Solutions to home work week 3

1. The enery levels of the harmonic oscillator are

$$E_n = \hbar\omega(n + \frac{1}{2}) \tag{1}$$

with integer quantum number $n \geq 0$. Because each level is non-degenerate, the partition function is

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega})^n \tag{2}$$

with $\beta = \frac{1}{kT}$. Because $0 < \exp[-\beta\hbar\omega] < 1$, we can use the result

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \tag{3}$$

Thus, the partition function of the quantum harmonic oscillator is

$$Z = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \tag{4}$$

With Z we can compute

- the entropy

$$\begin{aligned} S &= \frac{\langle E \rangle}{T} + k \ln Z \\ &= -\frac{1}{T}\frac{\partial}{\partial\beta} \ln Z + k \ln Z \\ &= -\frac{1}{T}\frac{\partial}{\partial\beta}\left(-\tfrac{1}{2}\beta\hbar\omega - \ln[1 - e^{-\beta\hbar\omega}]\right) + k\left(-\tfrac{1}{2}\beta\hbar\omega - \ln[1 - e^{-\beta\hbar\omega}]\right) \end{aligned} \tag{5}$$

Using the result for $\langle E \rangle$ from the homework 3, we get

$$\begin{aligned} S &= \tfrac{\hbar\omega}{2T}\left(\tfrac{1+e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right) - \tfrac{k\beta\omega}{2} - k\ln\left[1-e^{-\beta\hbar\omega}\right] \\ &= \tfrac{\hbar\omega}{2T}\left[\tfrac{1+e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} - \tfrac{1-e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right] - k\ln\left[1-e^{-\beta\hbar\omega}\right] \qquad (6) \\ &= -k\ln\left[1-e^{-\beta\hbar\omega}\right] + \tfrac{\hbar\omega}{T}\tfrac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \end{aligned}$$

Figure 1 is a plot of the Entropy as a function of temperature.

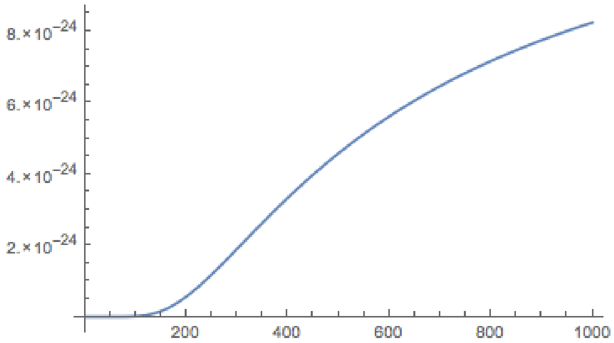

Figure 1: Entropy (y-axis) of a single quantum harmonic oscillator as a function of temperature (x-axis)

- The heat capacity at constant volume :

$$
\begin{aligned}
C_V &= \frac{\partial U}{\partial T} = \frac{\partial \langle E \rangle}{\partial T} \\
&= \frac{\partial}{\partial T}\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right) \\
&= \frac{\partial}{\partial \beta}\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)\frac{d\beta}{dT} \\
&= \frac{(\hbar\omega)^2 e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})kT^2} + \frac{(\hbar\omega)^2 e^{-2\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2 kT^2} \\
&= \frac{(\hbar\omega)^2\left(e^{-\beta\hbar\omega} - e^{-2\beta\hbar\omega} + e^{-2\beta\hbar\omega}\right)}{(1-e^{-\beta\hbar\omega})^2 kT^2} \\
&= \frac{(\hbar\omega)^2 \exp[-\frac{\hbar\omega}{kT}]}{(1-\exp[-\frac{\hbar\omega}{kT}])^2 kT^2}
\end{aligned}
\tag{7}
$$

Figure 2 is a logarithmic plot of the heat capacity for the oscillator.

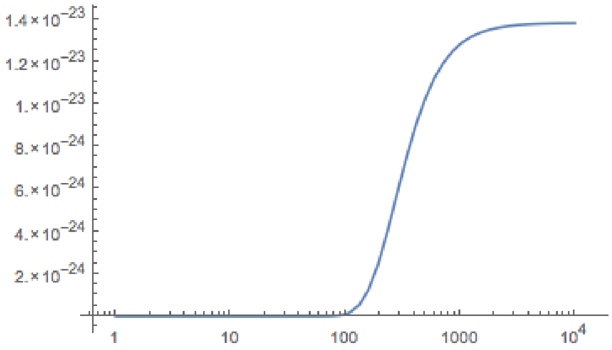

Figure 2: Heat capacity (y-axis) of a single quantum harmonic oscillator as a function of temperature (x-axis)

To get the entropy as a function of temperature above, we could also

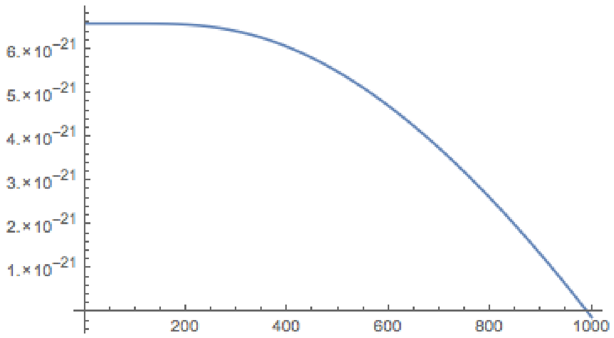

Figure 3: Helmholtz free energy (y-axis) of a single quantum harmonic oscillator as a function of temperature (x-axis)

have also use this result:

$$S = \int_0^T \frac{1}{T} \frac{\partial U}{\partial T} dT \tag{8}$$

but this is a more nasty integral.

- The Helmholtz free energy:

$$\begin{aligned} A &= -kT \ln Z = -\tfrac{1}{\beta} \ln Z \\ &= -\tfrac{1}{\beta} \left(-\tfrac{1}{2}\beta\hbar\omega - \ln[1 - e^{-\beta\hbar\omega}] \right) \\ &= \tfrac{\hbar\omega}{2} + \tfrac{\beta}{\ln}[1 - e^{-\beta\hbar\omega}] \\ &= \tfrac{\hbar\omega}{2} + kT \ln[1 - \exp[-\tfrac{\hbar\omega}{kT}] \end{aligned} \tag{9}$$

Figure 3 is a plot of the Helmholtz Free energy.

To get the entropy, we could have also used

$$S = -\frac{\partial A}{\partial T} \tag{10}$$

There are thus various ways to compute the variables.

2. First to get the angular frequency of HD , we need to recover the force constant from the frequencies of HH or DD. We have for the reduced masses of the three systems: $\mu_{\text{HH}} = 8.363 * 10^{-28}$ kg; $\mu_{\text{HD}} = 1.11488 * 10^{-27}$ kg; $\mu_{\text{DD}} = 1.67175 * 10^{-27}$ kg. From $\omega_{\text{HH}} = 131$ THz, we get $k = 14.3517\text{Nm}^{-1}$. As crosscheck, from $\omega_{\text{DD}} = 93$ THz, we get $k = 14.459\text{Nm}^{-1}$. Not totally the same, but close enough. We take the first value and hence correct slightly the ω_{DD} =92.6 THz. Probably 93 THz was rounded. Anyway, with $k = 14.3517\text{Nm}^{-1}$, we get for $\omega_{\text{HD}} = 113.5$ THz. With these values, we can compute the partition function of the reactants and products, assuming the two product HD molecules are distinguishable in our experiment. For the HH and DD reactants

$$Z_{\text{react}} = \frac{e^{-\frac{1}{2}\beta\hbar\omega_{\text{HH}}}}{1 - e^{-\beta\hbar\omega_{\text{HH}}}} \times \frac{e^{-\frac{1}{2}\beta\hbar\omega_{\text{DD}}}}{1 - e^{-\beta\hbar\omega_{\text{DD}}}} \tag{11}$$

and Helmholtz free energy

$$A_{\text{react}} = -kT \ln Z = -kT \ln \left[\frac{e^{-\frac{1}{2}\beta\hbar\omega_{\text{HH}}}}{1 - e^{-\beta\hbar\omega_{\text{HH}}}} \right] - kT \ln \left[\frac{e^{-\frac{1}{2}\beta\hbar\omega_{\text{DD}}}}{1 - e^{-\beta\hbar\omega_{\text{DD}}}} \right] \tag{12}$$

For the two HD products:

$$Z_{\text{prod}} = \frac{e^{-\frac{1}{2}\beta\hbar\omega_{\text{HD}}}}{1 - e^{-\beta\hbar\omega_{\text{HD}}}} \times \frac{e^{-\frac{1}{2}\beta\hbar\omega_{\text{HD}}}}{1 - e^{-\beta\hbar\omega_{\text{HD}}}} \tag{13}$$

and Helmholtz free energy

$$A_{\text{prod}} = -kT \ln Z = -2kT \ln \left[\frac{e^{-\frac{1}{2}\beta\hbar\omega_{\text{HD}}}}{1 - e^{-\beta\hbar\omega_{\text{HH}}}} \right] \tag{14}$$

To make them indistinguisbable, we need to divide by 2, but we forget about that for now and assume we can resolve the molecules.

The free energy difference is thus:

$$\begin{aligned}\Delta A &= A_{\text{prod}} - A_{\text{react}} \\ &= 2\tfrac{\hbar\omega_{\text{HD}}}{2} + 2kT\ln[1 - \exp[-\tfrac{\hbar\omega_{\text{HD}}}{kT}] \\ &\quad -\tfrac{\hbar\omega_{\text{HH}}}{2} - kT\ln[1 - \exp[-\tfrac{\hbar\omega_{\text{HH}}}{kT}] \\ &\quad -\tfrac{\hbar\omega_{\text{DD}}}{2} - kT\ln[1 - \exp[-\tfrac{\hbar\omega_{\text{DD}}}{kT}]\end{aligned} \tag{15}$$

Figure 4 shows how the reaction free energy depends on temperature.

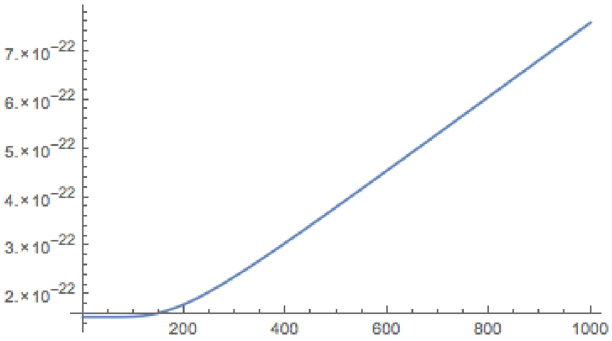

Figure 4: Reaction free energy (y-axis) as a function of temperature (x-axis)

because the free energy change is postive for all temperatures, the reaction is not spontaneous and we need to do work on the sytem to make is happen (*i. e.*, accelerate the molecules).

3. Because a *classical* harmonic oscillator has continuous energies, we can write the partition function as

$$Z = \int_{-\infty}^{\infty} \exp[-\frac{\beta}{2m}p^2 - \frac{\beta}{2}m\omega^2 x^2]dpdx \tag{16}$$

Becaue p and x are independent variables, we can cut this expression into a product:

$$Z = \int_{-\infty}^{\infty} \exp[-\frac{\beta}{2m}p^2]dp \times \int_{-\infty}^{\infty} \exp[-\frac{\beta}{2}m\omega^2 x^2]dx \tag{17}$$

Using the rules for integrals of Gaussian functions from the book ($a = \frac{\beta}{2m}$ in the first part and $a = \frac{\beta m\omega^2}{2}$ in the second part of the integral), we can do the integration:

$$\begin{aligned} Z &= \sqrt{\tfrac{2m\pi}{\beta}} \times \sqrt{\tfrac{2\pi}{m\beta\omega^2}} \\ &= \tfrac{2\pi}{\beta\omega} \end{aligned} \tag{18}$$

Note, however, we should have used $\frac{1}{h}$ as a prefactor of Z, but because we have not discussed this in the lecture, we leave it out for now. It has to do with the density of states and the relation with quantum mechanics. Also without h, Z is not unitless (i.e. now the unit of Z is Js, which is also the unit of h.

- The entropy is then (using the average energy $\langle E\rangle = kT$ from the next question .... I should have reveresed the order here...)

$$S = k + k\ln Z = k + k\ln\left[\frac{2\pi}{\beta\omega}\right] \tag{19}$$

- The average energy

$$\begin{aligned}\langle E\rangle &= -\tfrac{\partial}{\partial\beta}\ln Z \\ &= -\tfrac{\partial}{\partial\beta}\ln\left[\tfrac{2\pi}{\beta\omega}\right] \\ &= -\tfrac{\partial}{\partial\beta}\left(\ln[2\pi]-\ln[\beta\omega]\right) \qquad (20) \\ &= \tfrac{1}{\beta} \\ &= kT\end{aligned}$$

Thus the average enery is kT. This is an example of the *classical* equipartition theory that in equilibrium the available energy is equally shared between kinetic and potential energy, with $\frac{1}{2}kT$ per harmonic term in the Hamiltonian. We will discuss this further in the lecture.

- Finally, the Helmholtz free energy of this system is

$$A = -kT\ln Z = -kT\ln\left[\frac{2\pi}{\beta\omega}\right] \qquad (21)$$

Since we also have that $S = -\frac{\partial A}{\partial T}$, we could have also obtained the entropy by differentiation A:

$$-\frac{\partial A}{\partial T} = k\ln\left[\frac{2\pi kT}{\omega}\right] + k \qquad (22)$$