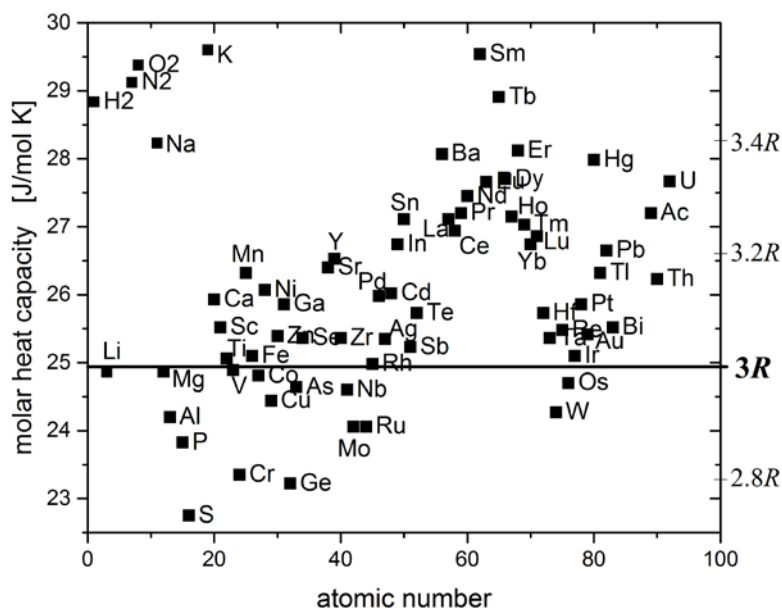# 3. Lattice vibration

2. Energy equipartition law and Dulong- Petit law

2.1 Dulong-Petit law

Dulong-Petit law is that molar isochoric heat capacity of solids is 3R (25J K^{-1} mol). Depending on the type of elements, heat capacities of solids are more or less the same.

Fig. 1. Molar heat capacity of most elements at 25 °C. It is the range between 2.8 R and 3.4 R: Plot as a function of atomic number with a y range from 22.5 to 30 J/mol K.

2.2 Derivation of Dulong-Petit law 1

Classic view of energy of a crystal

Atoms in a crystal are oscillating and being bounded by atomic bounding. That's why every single atom's energy can be described by the sum of kinetic energy of one atom and potential one. the kinetic energy of i-th atom in j-th direction is represented as $\varepsilon_{K,ij}$ and potential energy of i-th atom in j-th direction is represented as $\varepsilon_{P,ij}$, using p_{ij} (linear momentum of the i-th atom in the j-th direction), m_i (mass of the i-th atom), q_{ij} (deviation of the i-th atom from its equilibrium position in the j-th direction) and k_{ij} ("spring constant" for the potential energy in the j-th direction).

$$\varepsilon_{k,ij} = \frac{p_{ij}^2}{2m_i} \tag{3.3.1}$$

$$\varepsilon_{p,ij} = \frac{k_{ij}q_{ij}^2}{2} \tag{3.3.2}$$

2.3 Derivation of Dulong-Petit law 2

Sum of kinetic and potential energy

Energy of a crystal (E_T) means sum of kinetic energy in 3 directions and potential energy in 3directins of each atom in a crystal.

$$Et = \sum_{i=1}^{N} \sum_{j=1}^{3} \left(\varepsilon_{k,i\ j} + \varepsilon_{p,i\ j} \right)$$

$$= \sum_{i=1}^{N} \sum_{j=1}^{3} \left(\frac{p_{ij}^2}{2m_i} + \frac{k_{ij} q_{ij}^2}{2} \right)$$

$$= \sum_{l=1}^{3N} \left(\frac{p_l^2}{2m_l} + \frac{k_l q_l^2}{2} \right)$$

(I, j, l)=(1,1,1), (1,2,2), (1,3,3), (2,1,4), (2,2,5)(2,3,6)......(N,3,3N)   (3.3.3)

2.4 Derivation of Dulong-Petit law 3

Average kinetic energy

For n-th single atom in a crystal when its momentum is x, it's kinetic energy ($\varepsilon_{k,n,x}$) can expressed as follows.

$$\varepsilon_{k,n,x} = \frac{x^2}{2m_n} \quad (n = 1, 2, ... 3N) \tag{3.3.4}$$

The probability where the momentum of n-th single atom is x is defined as $P_{k,n,x}$ in order to calculate average kinetic energy. Now that x, $\varepsilon_{k,n,x}$, $P_{k,n,x}$ are defined, average kinetic energy of one atom in one direction (n-th) in a crystal is expressed as follows.

$$\langle \varepsilon_{k,n} \rangle = \int_{-\infty}^{\infty} \frac{x^2}{2m_n} P_{k,n,x}\, dx \tag{3.3.5}$$

Before finding $P_{k,n,x}$, let's calculate the partition function of N atoms in a crystal (Q),using K_B

. Because of crystal structure, N atoms and 3 directions are distinguished each other and when partition function of one atom in one direction is defined as q, Q can be expressed as follows.

$$q_i = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left[-\frac{\frac{p_i^2}{2m_l} + \frac{k_l q_i^2}{2}}{K_B T} \right] dp_i\, dq_i \tag{3.3.6}$$

$$Q = \prod_{i=1}^{3N} q_i$$

$$= \prod_{i=1}^{3N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left[-\frac{\frac{p_i^2}{2m_l} + \frac{k_l q_i^2}{2}}{K_B T} \right] dp_i\, dq_i \tag{3.3.7}$$

Now we are finding $P_{k,n,x}$. Because $P_{k,n,x}$ is depending on only n-th single atom, $p_{i\ (i=1,2,...3N,\ i\neq n)}$ and $q_{i(i=1,2,...3N)}$ can take from -∞ to ∞. That' why $P_{k,n,x}$ can be expressed as follows.

$$P_{k,n,x}$$

$$= \frac{1}{Q} \exp\left[\frac{-x^2}{2m_n}\bigg/ k_B T\right] \prod_{i=1(i\neq n)}^{3N} \int_{-\infty}^{\infty} \left\{\frac{-p_i^2}{2m_i}\bigg/ k_B T\right\} dp_i \ \prod_{i=1}^{3N} \int_{-\infty}^{\infty} \left\{\frac{-k_l q_i^2}{2}\bigg/ k_B T\right\} dq_i$$

$$= \frac{\exp\left[\frac{-x^2}{2m_n}\bigg/ k_B T\right]}{\int_{-\infty}^{\infty} \left\{\frac{-p_n^2}{2m_n}\bigg/ k_B T\right\} dp_n} \ (\because (3.3.7)) \tag{3.3.8}$$

From the equation (3.3.5) and (3.3.8) $< \varepsilon_{k,n} >$ will be calculated, using <u>Gaussian integral</u>.

$$< \varepsilon_{k,n} > = \int_{-\infty}^{\infty} \frac{x^2 \exp\left[\frac{-x^2}{2m_n}\bigg/ k_B T\right]}{2m_n \int_{-\infty}^{\infty} \left\{\frac{-p_n^2}{2m_n}\bigg/ k_B T\right\} dp_n} dx = \frac{\int_{-\infty}^{\infty} x^2 \exp\left[\frac{-x^2}{2m_n}\bigg/ k_B T\right] dx}{2m_n \int_{-\infty}^{\infty} \left\{\frac{-p_n^2}{2m_n}\bigg/ k_B T\right\} dp_n}$$

$$= \frac{\frac{1}{2}\sqrt{\pi\big/(1/2m_n k_B T)^3}}{2m_n\sqrt{\pi\big/(1/2m_n k_B T)}} (\because \text{ Gaussian integral}) = \frac{k_B T}{2}$$

$$\tag{3.3.9}$$

From equitation (3.3.9) the average of kinetic energy for one atom in one direction is $\frac{k_B T}{2}$.

2.5 Derivation of Dulong-Petit law 4

Average potential energy

Similarly, we are finding the average of the potential energy for one atom in one direction. When its equilibrium position (q_n) is x, it's potential energy ($\varepsilon_{p,n,x}$) can expressed as follows.

$$\varepsilon_{p,n,x} = \frac{k_n x^2}{2} (n = 1, 2, \ldots \ldots 3N) \tag{3.3.10}$$

3

The probability where atom's equilibrium position (q_n) is x is defined as $P_{p,n,x}$, and $q_{i\ (i=1,2,...3N,\ i\neq n)}$ and $p_{i(i=1,2,...3N)}$ are independent on q_n.

Now that x, $\varepsilon_{p,n,x}$ and $P_{p,n,x}$ are defined, Average kinetic energy of one atom in one direction (n-th) is expressed as follows.

$$< \varepsilon_{p,n} >= \int_{-\infty}^{\infty} \frac{k_n x^2}{2}\ P_{p,n,x}\ dx \tag{3.3.11}$$

Now we are finding $P_{p,n,x}$. Because $q_{i\ (i=1,2,...3N,\ i\neq n)}$ and $p_{i(i=1,2,...3N)}$ can take from $-\infty$ to ∞, $P_{p,n,x}$ can be expressed as follows.

$$P_{p,n,x}$$

$$= \frac{1}{Q}\exp\left[\frac{-k_n x^2}{2}\middle/ k_B T\right]\prod_{i=1}^{3N}\int_{-\infty}^{\infty}\left\{\frac{-p_i^2}{2m_i}\middle/ k_B T\right\}dp_i \prod_{i=1(i\neq n)}^{3N}\int_{-\infty}^{\infty}\left\{\frac{-k_l q_i^2}{2}\middle/ k_B T\right\}dq_i$$

$$= \frac{\exp\left[\frac{-k_n x^2}{2}\middle/ k_B T\right]}{\int_{-\infty}^{\infty}\left\{\frac{-k_l q_n^2}{2}\middle/ k_B T\right\}dq_n}\ (\because (3.3.7)) \tag{3.3.12}$$

From the equation (3.3.11) and (3.3.12) $< \varepsilon_{p,n} >$ will be calculated, using Gaussian integral.

$$< \varepsilon_{p,n} >= \int_{-\infty}^{\infty}\frac{k_n x^2 \exp\left[\frac{-k_n x^2}{2}\middle/ k_B T\right]}{2\int_{-\infty}^{\infty}\left\{\frac{-k_l q_n^2}{2}\middle/ k_B T\right\}dp_n}dx$$

$$= \frac{k_n \int_{-\infty}^{\infty} x^2 \exp\left[\frac{-k_n x^2}{2}\middle/ k_B T\right]dx}{2\int_{-\infty}^{\infty}\left\{\frac{-k_l q_n^2}{2}\middle/ k_B T\right\}dp_n}$$

$$= \frac{\frac{k_n}{2}\sqrt{\pi\middle/ (k_n/2\,k_B T)^3}}{2\sqrt{\pi\middle/ (k_n/2\,k_B T)}}(\because \text{ Gaussian integral})$$

$$= \frac{k_B T}{2} \tag{3.3.13}$$

From equitation (3.3.13) the average of potential energy for one atom in one direction is $\frac{k_B T}{2}$.

2.6 Derivation of Dulong Petit law 5

One atom has 6 energy freedoms (3 for kinetic energy and 3 for potential energy). That's why the total energy of one atom (E_{one}) at T is:

$$E_{one} = (3+3) \times \frac{k_B T}{2}$$
$$= 3kBT \tag{3.3.14}$$

. From this the energy of one-mole solids at T (E) is expressed as follows. N_A means Avogadro's constant.

$$E = E_{one} \times N_A$$
$$= 3RT \tag{3.3.15}$$

Because the molar isochoric heat capacity (C_v) is E divided by T at constant V, it is represented as follows.

$$C_V = \left(\frac{\partial E}{\partial T}\right)_v$$

$$= 3R \tag{3.3.16}$$

In the case where interatomic integrations can be neglected C_V is nearly 3R. Realistically, this situation is under high temperatures.