Handout: Entropy of a harmonic oscillator

In deriving the intrinsic vacancy density we require the entropy of a harmonic oscillator. This handout contains some basic thermodynamic relations and derives this quantity.

3.1 Partition function

A very useful function in thermodynamics is the *partition function* Z:

$$Z = \sum_{states\ s} \exp -\beta E_s \tag{3.1}$$

Where E_s is the energy of state s and we define $\beta = 1/k_B T$. Note that therefore $dB = (-1/k_B T^2)dT$.

3.2 Probability of occupation

The partition function provides a normalising constant for the measure of the probability that some state s is occupied.

$$p_s = \frac{1}{Z} \exp -\beta E_s \tag{3.2}$$

3.3 Mean total energy

The mean of a function x is the sum of all x times their probabilities: $\int xp(x)dx$. Hence, the mean energy is:

$$\overline{U} = \sum E_s p_s = \frac{1}{Z} \sum E_s \exp -\beta E_s \tag{3.3}$$

Notice that the term being summed is equal to $-\partial Z/\partial \beta$. Hence:

$$\overline{U} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial (\ln Z)}{\partial \beta} = k_B T^2 \frac{\partial (\ln Z)}{\partial T} \tag{3.4}$$

3.4 Heat capacity

The heat capacity is defined as the energy change required to change the temperature of a substance (or vice versa):

$$\frac{\partial U}{\partial T} = \frac{\partial U}{\partial \beta}\frac{\partial \beta}{\partial T} = \frac{1}{k_B T^2}\frac{\partial U}{\partial \beta} = \frac{1}{k_B T^2}\frac{\partial^2 (\ln Z)}{\partial \beta^2} \tag{3.5}$$

3.5 Entropy

Entropy, a powerful concept used physics, information theory, mathematics etc. to described the disorder of a system is commonly defined as:

$$S = -k_B \sum_s p_s \ln p_s \tag{3.6}$$

$$S = -k_B \sum_s \frac{1}{Z} \exp(-\beta E_s) \ln\left(\frac{1}{Z} \exp -\beta E_s\right) \tag{3.7}$$

$$S = -k_B \sum_s \frac{1}{Z} \exp(-\beta E_s) \left[-\beta E_s - \ln Z\right] \tag{3.8}$$

$$S = k_B \beta \frac{1}{Z} \sum_s E_s \exp(-\beta E_s) + k_B \frac{\ln Z}{Z} \sum_s \exp(-\beta E_s) \tag{3.9}$$

The first of these sums is equal to the mean energy $\overline{U}$ (see above). The second sum is equal to Z. Thus:

$$S = k_B(\beta \overline{U} + \ln Z) \tag{3.10}$$

This can be more neatly expressed as:

$$S = \frac{\partial}{\partial T}\left(k_B T \ln Z\right) \tag{3.11}$$

(which you can confirm by performing the derivative and confirming it gives the right result)

3.6 Harmonic oscillator

3.6.1 HO: Partition function

A harmonic oscillator has a set of quantised states with energies equal to:

$$E_n = (n + \frac{1}{2})\hbar\omega \tag{3.12}$$

Following the above definitions:

$$Z = \sum_n \exp\left[-\beta\left(n + \frac{1}{2}\right)\hbar\omega\right] \tag{3.13}$$

$$Z = \exp\left(-\frac{\beta\hbar\omega}{2}\right) \sum_n \exp(-\beta n \hbar\omega) \tag{3.14}$$

This sum has a fixed solution:

$$Z = \frac{\exp\left(-\frac{\beta\hbar\omega}{2}\right)}{1-\exp(-\beta\hbar\omega)} \tag{3.15}$$

So,

$$\ln Z = -\frac{\beta\hbar\omega}{2} - \ln\left[1-\exp(-\beta\hbar\omega)\right] \tag{3.16}$$

3.6.2 HO: Entropy

$$S = \frac{\partial}{\partial T}\left(k_B T \ln Z\right) \tag{3.17}$$

$$S = -\frac{\partial}{\partial T}\left(\frac{\hbar\omega}{2} - k_B T \ln\left[1-\exp(-\beta\hbar\omega)\right]\right) \tag{3.18}$$

$$S = -k_B \ln\left[1-\exp(-\beta\hbar\omega)\right] + \frac{\frac{\hbar\omega}{T}\exp(-\beta\hbar\omega)}{1-\exp(-\beta\hbar\omega)} \tag{3.19}$$

Making the ‘high temperature’ approximation, the energy splitting of the harmonic oscillator states $\hbar\omega$ is much less than the thermal energy $k_B T$. Hence, $\hbar\omega\beta << 1$, and

$$S \approx -k_B \ln\left[\beta\hbar\omega\right] + \frac{\frac{\hbar\omega}{T}(1-\beta\hbar\omega)}{\beta\hbar\omega} \tag{3.20}$$

$$S \approx -k_B \ln\left[\frac{\hbar\omega}{k_B T}\right] + k_B(1-\beta\hbar\omega) \tag{3.21}$$

$$S \approx -k_B \ln\left[\frac{\hbar\omega}{k_B T}\right] + k_B \tag{3.22}$$

$$S \approx k_B\left(1 + \ln\left[\frac{k_B T}{\hbar\omega}\right]\right) \tag{3.23}$$

QED