Solutions to home work week 3

1. At equilibrium, we have that

$$\left(\frac{\partial S_{AB}}{\partial V_A}\right)_{N_A,N_B,E_A,E_B} = \left(\frac{\partial S_A}{\partial V_A}\right)_{N_A,E_A} + \left(\frac{\partial S_B}{\partial V_B}\right)_{N_B,E_B} \frac{dV_B}{dV_A} = 0 \quad (1)$$

   From the fact that the total volume is conserved $V_A + V_B = V_{AB}$, we have that $dV_A + dV_B = 0$ and therefore

$$\frac{dV_B}{dV_A} = -1 \quad (2)$$

   Thus, at equilibrium, we have that

$$\left(\frac{\partial S_A}{\partial V_A}\right)_{N_A,E_A} = \left(\frac{\partial S_B}{\partial V_B}\right)_{N_B,E_B} \quad (3)$$

   We know (intuitively) that the pressures are the same in equilibrium. Furthermore, the units of these derivatives are are $\mathrm{JK}^{-1}\mathrm{m}^{-3}$, while pressure has Jm^{-3}, we apparently need to multiply by temperature:

$$P_A = T_A \left(\frac{\partial S_A}{\partial V_A}\right)_{N_A,E_A} \quad (4)$$

2. There are two energy levels per nucleus. If we set (arbitrary, but convenient) the lower level to 0 ($E_0 = 0$ J), the probability for a single nucleus to be in the higher energy level ($E_1 = 3\ 10^{-20}$ J) is

$$p_1 = \frac{\exp[-\beta E_1]}{1 + \exp[-\beta E_1]} \quad (5)$$

   where we used that $\exp[0] = 1$. Thus, of the N nuclei, there will be $p_1 N$in the higher energy state with enery E_1,

$$N_1 = Np_1 = \frac{N\exp[-\beta E_1]}{1+\exp[-\beta E_1]} \tag{6}$$

and p_0N in the lower energy state with energy E_0:

$$N_0 = Np_0 = \frac{N}{1+\exp[-\beta E_1]} \tag{7}$$

With $N = $ 1,000,000 and $k = 1.3806\ 10^{-23}$ JK^{-1}, we have at

- 0 K: $N_0 = 1000000$ and $N_1 = 0$
- 10 K: $N_0 = 1000000$ and $N_1 = 0$
- 100 K: $N_0 = 1000000$ and $N_1 = 0$
- 300 K: $N_0 = 999286$ and $N_1 = 714$.
- 1000 K: $N_0 = 897796$ and $N_1 = 102204$
- 10,000 K: $N_0 = 554111$ and $N_1 = 445889$

3. For the quantum harmonic oscillator, the partition function:

$$\begin{aligned} Z &= \textstyle\sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} \\ &= e^{-\frac{1}{2}\beta\hbar\omega} \textstyle\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \\ &= e^{-\frac{1}{2}\beta\hbar\omega} \textstyle\sum_{n=0}^{\infty} (e^{-\beta\hbar\omega})^n \end{aligned} \tag{8}$$

Since $\exp[-\beta\hbar\omega] \leq 1$, we can use $\sum_i x^n = \frac{1}{1-x}$:

$$Z = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \tag{9}$$

To calculate the ratio between the occupancies (*i. e.*, probabilities) of energy levels 0 and 1, we use the Boltzmann factors:

$$p_n = \frac{e^{-(n+\frac{1}{2})\beta\hbar\omega}}{Z} \tag{10}$$

with Z in equation 9. However, we only need the ratio here, *i. e.*,:

$$\begin{aligned} \frac{p_1}{p_0} &= \frac{e^{-1\frac{1}{2}\beta\hbar\omega}}{e^{-\frac{1}{2}\beta\hbar\omega}} \\ &= e^{-\beta\hbar\omega} \end{aligned} \tag{11}$$

Thus the ratios are at

- 1 K: 0
- 10 K: 0
- 100 K: 0
- 1,000 K: 0.38
- 10,000 K: 0.91

The average energy is obtained as the derivative of the logarithm of the partition function (equation 9) with respect to β;

$$\begin{aligned} \langle E \rangle &= -\frac{\partial}{\partial\beta}\ln Z \\ &= -\frac{\partial}{\partial\beta}\ln\left[\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right] \\ &= -\frac{\partial}{\partial\beta}\left(\ln\left[e^{-\frac{1}{2}\beta\hbar\omega}\right] - \ln\left[1-e^{-\beta\hbar\omega}\right]\right) \\ &= \frac{\partial}{\partial\beta}\frac{1}{2}\beta\hbar\omega + \frac{\partial}{\partial\beta}\ln\left[1-e^{-\beta\hbar\omega}\right] \\ &= \frac{1}{2}\hbar\omega + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \end{aligned} \tag{12}$$

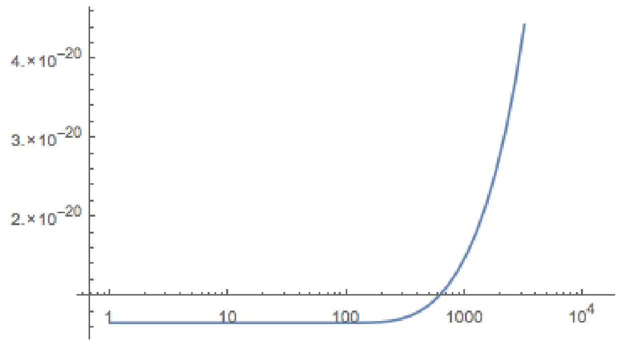

Figure 1: Average energy (y-axis, J) of a single harmonic oscillator as a function of temperature (x-axis, K)

Thus, irrespective of temperature, the energy always contains the zero-point energy ($\frac{1}{2}\hbar\omega$), and higher levels contribute to the energy only if the temperature is sufficiently high, as shown in figure 1.