Statistics of phonons

For each phonon mode ξ, any number of phonons can exist:

$$E_\xi = \hbar\omega_\xi \left(n_\xi + \frac{1}{2}\right), \quad n_\xi = 0, 1, 2, \ldots$$

Therefore, phonons are bosons and follow the Bose-Einstein statistics.

In thermal equilibrium, the number of phonons for each mode is determined by a minimum of Helmholtz's free energy $\left(\frac{\partial F}{\partial N}\right)_{T,V} = 0$.

Reminder: $dF = -PdV - SdT + \mu dN \Rightarrow \left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu$.

Therefore, the chemical potential for phonon gas is zero, $\mu = 0$ (because, the number of phonons is not fixed).

Let us determine the average number of phonons $\bar{n}_\xi$ for the mode ξ.

Boltzmann's probability: $W_{n_\xi} = \frac{1}{Z_\xi} e^{-E_{n_\xi}/kT}$

Partition Function: $Z_\xi = \sum_{n_\xi=0}^{\infty} e^{-E_{n_\xi}/kT} = e^{-\frac{\hbar\omega_\xi}{2kT}} \cdot \sum_{n_\xi=0}^{\infty} \left(e^{-\frac{\hbar\omega_\xi}{kT}}\right)^{n_\xi} = \frac{e^{-\frac{\hbar\omega_\xi}{2kT}}}{1-e^{-\frac{\hbar\omega_\xi}{kT}}}$

$$\bar{n}_\xi = \sum_{n_\xi=0}^{\infty} n_\xi \cdot W_{n_\xi} = \frac{1}{Z_\xi} \cdot \sum_{n_\xi=0}^{\infty} n_\xi \cdot e^{-\frac{\hbar\omega_\xi}{2kT}} \cdot e^{-\frac{\hbar\omega_\xi}{kT} \cdot n_\xi} \qquad \left(\frac{\hbar\omega_\xi}{kT} = x\right)$$

$$= \frac{e^{-x/2}}{Z_\xi} \cdot \sum_{n_\xi=0}^{\infty} \underbrace{n_\xi \cdot e^{-n_\xi \cdot x}}_{-\frac{\partial}{\partial x} \cdot e^{-n_\xi x}} = \frac{e^{-\frac{x}{2}}}{Z_\xi} \cdot \left(-\frac{\partial}{\partial x}\right) \underbrace{\sum_{n_\xi=0}^{\infty} \left(e^{-x}\right)^{n_\xi}}_{\frac{1}{1-e^{-x}}}$$

$$= \frac{e^{-x/2}}{Z_\xi} \cdot (-1) \cdot \frac{-1}{(1-e^{-x})^2} \cdot \left(-e^{-x}\right) \cdot (-1) =$$

$$= \frac{e^{-x/2}}{e^{-x/2}/1-e^{-x}} \cdot \frac{e^{-x}}{(1-e^{-x})^2} = \frac{e^{-x}}{1-e^{-x}} = \frac{1}{e^{+x}-1} \Rightarrow \boxed{\bar{n}_\xi = \frac{1}{e^{\frac{\hbar\omega_\xi}{kT}} - 1}}$$