Density of States

A result of thermodynamics is that is a system is in thermodynamical equilibrium at some temperature T, then the probability to find a particle with energy E_n is given by

$$P_n \propto \exp\left(-\frac{E_n}{k_B T}\right)$$

Boltzmann dist. of prob.

k_B: Boltzmann constant

$[k_B] = J/K$

The proportionality symbol indicates a common factor

$$\sum_n P_n = \sum_n \varepsilon\, e^{-E_n/k_B T} = 1$$

$$\varepsilon \sum_n e^{-E_n/k_B T} = 1$$

$$\boxed{\varepsilon = \frac{1}{\sum_n e^{-E_n/k_B T}}}$$

The probabilities then are:

$$P_n = \frac{e^{-E_n/k_B T}}{\sum_n e^{-E_n/k_B T}}$$

For a quantum harmonic oscillator of frequency ω, we know that $E_n = \hbar\omega n$

$$P_n = \frac{e^{-\hbar\omega n/k_B T}}{\sum_n e^{-\hbar\omega n/k_B T}}$$

$$e^{-\hbar\omega n/k_BT} = \left(e^{-\hbar\omega/k_BT}\right)^n$$

$$\sum_n x^n = \frac{1}{1-x} \qquad \frac{1}{\sum_n x^n} = 1-x$$

Then $P_n = e^{-\hbar\omega n/k_BT}\left(1 - e^{-\hbar\omega/k_BT}\right)$

The probability to have our oscillator on n^{th} excited state is

$$\langle n\rangle = \sum_n n P_n = \sum_n n\, e^{-\hbar\omega n/k_BT}\left(1 - e^{-\hbar\omega/k_BT}\right)$$

$$= \left(1 - e^{-\hbar\omega/k_BT}\right)\sum_n n\, e^{-\hbar\omega n/k_BT}$$

$$\sum_n n x^n$$

$$\frac{d}{dx}\sum_n x^n = \sum_n \frac{d}{dx} x^n = \sum_n n x^{n-1}$$

$$x\frac{d}{dx}\sum_n x^n = \sum_n n x^n$$

$$\frac{d}{dx}\sum_n x^n = \frac{d}{dx}\frac{1}{1-x} = \frac{1}{(1-x)^2}$$

$$\sum_n n x^n = x\frac{d}{dx}\sum_n x^n = \frac{x}{(1-x)^2}$$

$$\langle n\rangle = \left(1 - e^{-\hbar\omega/k_BT}\right)\frac{e^{-\hbar\omega/k_BT}}{\left(1 - e^{-\hbar\omega/k_BT}\right)^2}$$

$$= \frac{e^{-\hbar\omega/k_BT}}{1 - e^{-\hbar\omega/k_BT}} = \frac{e^{-\hbar\omega/k_BT}}{e^{-\hbar\omega/k_BT}\left(e^{\hbar\omega/k_BT} - 1\right)}$$

$$\boxed{\langle n\rangle = \frac{1}{e^{\hbar\omega/k_BT} - 1}}$$

Planck Distribution

The total energy of the quantum oscillator is given by

$$U = \sum_k \sum_p \langle n \rangle_{k,p} \hbar \omega_{k,p} = \sum_k \sum_p \frac{\hbar \omega_{k,p}}{e^{\hbar\omega_{kp}/k_B T} - 1}$$

The summation is done over all wavevectors k and over all polarization p.

Although there are 3 polarization per wavevector, the latter are rather a cont. variable. $\sum_k \to \int dk$

We have to take into account the weight that wavector has in a range of frequencies ω to $\omega + d\omega$

weight is given by $D(\omega) d\omega$

$$\boxed{U = \sum_p \int d\omega \, D(\omega) \frac{\hbar \omega_{k,p}}{e^{\hbar\omega_{kp}/k_B T} - 1}}$$

Total energy of the collection of oscillators

Once the energy is know, we can obtain e.g. the heat capacity of the crystal

Heat capacity: $\dfrac{\text{How energy varies}}{\text{when we charge temperature}}$

$$C_{latt} = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} \sum_p \int d\omega \, D(\omega) \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

$$= \sum_p \int d\omega \, D(\omega) \, \hbar\omega \frac{\partial}{\partial T} \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

$$\frac{\partial}{\partial T} \frac{1}{e^{\hbar\omega/k_B T} - 1} = \frac{1}{(e^{\hbar\omega/k_B T} - 1)^2} e^{\hbar\omega/k_B T} \frac{\hbar\omega}{k_B T^2} \frac{\hbar\omega}{k_B} \frac{k_B}{\hbar\omega}$$

$$= \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{k_B}{\hbar\omega}$$

$$C_{latt} = \sum_p \int d\omega\, D(\omega)\, \hbar\omega \frac{e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT}-1)^2} \left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{k_B}{\hbar\omega}$$

$$\boxed{C_{latt} = k_B \sum_p \int d\omega\, D(\omega) \left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT}-1)^2}}$$

The central problem is to find $D(\omega)$
the number of modes per unit frequency range
This function is called the Density of states