Statistical Physics: Workshop Problems 2

(1) A particle can be in one of six degenerate states, $i = 1, 2, \dots, 6$. The probability that the particle is in state i is p_i and the probabilities are normalised, $\sum_{i=1}^{6} p_i = 1$. The Gibbs statistical entropy of the particle for the probability distribution $\{p_1, p_2, \dots, p_6\}$ is

$$S(\{p_i\}) = -k_{\mathrm{B}} \sum_{i=1}^{6} p_i \ln p_i.$$

Show that the set of probabilities that maximise the entropy under the constraint of normalisation (use a Lagrange multiplier), satisfy $p_i = 1/6$. Comment on the principle of equal *a priori* probabilities for a microcanonical ensemble.

(2) In a non-degenerate system the partition function Z is given by a sum over the single-particle states

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

where ϵ_j is the energy of the non-degenerate single-particle state j.

(a) What is the expression for Z when each energy level has degeneracy two?

(b) Given the (hopefully simple) result in (a) state the partition function for the case where energy levels have degeneracy $g(j)$?

(3) (a) Consider a three-dimensional (3D) simple harmonic oscillator (SHO). The energy levels are

$$\epsilon_n = (n + 3/2)h\nu.$$

The degeneracy of the n-th level is

$$g(\epsilon_n) = (n+1)(n+2)/2.$$

Show that the partition function Z_{3D} for the 3D SHO is given by

$$\log Z_{3D} = 3 \log Z_{1D}$$

where Z_{1D} is the partition function of the equivalent 1D SHO.

Hint 1: One can evaluate the infinite sum in the definition of the partition function for Z_{3D} and compare to Z_{1D}. However a simpler method is to note that 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: $n = j + k + l$, with $j, k, l = 0, 1, \dots$. The energy ϵ_n is given by $\epsilon_n = \epsilon_j + \epsilon_k + \epsilon_l = (j + 1/2)h\nu + (k + 1/2)h\nu + (l + 1/2)h\nu$. Note that the single-particle energy levels of the 3D oscillator are degenerate but the single-particle energy levels of the 1D oscillators are not degenerate.

Hint 2: If you want to ignore Hint 1 then note that

$$\sum_{n=0}^{\infty} (n+1)(n+2)e^{-nx} = \frac{2e^{3x}}{(e^x - 1)^3}.$$

(b) From the partition function find the internal energy U, free energy F and the entropy S for a system of N distinguishable 3D SHOs.

(4) What is the heat capacity, C_V, for a system of N 3D SHOs? (This is the Einstein heat capacity of a solid.) Show that it gives a constant heat capacity for high temperatures. Using this result, explain the Dulong and Petit law, that the molar heat capacity of any solid is approximately ~ 25 J/(mol K).