/kT})
 \end{aligned}$$

as required.

d. By the definition of the Helmholtz free energy,

as required.

d. By the definition of the Helmholtz free energy,

$$F = U - TS \Rightarrow U = F + TS$$

Therefore,

$$\begin{aligned} U &= k_B T \ln(1 - e^{-\hbar\omega/kT}) + k_B \left[\frac{(\hbar\omega/kT)}{e^{\hbar\omega/kT} - 1} - \ln(1 - e^{-\hbar\omega/kT}) \right] \\ &= \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \end{aligned}$$

which agrees exactly with the value found in problem 3.

e. We have the thermodynamic identity

$$dU = T dS - p dV$$

when volume is kept constant, $dV = 0$ and so

$$(dU = T dS)_V$$

Differentiating both sides with respect to T gives

$$\begin{aligned} \left(\frac{\partial U}{\partial T} \right)_V &= \left(\frac{\partial}{\partial T} (T dS) \right)_V \\ &= \left(T \frac{\partial S}{\partial T} + dS \right)_V \end{aligned}$$

but $dS = \frac{Q}{T}$ where Q is an infinitesimal quantity of

heat applied, so

$$\left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V = C_V$$

Using the formula in terms of thermal energy,

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \right) \\ &= \hbar\omega \frac{\partial}{\partial T} (e^{\hbar\omega/kT} - 1)^{-1} \\ &= \hbar\omega \cdot - \frac{\hbar\omega e^{\hbar\omega/kT}}{kT^2} \cdot -(e^{\hbar\omega/kT} - 1)^{-2} \\ &= e^{-\hbar\omega/kT} \left(\frac{\hbar\omega}{\sqrt{kT} (e^{\hbar\omega/kT} - 1)} \right)^2 \end{aligned}$$