3. Lattice Vibration

3.2. Energy Equipartition Law and Dulong-Petit Law

3.2.1 Equipartition of Energy

The equipartition of energy relates the temperature of a system to its average energies. The law of equipartition (law of statistical mechanics) explain that when one system is in thermal equilibrium, on the average, an equal amount of energy will be associated with each degree of freedom, in other words, the energy will be proportional to the number of dimensions necessary to describe the position of a particle that moves in space. This law is based on the work of James Clerk Maxwell and Ludwing Boltzmann, and states that a system of particles at absolute temperature will have an average energy of $\frac{1}{2}\,k_B T$ associated with each degree of freedom, in which $k_B$is the Boltzmann constant. This explain how the equipartition theorem is able to makes quantitative predictions regarding the heat capacity, it gives the total average kinetic and potential energies for a system at a given temperature, from which the system's heat capacity can be computed.

3.2.2 Dulong-Petit law

The Dulong–Petit law is a thermodynamic law which represent the classical expression for the molar specific heat of certain crystals. The Dulong-Petit Law is based on the result of experiments on three dimensional solid crystals to determine the heat capacities of a variety of these solids. The results proved that all investigated solids had a heat capacity of approximately 3R (25 $J\,K^{-1}gmol^{-1}$) at room temperature. The equipartition theory provides a simple explanation for the Dulong-Petit law: an atom in a solid is considered to be a localized harmonic oscillator, with three modes of vibration. There are two degrees of freedom associated with each mode of vibration, or a total of six degrees of freedom, thus the simplified form to describe the specific heat $C_v = \frac{1}{2}RD$, in which D is the degrees of freedom, gives for a monoatomic solid:

$$C_v = \frac{1}{2}RD = \frac{1}{2}R(6) = 24{,}987\ \frac{J}{gmol\ K} \qquad \mathbf{(3.2.1)}$$

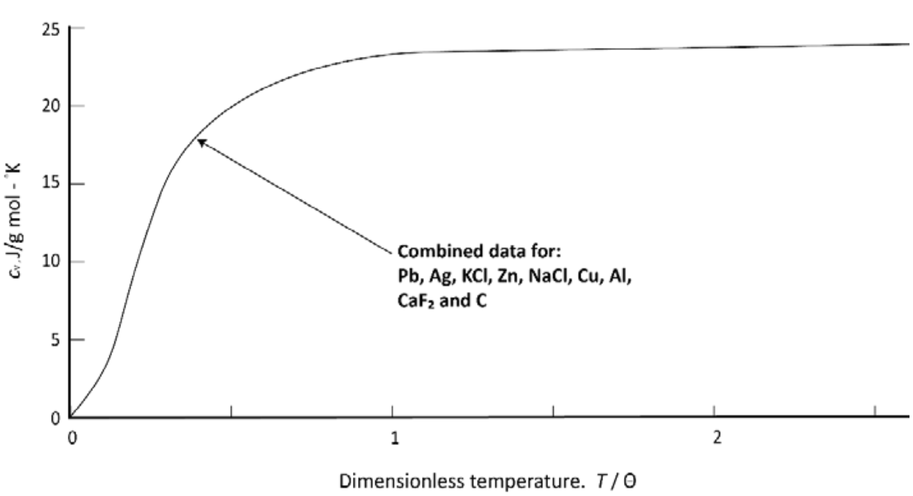

Figure 3.2.1. Correlated data from nine different substances onto a single curve, with the aid of a dimensionless temperature, T/θ. Source: Chang (1979).

2.3 Derivation of Dulong-Petit law

The atoms in solid are oscillating and being bound by atomic bounding, the energy is given by the kinetic and potential energy. The kinetic energy of the atom *i-th* in the direction *j-th* is expressed by $\varepsilon_{K,ij} = p_{ij}^2 / 2m_i$, and the potential energy by $\varepsilon_{P,ij} = \frac{1}{2} k_{ij} q_{ij}^2$, in which p_{ij}^2 represent the linear momentum of the *i-th* atom in the *j-th* direction, m_i is the mass of the *i-th* atom, q_{ij}^2 is the deviation of the *i-th* atom from its equilibrium position in the *j-th* direction and $k_{ij}$is the spring constant for the potential energy in the *j-th* direction. Hence, the total energy of the crystal E_T is equal to the sum of the kinetic energy in the 3 directions and the potential energy in the 3 directions of all atoms, as is expressed in the equation (3.2.2).

$$E_T = \sum_{i=1}^{N} \sum_{j=1}^{3} (\varepsilon_{K,ij} + \varepsilon_{P,ij}) = \sum_{i=1}^{N} \sum_{j=1}^{3} (\frac{p_{ij}^2}{2m_i} + \frac{1}{2} k_{ij} q_{ij}^2) = \sum_{l=1}^{3N} \frac{p_l^2}{2m_l} + \frac{1}{2} k_l q_l^2 \quad \mathbf{(3.2.2)}$$

$$I = 3X0+1, 3x0+2, 3x0+3, 3x1+1, 3x1+2, 3x2+1, 3x2+2, 3x2+3, \dots,$$

$$3(N-1)+1, 3(N-1)+2, and\ 3(N-1)+3 = 1,2,3,4,5,6,\dots,3N-2, 3N-1, 3N$$

The average kinetic energy of one atom in one direction can be obtained using the Boltzmann distribution. This explain the average kinetic energy of one atom, is given by the rate of the multiple integrals of the kinetic energy multiplied by the factor $exp[-E_T/k_BT]$ with regards to the multiple integrals of the factor $exp[-E_T/k_BT]$, the simplified description of the average kinetic energy is given by the equation (3.2.4). A similar deduction can be used for the potential energy of one atom in one direction, obtaining a similar value as is shown by the equation (3.2.5)

$$\langle \varepsilon_{K,n} \rangle = \frac{\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \varepsilon_{K,n}\ exp[-E_T/k_BT] dp_1 dq_1 \dots . dp_{3N} dq_{3N}}{\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty}\ exp[-E_T/k_BT] dp_1 dq_1 \dots . dp_{3N} dq_{3N}}$$

$$= \frac{\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \frac{p_n^2}{2m_n}\ exp\left[-\sum_{l=1}^{3N} (\frac{p_l^2}{2m_l} + \frac{1}{2} k_l q_l^2)/k_BT\right] dp_1 dq_1 \dots . dp_{3N} dq_{3N}}{\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty}\ exp\left[-\sum_{l=1}^{3N} (\frac{p_l^2}{2m_l} + \frac{1}{2} k_l q_l^2)/k_BT\right] dp_1 dq_1 \dots . dp_{3N} dq_{3N}}$$

$$= \frac{\int_{-\infty}^{\infty} \frac{p_n^2}{2m_n} exp\left[-\frac{p_n^2/2m_n}{k_BT}\right] dp_n \prod_{l=1,l\neq n}^{3N} \int_{-\infty}^{\infty} exp\left[-\frac{p_l^2/2m_l}{k_BT}\right] dp_l \prod_{l=1,}^{3N} \int_{-\infty}^{\infty} exp\left[-\frac{\frac{1}{2}k_l q_l^2}{k_BT}\right] dq_l}{\int_{-\infty}^{\infty} exp\left[-\frac{p_n^2/2m_n}{k_BT}\right] dp_n \prod_{l=1,l\neq n}^{3N} \int_{-\infty}^{\infty} exp\left[-\frac{p_l^2/2m_l}{k_BT}\right] dp_l \prod_{l=1,}^{3N} \int_{-\infty}^{\infty} exp\left[-\frac{\frac{1}{2}k_l q_l^2}{k_BT}\right] dq_l}$$

$$= \frac{\frac{1}{2m_n} \int_{-\infty}^{\infty} p_n^2\, exp\left[-\frac{1}{2m_n k_BT} p_n^2\right] dp_n}{\int_{-\infty}^{\infty} p_n^2\, exp\left[-\frac{1}{2m_n k_BT} p_n^2\right] dp_n} \qquad \mathbf{(3.2.3)}$$

$$\langle \varepsilon_{K,n} \rangle = \frac{\frac{1}{2m_n} \int_{-\infty}^{\infty} p_n^2\, exp\left[-\frac{1}{2m_n k_B T} p_n^2\right] dp_n}{\int_{-\infty}^{\infty} p_n^2\, exp\left[-\frac{1}{2m_n k_B T} p_n^2\right] dp_n} = \frac{\frac{1}{2m_n} \sqrt[1/2]{\pi/\left(\frac{1}{2m_n k_B T}\right)^3}}{\sqrt{\pi/2m_n k_B T}} = \frac{1}{2} k_B T \ \mathbf{(3.2.4)}$$

$$x = p_n, a = \frac{1}{2m_n k_B T}, \int_{-\infty}^{\infty} \exp(ax^2)\, dx = \sqrt{\pi/_{a}}, \int_{-\infty}^{\infty} x^2 \exp(-ax^2)\, dx = \frac{1}{2}\sqrt{\pi/_{a^3}}$$

$$\langle \varepsilon_{P,n} \rangle = \frac{\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \varepsilon_{P,n}\ exp[-E_T/k_B T] dp_1 dq_1 \dots . dp_{3N} dq_{3N}}{\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty}\ exp[-E_T/k_B T] dp_1 dq_1 \dots . dp_{3N} dq_{3N}}$$

$$= \frac{\int_{-\infty}^{\infty} \frac{q_n^2 k_n}{2}\ exp\left[-\frac{\frac{q_n^2 k_n}{2}}{k_B T}\right] dp_n \prod_{l=1, l \neq n}^{3N} \int_{-\infty}^{\infty} exp\left[-\frac{\frac{q_l^2 k_l}{2}}{k_B T}\right] dp_l \prod_{l=1,}^{3N} \int_{-\infty}^{\infty} exp\left[-\frac{p_n^2/_{2m_n}}{k_B T}\right] dq_l}{\int_{-\infty}^{\infty} exp\left[-\frac{\frac{q_n^2 k_n}{2}}{k_B T}\right] dp_n \prod_{l=1, l \neq n}^{3N} \int_{-\infty}^{\infty} exp\left[-\frac{\frac{q_l^2 k_l}{2}}{k_B T}\right] dp_l \prod_{l=1,}^{3N} \int_{-\infty}^{\infty} exp\left[-\frac{p_n^2/_{2m_n}}{k_B T}\right] dq_l}$$

$$\langle \varepsilon_{P,n} \rangle = \frac{\frac{k_n}{2} \int_{-\infty}^{\infty} q_n^2\, exp\left[-\frac{k_n}{2k_B T} q_n^2\right] dp_n}{\int_{-\infty}^{\infty} exp\left[-\frac{k_n}{2k_B T} q_n^2\right] dp_n} = \frac{\frac{k_n}{2} \sqrt[1/2]{\pi/\left(\frac{k_n}{2k_B T}\right)^3}}{\sqrt{\pi/\left(\frac{k_n}{2k_B T}\right)}} = \frac{1}{2} k_B T \quad (3.2.5)$$

$$x = q_n, a = \frac{k_n}{2k_B T}$$

Thus, from the present deduction, for one freedom of both kinetic and potential energy has an average energy value of $\frac{1}{2} k_B T$, as it was explained in 3.2.1. Since one atom has 6 energy freedoms, 3 for kinetic and 3 for potential energy, the total energy of one atom tends to be $3k_B T$, and *3RT* per one mole of solid at T.

2.4 Limitation of Dulong-Petit law

The accuracy of Petit and Dulong law decrease at low temperatures and also fails to explain why certain substances deviate very strongly from these laws. The figure 3.2.1, shows how the specific heat of the variety of solids, when they are plotted against temperature, tend to limit the Specific heat as the temperature is increased. As the temperature goes up, the specific heat goes up until it approaches the Dulong and Petit prediction at high temperature. Nonetheless the explanation for Petit and Dulong's experiment was not sufficient when it was discovered that heat capacity decreased and going to zero as a function of T3 (or, for metals, T) as temperature approached absolute zero. Some applications and Cv values for certain materials are given in table 3.2.1.

Table 3.2.1. Application of Laws of DuLong and Petit

Molar C_v for Monoatomic Solids			**Molar C_v for Diatomic and Triatomic Solids**		
Substance	**T, °C**	***$C_{v,}$, KJ/ gmole* °C**	**Substance**	**T, °C**	***$C_{v,}$ /2 or 3, KJ/ gmole* °C**
Ag	0	25.1	AgCl	28	26.2
Au	0	25.4	CuO	22	21.8
Cr	0	22.4	KCl	23	25.9
Fe	0	24.5	CuS	25	24.9
Ni	0	25.3	PbO_2	24	21.6
Sb	0	25.1	CaF_2	15-99	23.5
Graphite	0	7.6	ZnO	16—99	21.3
Diamond	0	5.2	$PbCl_2$	0-20	25.4

2.5 References

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