

Statistical Physics: Workshop Problems 2

- (1) To obtain the set of probabilities that maximise the entropy under the constraint of normalisation, we must maximise

$$\left[-\sum_{i=1}^6 p_i \ln p_i - \alpha \sum_{i=1}^6 p_i \right]$$

where α is the Lagrange multiplier constraining total probability. Set to zero the derivative of this expression with respect to one of the $\{p_1, p_2, \dots, p_6\}$. For example pick p_3

$$0 = \frac{\partial}{\partial p_3} \left[\right] \Rightarrow 0 = -\ln p_3 - \frac{p_3}{p_3} - \alpha \Rightarrow \ln p_3 = -1 - \alpha \Rightarrow p_3 = e^{-1-\alpha}.$$

However, p_3 is not special and the same result must hold for all the other p_i , With i being any of 1, 2, 3, 4, 5, 6 we have

$$p_i = e^{-1-\alpha}, \quad \text{for } i = 1, 2, \dots, 6.$$

From the constraint of normalisation, we have

$$\sum_{i=1}^6 p_i = 1 \Rightarrow e^{-1-\alpha} \sum_{i=1}^6 1 = 1 \Rightarrow e^{-1-\alpha} \times 6 = 1 \Rightarrow e^{-1-\alpha} = 1/6$$

We conclude that $p_i = 1/6$ for all $i = 1, 2, \dots, 6$.

By assigning equal probability to all events we maximise the entropy under just the constraint of normalisation of the probability and in the lack of any other knowledge. The same idea is used in the principle of equal *a priori* probabilities. In the microcanonical ensemble, all microstates have the same energy and in the lack of any other information we choose equal probabilities which maximise the entropy.

- (2) (a) When each energy level is doubly degenerate the partition function will be

$$Z = \underbrace{e^{-\beta\epsilon_1}}_{\text{s.p. state 1}} + \underbrace{e^{-\beta\epsilon_1}}_{\text{s.p. state 2}} + \underbrace{e^{-\beta\epsilon_2}}_{\text{s.p. state 3}} + \underbrace{e^{-\beta\epsilon_2}}_{\text{s.p. state 4}} + \dots = \sum_j 2e^{-\beta\epsilon_j}$$

- (b) Obviously, in the general case, this becomes

$$Z = \sum_j g(j) e^{-\beta\epsilon_j}$$

- (3) (a) The single-particle partition function is

$$\begin{aligned} Z_{3D} &= \sum_{n=0}^{\infty} g(\epsilon_n) e^{-\beta(n+3/2)h\nu} \\ &= \sum_{n=0}^{\infty} \frac{1}{2} (n+1)(n+2) e^{-\beta(n+3/2)h\nu}. \end{aligned}$$

This sum over n is complicated by the presence of the coefficient $g(\epsilon_n)$ but still it can be found using properties of sums of geometric series. One can do that, but instead we will use the hint in the question.

The single-particle state n of a 3D SHO is given by specifying the states j, k, l of three 1D SHOs in the directions x, y, z :

$$n = j + k + l, \text{ with } j, k, l = 0, 1, \dots$$

Let's see what happens with the degeneracy

$$\begin{aligned} g(n=0) &= 1, & n=0 &= 0+0+0 \\ g(n=1) &= 3, & n=1 &= 1+0+0 \\ & & &= 0+1+0 \\ & & &= 0+0+1 \\ & & &\dots \end{aligned}$$

So, when we change the sum over n to a sum over j, k, l (three 1D oscillators), the degeneracy $g(n)$ is taken care of by the three separate sums

$$\sum_{n=0}^{\infty} g(n) e^{(\dots)} \rightarrow \sum_{j,k,l=0}^{\infty} 1 e^{(\dots)}.$$

The energy ϵ_n is given by

$$\epsilon_n = \epsilon_j + \epsilon_k + \epsilon_l = (j + 1/2)h\nu + (k + 1/2)h\nu + (l + 1/2)h\nu.$$

The single-particle partition function for the 3D SHO becomes

$$\begin{aligned} Z_{3D} &= \sum_{j,k,l=0}^{\infty} e^{-\beta(j+1/2)h\nu} e^{-\beta(k+1/2)h\nu} e^{-\beta(l+1/2)h\nu} \\ Z_{3D} &= \sum_{j=0}^{\infty} e^{-\beta(j+1/2)h\nu} \sum_{k=0}^{\infty} e^{-\beta(k+1/2)h\nu} \sum_{l=0}^{\infty} e^{-\beta(l+1/2)h\nu} = \left(\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right)^3 = Z_{1D}^3 \end{aligned}$$

The logarithm of the partition function is

$$\ln Z_{3D} = 3 \ln Z_{1D}.$$

- (b) This means that the thermodynamic functions, i.e., U, F, S , for N 3D SHOs will be the same as the corresponding thermodynamic functions of $3N$ 1D SHOs. Therefore

$$\begin{aligned} U &= -N \frac{\partial \log Z}{\partial \beta} \\ &= \frac{3N h\nu}{2} + \frac{3N h\nu}{\exp(\beta h\nu) - 1}, \\ F &= -\frac{N}{\beta} \log Z \\ &= \frac{3N h\nu}{2} + \frac{3N}{\beta} \ln(1 - \exp(-\beta h\nu)), \\ S &= k_B \beta (U - F) \\ &= 3N k_B \left[\frac{\beta h\nu}{\exp(\beta h\nu) - 1} - \ln(1 - \exp(-\beta h\nu)) \right]. \end{aligned}$$

(4) Carrying on from the previous problem we have

$$\begin{aligned} C_V &= \left[\frac{\partial U}{\partial T} \right]_V \\ &= \frac{3Nk_B(\beta h\nu)^2 \exp(\beta h\nu)}{(\exp(\beta h\nu) - 1)^2}. \end{aligned}$$

In the above, note that

$$\frac{\partial}{\partial T} = -k_B\beta^2 \frac{\partial}{\partial \beta}.$$

At high temperatures $\beta \rightarrow 0$ and $\exp(\beta h\nu) \rightarrow 1$. We expand the denominator in a Taylor series

$$\frac{1}{(\exp(\beta h\nu) - 1)^2} \simeq \frac{1}{(1 + \beta h\nu - 1)^2} = \frac{1}{(\beta h\nu)^2}$$

so the heat capacity becomes

$$C_V = 3Nk_B.$$

The heat capacity for a mole of a solid at high temperature is (N_A is Avogadro's number)

$$C_V^{mol} = 3N_Ak_B = 3 \times 6.022 \times 10^{23} \times 1.38064852 \times 10^{-23} J/K = 24.9 J/K.$$