3. Lattice vibration

3.4. Einstein model for heat capacity

This section is dedicated to modeling the temperature dependence of (isochoric) heat capacity (C) for crystals by using Einstein model. Here, crystal is approximated as an assemblage of harmonic oscillators (Fig. 3.4.1). We need to derive the total (internal) energy (E_{total}) of the system to obtain C, because C is a derivative of E_{total} with respect to temperature (T). Firstly, we will recall the energy level of the quantum harmonic oscillator, which are derived in the section 3.3. Then we will derive the average quantum number of the harmonic oscillators in solids. Lastly, C will be acquired from the total vibrational energy E_{total} of the system.

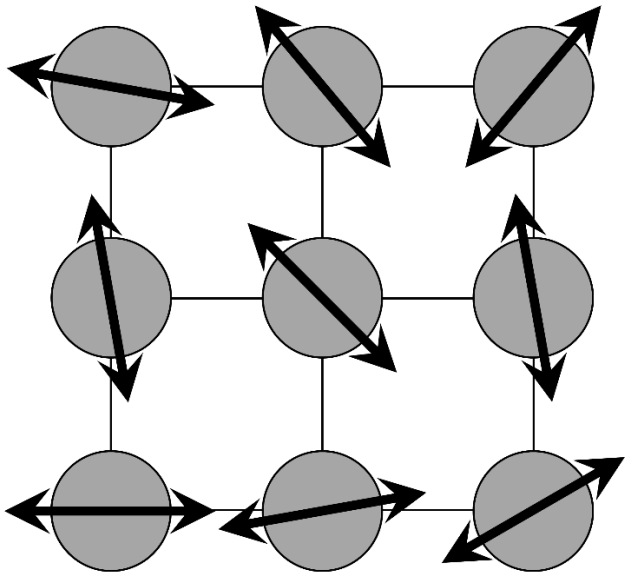


Fig. 3.4.1. The simplest model for crystal lattice. Each atom vibrates around a stable lattice point.

3.4.1 Energy level of quantum harmonic oscillator

In this section, we will obtain the total vibrational energy E_{total} of crystals based on quantum mechanics and statistical mechanics. To begin with, let us recall the energy level of a quantum harmonic oscillator. As derived in the section 3.3, the energy level of the harmonic oscillator which has a particular vibrational mode and the angular frequency (ω) can be written as:

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{3.4.1}$$

Here, n (= 0, 1, 2, …) is quantum number and $\hbar$ is the reduced Planck constant (Fig. 3.4.2). In the case of n = 0, the harmonic oscillator is in the fundamental mode and so has the ground-state energy level: $\varepsilon_0 = \hbar\omega/2$. Considering that there are N_n atoms whose energy level is ε_n at given ω and T in the N-atom crystal, the probability that the presence of atoms in the n-th state can be expressed by using Boltzmann distribution:

$$\frac{N_n}{N} = \frac{e^{-\varepsilon_n/k_{\text{B}}T}}{\sum_{s=0}^{\infty} e^{-\varepsilon_s/k_{\text{B}}T}} = \frac{e^{-\hbar\omega/2k_{\text{B}}T}e^{-n\hbar\omega/k_{\text{B}}T}}{e^{-\hbar\omega/2k_{\text{B}}T}\sum_s e^{-s\hbar\omega/k_{\text{B}}T}} = \frac{e^{-n\hbar\omega/k_{\text{B}}T}}{\sum_s e^{-s\hbar\omega/k_{\text{B}}T}} \tag{3.4.2}$$

where k_{B} is Boltzmann constant. Eq. (3.4.2) regards the total number of all possible energy levels as infinity. It is natural and accurate enough considering that real matters contain ~10^{23} atoms and/or

molecules. Then we can derive the average quantum number $\langle n \rangle$ of the system as an expected value for n-th state using Eq. (3.4.2):

$$\langle n \rangle = \sum_s s \frac{N_s}{N} = \frac{\sum_s s e^{-s\hbar\omega/k_B T}}{\sum_p e^{-p\hbar\omega/k_B T}} \tag{3.4.3}$$

By introducing a parameter $x \equiv e^{-\hbar\omega/k_B T}$, Eq. (3.4.3) becomes:

$$\langle n \rangle = \frac{\sum_s s x^s}{\sum_p x^p} = \frac{x/(1-x)^2}{1/(1-x)} = \frac{x}{1-x} \tag{3.4.4}$$

Then $\langle n \rangle$ is obtained as a function of temperature:

$$\langle n \rangle = \frac{e^{-\hbar\omega/k_B T}}{1 - e^{-\hbar\omega/k_B T}} = \frac{e^{-\hbar\omega/k_B T} e^{\hbar\omega/k_B T}}{(1 - e^{-\hbar\omega/k_B T}) e^{\hbar\omega/k_B T}} = \frac{1}{e^{\hbar\omega/k_B T} - 1} \tag{3.4.5}$$

This function form represents the Planck distribution. Since $\langle n \rangle \gg 1$ for many ω and T, the average energy of an oscillator with ω at T is expressed as:

$$\langle \varepsilon(\omega) \rangle = \left(\langle n \rangle + \frac{1}{2} \right) \hbar\omega \approx \langle n \rangle \hbar\omega = \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \tag{3.4.6}$$

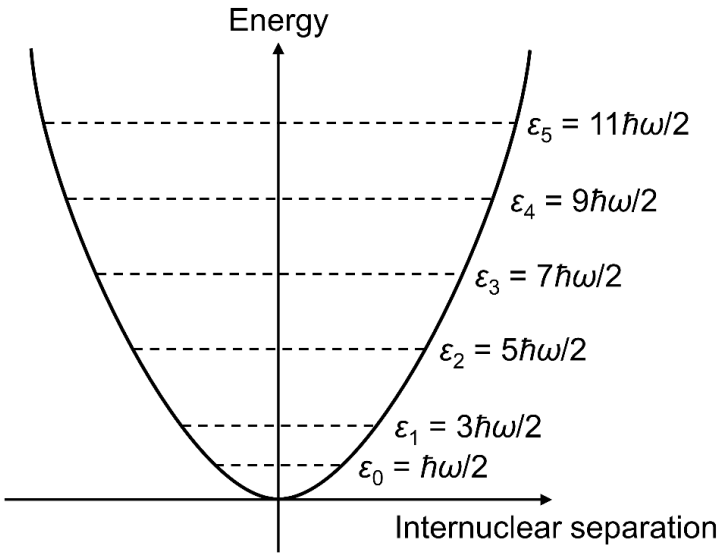


Fig. 3.4.2. Quantum harmonic oscillator potential (solid curve) and its energy levels (dashed lines).

Let us derive the total vibrational energy of many-particle solids. Although ω was given in the above-mentioned theory, atoms' ω of matters should have a certain variety. Hence, defining the population of vibrational modes with a frequency ω_i as $D(\omega_i)$ (density of states), we can access the subtotal vibrational energy E_i for ω_i:

$$E_i = D(\omega_i) \langle \varepsilon(\omega_i) \rangle \tag{3.4.7}$$

By combining Eqs. (3.4.6) and (3.4.7), the total energy can be calculated as:

$$E_{\text{total}} = \sum_i E_i = \sum_i D(\omega_i) \langle \varepsilon(\omega_i) \rangle = \sum_i D(\omega_i) \frac{\hbar\omega_i}{e^{\hbar\omega_i/k_B T} - 1} \tag{3.4.8}$$

If we know the enough fine $D(\omega)$ data, E_{total} can be described by an integration as well:

$$E_{\text{total}} = \int D(\omega)\langle\varepsilon(\omega)\rangle \mathrm{d}\omega = \int D(\omega)\frac{\hbar\omega}{e^{\hbar\omega/k_{\mathrm{B}}T}-1}\mathrm{d}\omega \tag{3.4.9}$$

3.4.2 Heat capacity

Let us derive the heat capacity from the equations obtained until here. In statistical mechanics, heat capacity C can be derived by the thermodynamic relationship with the internal energy: a temperature derivative of the total energy E_{total}. Thus, C can be written as follows from Eq. (3.4.9):

$$C = \frac{\mathrm{d}E_{\text{total}}}{\mathrm{d}T} = \frac{\mathrm{d}}{\mathrm{d}T}\int D(\omega)\frac{\hbar\omega}{e^{\hbar\omega/k_{\mathrm{B}}T}-1}\mathrm{d}\omega \tag{3.4.10}$$

where density of states $D(\omega)$ is assumed to be a function of ω only and is independent of T. Then,

$$C = \int D(\omega)\frac{\mathrm{d}}{\mathrm{d}T}\frac{\hbar\omega}{e^{\hbar\omega/k_{\mathrm{B}}T}-1}\mathrm{d}\omega \tag{3.4.11}$$

$$= \int D(\omega)\frac{-\hbar^2\omega^2/k_{\mathrm{B}}T^2 e^{\hbar\omega/k_{\mathrm{B}}T}}{-(e^{\hbar\omega/k_{\mathrm{B}}T}-1)^2}\mathrm{d}\omega$$

$$= \int D(\omega)k_{\mathrm{B}}\frac{(\hbar\omega/k_{\mathrm{B}}T)^2 e^{\hbar\omega/k_{\mathrm{B}}T}}{(e^{\hbar\omega/k_{\mathrm{B}}T}-1)^2}\mathrm{d}\omega \tag{3.4.12}$$

When we define a variable $y \equiv \hbar\omega/k_{\mathrm{B}}T$, Eq. (3.4.12) can be written as a simpler form:

$$C = k_{\mathrm{B}}\int D(\omega)\frac{y^2 e^y}{(e^y-1)^2}\mathrm{d}\omega \tag{3.4.13}$$

3.4.3 Einstein model and its problem

Einstein model is the simplest model which describes thermal properties of crystals at various temperatures. It assumes all atoms are mutually independent and oscillate with the same frequency ω_α. On such assumption, the density of states of Einstein solids is given by:

$$D(\omega) = \begin{cases} 1 & \text{if } \omega = \omega_\alpha \\ 0 & \text{if } \omega \neq \omega_\alpha \end{cases} \tag{3.4.14}$$

By substituting ω_α to Eq. (3.4.6), the average energy of one-dimensional oscillation of an atom in Einstein solids $\langle\varepsilon_{\text{Es}}\rangle$ is:

$$\langle\varepsilon_{\text{Es}}\rangle = \frac{\hbar\omega_\alpha}{e^{\hbar\omega_\alpha/k_{\mathrm{B}}T}-1} \tag{3.4.15}$$

In the case of a three-dimensional crystal which contains N atoms, the vibration of atoms have $3N$ directional components (degree of freedom) in total because the oscillation of each atom has three components. Its total energy E_{Es} is thus expressed as:

$$E_{\text{Es}} = 3N\langle\varepsilon_{\text{Es}}\rangle = \frac{3N\hbar\omega_\alpha}{e^{\hbar\omega_\alpha/k_{\mathrm{B}}T}-1} \tag{3.4.16}$$

Therefore, the heat capacity of Einstein solids is given by the following equation:

$$C = \frac{\mathrm{d}E_{\text{Es}}}{\mathrm{d}T} = \frac{3Nk_{\mathrm{B}}(\hbar\omega_\alpha/k_{\mathrm{B}}T)^2 e^{\hbar\omega_\alpha/k_{\mathrm{B}}T}}{(e^{\hbar\omega_\alpha/k_{\mathrm{B}}T}-1)^2} \tag{3.4.17}$$

The detail of the calculation is already given in the section 3.4.2. By defining the temperature T_α as:

$$T_\alpha \equiv \frac{\hbar\omega_\alpha}{k_{\mathrm{B}}} \tag{3.4.18}$$

Eq. (3.4.17) turns into:

$$C = 3Nk_{\mathrm{B}}\left(\frac{T_\alpha}{T}\right)^2 \frac{e^{T_\alpha/T}}{(e^{T_\alpha/T}-1)^2} \tag{3.4.19}$$

Here, T_α is Einstein temperature, which characterizes thermal properties of crystals at low-T when $T_\alpha \ll 1$ and those at high-T when $T_\alpha \gg 1$. In order to catch the high- and low-T limit of the heat capacity, let us write the exponential term $e^{T_\alpha/T}$ as a power series. The Laurent series of $e^{T_\alpha/T}$ about $T_\alpha/T = 0$ is:

$$e^{T_\alpha/T} = 1 + \frac{T_\alpha}{T} + \frac{1}{2!}\left(\frac{T_\alpha}{T}\right)^2 + \frac{1}{3!}\left(\frac{T_\alpha}{T}\right)^3 + \cdots \tag{3.4.20}$$

Thus, the high-T limit ($T \to \infty$, $T_\alpha/T \to +0$) of this term is:

$$e^{T_\alpha/T} \xrightarrow{T_\alpha/T \to +0} 1 + \frac{T_\alpha}{T} \to 1 \tag{3.4.21}$$

From Eqs. (3.4.19) and (3.4.21) the heat capacity at high temperature is then written as follows:

$$C_{V,\mathrm{Es}} \xrightarrow{T_\alpha/T \to +0} 3Nk_{\mathrm{B}}\left(\frac{T_\alpha}{T}\right)^2 \frac{1 - T_\alpha/T}{(1 + T_\alpha/T - 1)^2} = 3Nk_{\mathrm{B}}\left(1 - \frac{T_\alpha}{T}\right) \to 3Nk_{\mathrm{B}} \tag{3.4.22}$$

In the case that N equals to one mole,

$$C_{V,\mathrm{Es}} \to 3R \tag{3.4.23}$$

where R is the gas constant. This result consistent with the fact that molar heat capacity of many solids is close to $3R \approx 25$ J(mol K)$^{-1}$ by experiments (Dulong-Petit law) at high T such as $\geq \sim 2T_\alpha$. In addition, the high-T limit of $C_{V,\mathrm{Es}}$ equals the isochoric heat capacity of an ideal gas. This coincidence is convincing when we look at the definition that an ideal gas has no intermolecular interaction. In contrast, for the low-T limit ($T \to +0$, $T_\alpha/T \to \infty$) of $e^{T_\alpha/T}$ is:

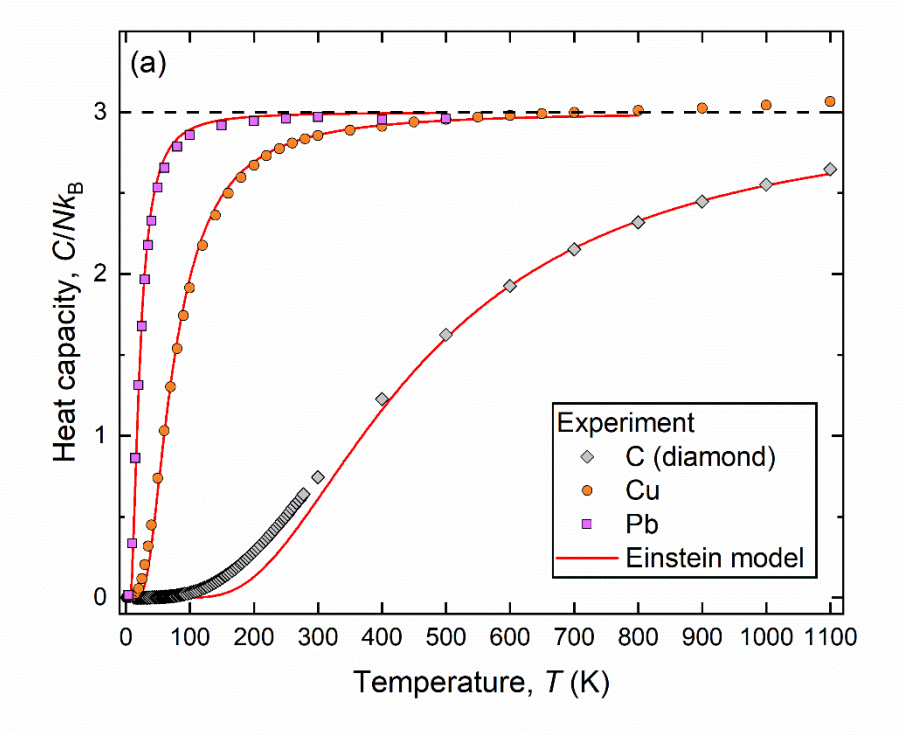
$$e^{T_\alpha/T} - 1 \xrightarrow{T_\alpha/T \to \infty} e^{T_\alpha/T} \tag{3.4.24}$$

Hence, the low-T limit of $C_{V,\mathrm{Es}}$ is:

$$C_{V,\mathrm{Es}} \xrightarrow{T_\alpha/T \to \infty} 3Nk_{\mathrm{B}}\left(\frac{T_\alpha}{T}\right)^2 \frac{e^{T_\alpha/T}}{(e^{T_\alpha/T})^2} = 3Nk_{\mathrm{B}}\frac{(T_\alpha/T)^2}{e^{T_\alpha/T}} \to 0 \tag{3.4.25}$$

Unlike the case of $C_{V,\mathrm{Es}}$ at high T (Eqs. (3.4.22) and (3.4.23)), $C_{V,\mathrm{Es}}$ at low T near 0 K contains the reduced Planck constant $\hbar$ inside T_α (cf. the second formula from the right side of Eq. (3.4.25)). This demonstrates that we should take quantum effects into consideration to understand low-T solids' heat capacity. Contrastively, the heat capacity at high T is nearly constant and can be sufficiently explained by classical mechanics. Fig. 3.4.3 shows $C_{V,\mathrm{Es}}$ at various temperatures together with experimental results for several monatomic crystals. The Einstein model took a different approach from previous ideas at that time and succeeded in explaining the low-T behavior of the heat capacity of crystals.

Although heat capacity predicted by the Einstein model is roughly consistent with experimental results, there are significant discrepancies at low T (Fig. 3.4.3). This is due to the following factors: (1) the frequency of atoms is assumed to be common, and (2) each harmonic oscillator is independent. The sharp change in $C_{V,\mathrm{Es}}$ at low T indicates that, unlike real solids, atoms in the Einstein solid remain in the ground state (ε_0) and do not excite near 0 K. Once the system reaches an enough high temperature around $\sim T_\alpha/10$, many atoms are raised to the excited state (ε_1), and $C_{V,\mathrm{Es}}$ rises as a result. If we consider various ω and coupled oscillation of lattices, the model heat capacity will be significantly improved for many monatomic crystals.



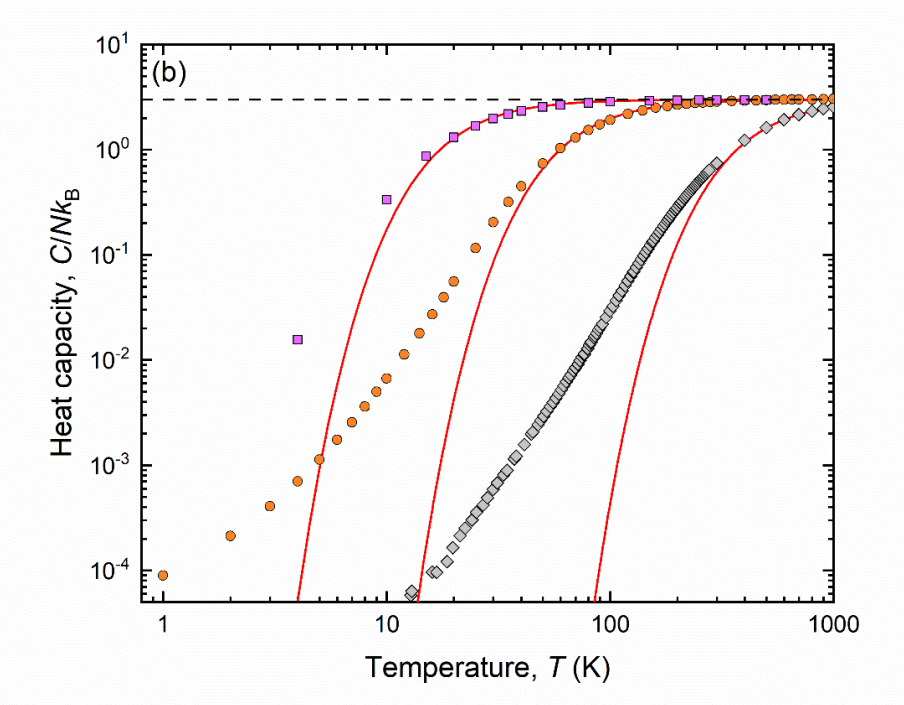


Fig. 3.4.3. Comparisons of the experimental molar heat capacity data to the Einstein model for C (diamond) (Desnoyehs and Morrison, 1958; Victor, 1962), Cu (White and Collocott, 1984), and Pb (Stedman et al., 1967) in (a) linear and (b) logarithmic representations. The horizontal dashed line at 3 indicates the Dulong-Petit limit.

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