

Chapter 3. Lattice vibration

Section 4. Einstein model for heat capacity.

- Goal of this section: To obtain a [heat capacity](#) model of a crystal by assuming that the lattice vibrates with a single [frequency](#).
- Flow derivation
- The energy levels of one-dimensional [quantum harmonic oscillator](#).
- The average quantum number of the harmonic oscillators.
 - ✓ [Planck distribution](#)
- Total vibrational energy
- Differentiation of the total vibrational energy by temperature to obtain a heat capacity.

3.4.1 Total vibrational energy

Sub-total vibrational energy at a given frequency (ω_i), equals the number of vibrational modes ($D(\omega)$), multiplied average vibrational energy ($\langle \varepsilon(\omega) \rangle$).

$$E_i = D(\omega_i) \langle \varepsilon(\omega_i) \rangle \quad (3.4.1)$$

The total energy of [the lattice vibration](#) equals the [sum of sub-total vibrational energy at each frequency](#). The equivalent estimation is integrating the total frequency of the product of number of vibrational modes and the average vibrational energy.

$$E_{total} = \sum_i E_i = \int E(\omega) d\omega = \int D(\omega) \langle \varepsilon(\omega) \rangle d\omega \quad (3.4.2)$$

3.4.2 Energy level of quantum mechanical harmonic oscillator

[Quantum-mechanical harmonic oscillator model has the energy levels of a particular mode with the angular frequency \$\omega\$ and its harmonics \$\varepsilon_n\$](#) , as expressed in equation 3.4.3:

$$\varepsilon_n = \left(n + \frac{1}{2}\right) \hbar \omega \quad (3.4.3)$$

Where n : quantum number. $n = 0$ term: zero-point energy or fundamental mode:

$$\varepsilon_0 = \frac{1}{2} \hbar \omega$$

This fundamental expression also represents a single wavelength as shown in figure 1, the sequential higher quantic energy levels $n = 1, 2, 3 \dots$ increase as a function of equation 3.4.3 and also implied representation of an increased number of wavelengths.

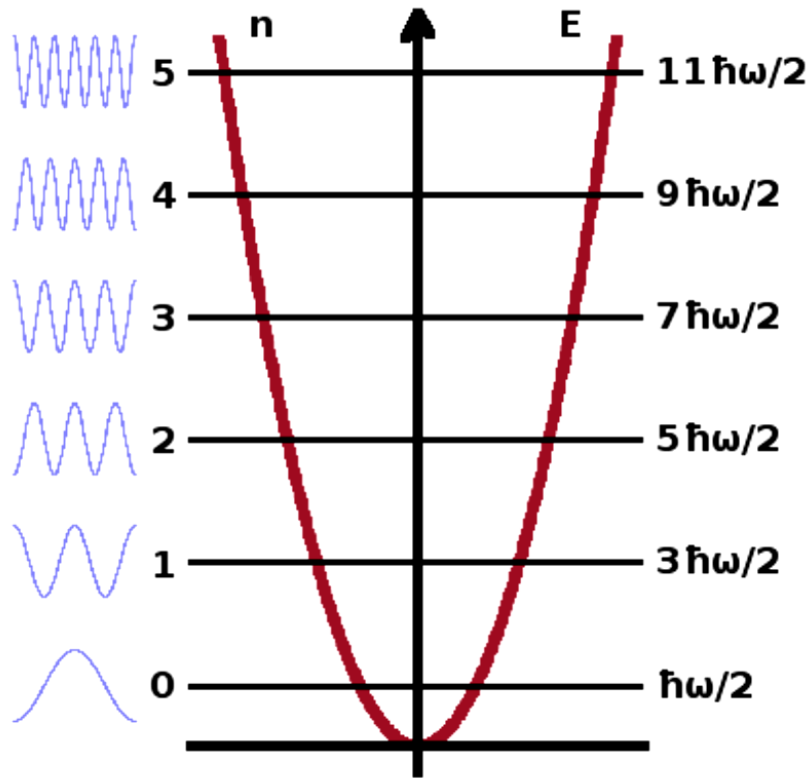


Figure 1. Representation of the quantic energy levels n of a quantum model mechanical harmonic oscillator. Source:

3.4.3 Relative population of each energy level

Let us consider the fraction $\frac{N_n}{N}$ of an oscillator with the n -th energy at a given frequency ω and a temperature, T . This can be obtained by estimating the probability to have the n -th level of energy divided by the sum of probabilities for all levels.

The probability can be estimated using the Boltzmann distribution: $P_n \propto \exp\left(-\frac{\varepsilon_n}{k_B T}\right)$

$$\frac{N_n}{N} = \frac{\exp\left(\frac{-(n + \frac{1}{2})\hbar\omega}{k_B T}\right)}{\sum_{s=0}^{\infty} \exp\left(\frac{-(s + \frac{1}{2})\hbar\omega}{k_B T}\right)} = \frac{\exp(-\frac{n\hbar\omega}{k_B T})}{\sum_s \exp(-\frac{s\hbar\omega}{k_B T})} \quad (3.4.4)$$

The result of equation 3.4.4 is due to the cancellation of the $\frac{1}{2}$ constant factor found in the numerator and denominator.

3.4.4 Planck distribution

To obtain the average quantum number $\langle n \rangle$. This is equal to the sum of the product of the quantum number S and the relative population of each energy level as expressed in the following equation:

$$\begin{aligned} \langle n \rangle &= \sum_s S \frac{N_s}{N} = \sum_s S \frac{s \exp(-\frac{s\hbar\omega}{k_B T})}{\sum_p \exp(-\frac{p\hbar\omega}{k_B T})} = \frac{\sum_s s \left\{ \exp(-\frac{\hbar\omega}{k_B T}) \right\}^s}{\sum_p \left\{ \exp(-\frac{\hbar\omega}{k_B T}) \right\}^p} = \frac{\sum_s s x^s}{\sum_p x^p} \\ &= \left(\frac{x}{(1-x)^2} \right) / \frac{1}{1-x} = \frac{x}{1-x} \end{aligned} \quad (3.4.5)$$

Being $x = \exp\left(-\frac{\hbar\omega}{k_B T}\right)$. Therefore, multiplying and dividing by the inverse conjugate equation (3.4.5) can be expressed like equation 3.4.6 as shown below:

$$\langle n \rangle = \frac{\exp\left(-\frac{\hbar\omega}{k_B T}\right)}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} = \frac{\exp\left(-\frac{\hbar\omega}{k_B T}\right) \exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left\{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)\right\} \exp\left(\frac{\hbar\omega}{k_B T}\right)} = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \quad (3.4.6)$$

Planck distribution. Is the average energy of an oscillator with an angular frequency ω at a temperature T :

$$\langle \varepsilon(\omega) \rangle = \left(\langle n \rangle + \frac{1}{2} \right) \hbar\omega \approx \langle n \rangle \hbar\omega = \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \quad (3.4.7)$$

3.4.5 Total vibrational energy

The total vibrational energy of the lattice, is the sum of the average energy of the quantum oscillator:

$$E_{total} = \sum_i \langle \varepsilon(\omega_i) \rangle = \sum_i \frac{\hbar\omega_i}{\exp\left(\frac{\hbar\omega_i}{k_B T}\right) - 1} \quad (3.4.8)$$

Each frequency can have more than one mode due to different \vec{k} and polarization. Approximating equation (3.4.5) by integrating:

$$E_{total} = \int D(\omega) \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega \quad (3.4.9)$$

Where $D(\omega)$: density states as a function of ω . The Planck distribution takes care of the distribution at a given ω .

3.4.6 Heat Capacity

Heat capacity C : T derivate of E_{total}

$$C = \frac{dE_{vib}}{dT} = \frac{d}{dT} \int D(\omega) \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega \quad (3.4.10)$$

We assume that density states $D(\omega)$: approximately independent from temperature T

$$\begin{aligned} C &= \int D(\omega) \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega \\ &= \int D(\omega) \left(-\frac{\hbar\omega}{\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2} \right) \frac{d}{dT} \left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1 \right) d\omega \\ &= \int D(\omega) \left(-\frac{\hbar\omega}{\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2} \right) \left(\exp\left(\frac{\hbar\omega}{k_B T}\right) \right) \left(-\frac{\hbar\omega}{k_B T^2} \right) d\omega \\ &= \int D(\omega) \frac{h^2 \omega^2 \exp\left(\frac{\hbar\omega}{k_B T}\right)}{k_B T^2 \left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2} d\omega \end{aligned} \quad (3.4.11)$$

$$= \int D(\omega) k_B \frac{\left(\frac{\hbar\omega}{k_B T}\right)^2 \exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2} d\omega = k_B \int D(\omega) \frac{x^2 e^x}{(e^x - 1)^2} d\omega \quad (3.4.12)$$

$$x = \frac{\hbar\omega}{k_B T} \quad (3.4.13)$$

3.4.7 Einstein solid -1

Einstein solid: the simplest model of heat capacity in which the results of statistical and quantum mechanics are considered.

Assumption: is that all atoms oscillate with the same frequency

$$\omega = \omega_\alpha$$

Only

Therefore, Einstein frequency is defined as:

$$\nu_\alpha = \frac{\omega_\alpha}{2\pi}$$

$$D(\omega) = D(\omega_\alpha) = \text{constant}$$

(3.4.14)

The average energy of one-dimensional oscillation of an atom:

$$\langle \varepsilon_{Es} \rangle = \frac{\hbar\omega_\alpha}{\exp(\hbar\omega_\alpha/k_B T) - 1}$$

(3.4.15)

3.4.8 Einstein solid -2

The total energy of the crystal consisting of 3-dimensional N atoms:

$$E_{Es} = 3N\langle \varepsilon_{Es} \rangle = \frac{3N\hbar\omega_\alpha}{\exp(\hbar\omega_\alpha/k_B T) - 1}$$

(3.4.16)

The heat capacity of the crystal:

$$\begin{aligned} C_{V,Es} &= \frac{3Nk_B \left(\frac{\hbar\omega_\alpha}{k_B T}\right)^2 \exp\left(\frac{\hbar\omega_\alpha}{k_B T}\right)}{\left[\exp\left(\frac{\hbar\omega_\alpha}{k_B T}\right) - 1\right]^2} \\ &= 3Nk_B \left(\frac{T_\alpha}{T}\right)^2 \frac{\exp\left(\frac{T_\alpha}{T}\right)}{\left[\exp\left(\frac{T_\alpha}{T}\right) - 1\right]^2} \end{aligned}$$

(3.4.17)

Resulting in the Einstein temperature:

$$T_\alpha = \frac{\hbar\omega_\alpha}{k_B}$$

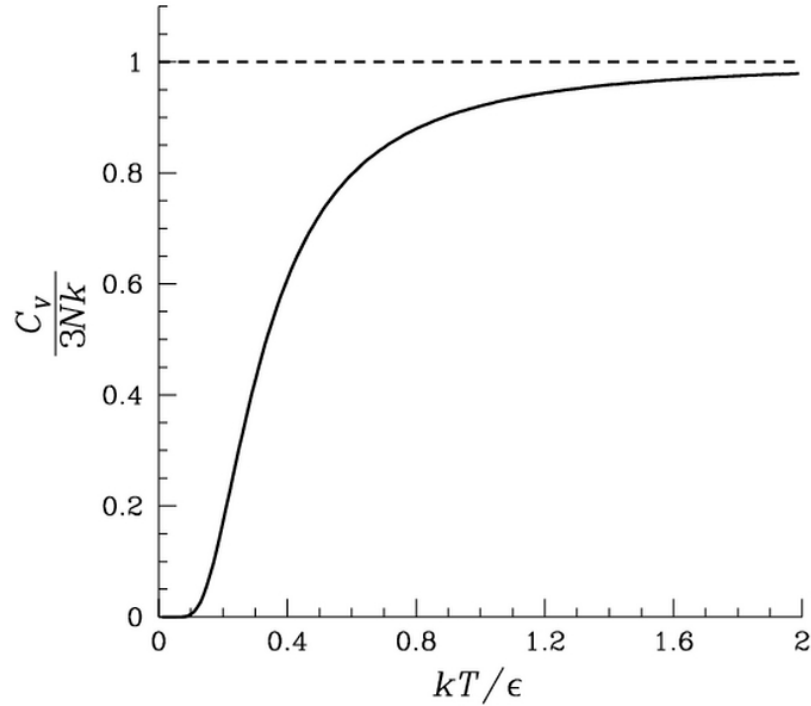


Figure 2. Heat capacity of an Einstein solid as a function of temperature T . Experimental value of $3Nk$ is recovered at high temperatures. Source: Wikipedia [Einstein solid - Wikipedia](#)

3.4.9 High T limits of Einstein heat capacity

High Temperature Limit: $T \rightarrow \infty$. When temperatures tend to infinity:

$$\begin{aligned} \frac{T_\alpha}{T} &\rightarrow 0 \\ \exp\left(\frac{T_\alpha}{T}\right) &\rightarrow 1 + \frac{T_\alpha}{T} \rightarrow 1 \\ C_{V,Es} &= \frac{3Nk_B \left(\frac{T_\alpha}{T}\right)^2 \exp\left(\frac{T_\alpha}{T}\right)}{\left[\exp\left(\frac{T_\alpha}{T}\right) - 1\right]^2} \rightarrow \frac{3Nk_B \left(\frac{T_\alpha}{T}\right)^2 \left(1 + \frac{T_\alpha}{T}\right)}{\left[\left(1 + \frac{T_\alpha}{T}\right) - 1\right]^2} \rightarrow 3Nk_B \end{aligned} \quad (3.4.18)$$

For one mole solid

$$C_{V,Es} = 3Nk_B \quad (3.4.19)$$

Approaches to Dulong-Petit law. Being $3R$: Dulong-Petit limit.

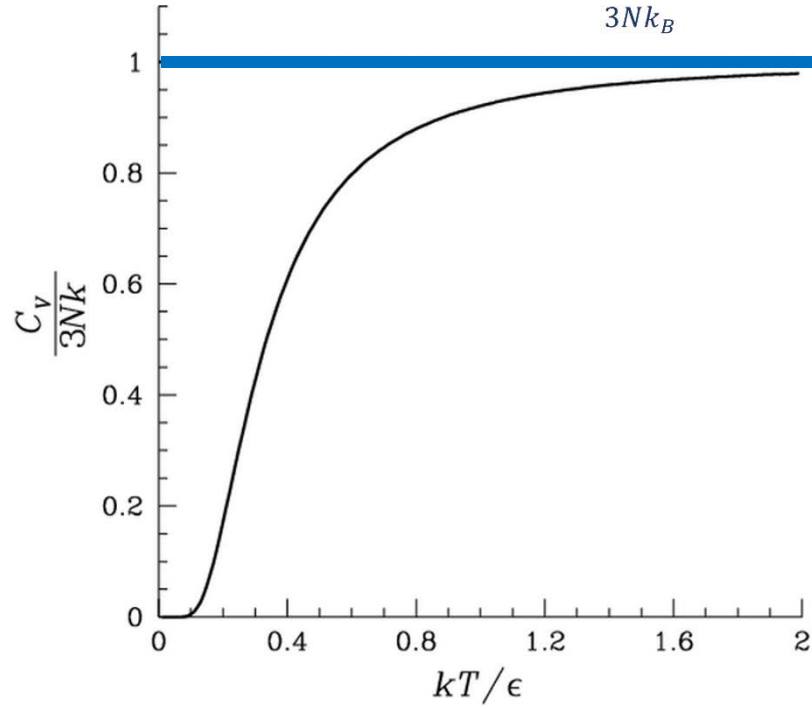


Figure 3. Heat capacity of an Einstein solid as a function of temperature T . Experimental value of $3Nk$ is recovered at high temperatures. Source: Wikipedia [Einstein solid - Wikipedia](#)

3.4.10 Low T limits of Einstein heat capacity

Low Temperature Limit: $T \rightarrow 0$

$$\begin{aligned}
 \frac{T_\alpha}{T} &\rightarrow \infty \\
 \exp\left(\frac{T_\alpha}{T}\right) - 1 &\rightarrow \exp\left(\frac{T_\alpha}{T}\right) \\
 C_{V,Es} &= \frac{3Nk_B \left(\frac{T_\alpha}{T}\right)^2 \exp\left(\frac{T_\alpha}{T}\right)}{\left[\exp\left(\frac{T_\alpha}{T}\right) - 1\right]^2} \rightarrow \frac{3Nk_B \left(\frac{T_\alpha}{T}\right)^2}{\exp\left(\frac{T_\alpha}{T}\right)} \rightarrow 0 \\
 \exp\left(\frac{T_\alpha}{T}\right) &\gg \left(\frac{T_\alpha}{T}\right)^2
 \end{aligned}
 \tag{3.4.20}$$

$C_{V,Es}$ rapidly decreases to zero with $T \rightarrow 0$

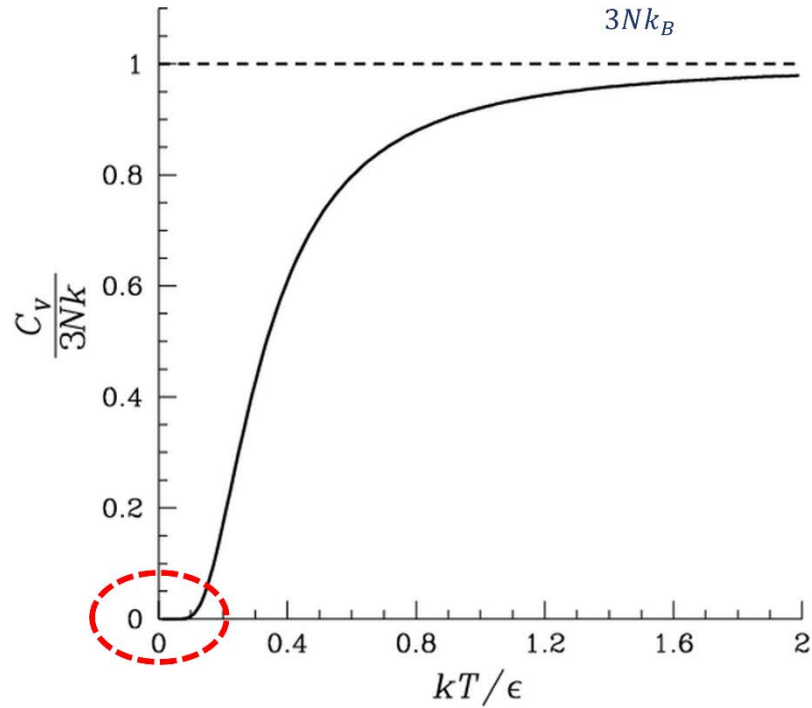


Figure 4. Heat capacity of an Einstein solid as a function of temperature T . Experimental value of $3Nk$ is recovered at high temperatures. At very low temperature it is observed that the results tend to zero, Source: Wikipedia [Einstein solid - Wikipedia](#)

3.4.11 Under estimation of low T heat capacity by Einstein model

Einstein model versus real solids

Systematic deviation of heat capacity at low T

The lattice vibration with a given a frequency ω cannot be excited at low temperature T due to the low thermal energy.

The oscillation of solids: far from single frequency ω

Maybe the frequency ω vibration excited at low temperature T should be low

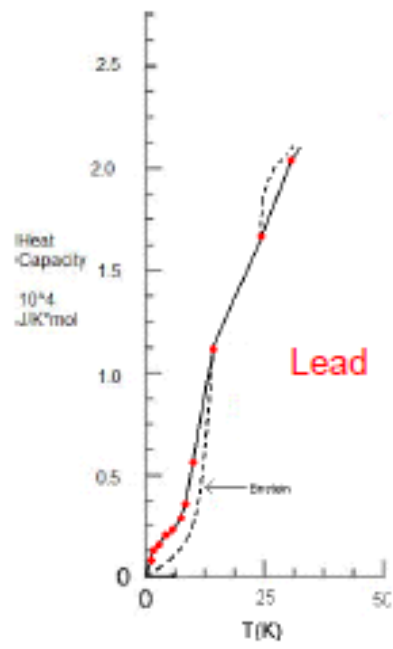


Figure 5. This plot shows the experimental heat capacity values of lead compared to the expected values calculated from Einstein's heat capacity model.