Mineral Physics I
Chapter 3. Lattice vibration
Section 2. Energy equipartition law and Dulong-Petit law

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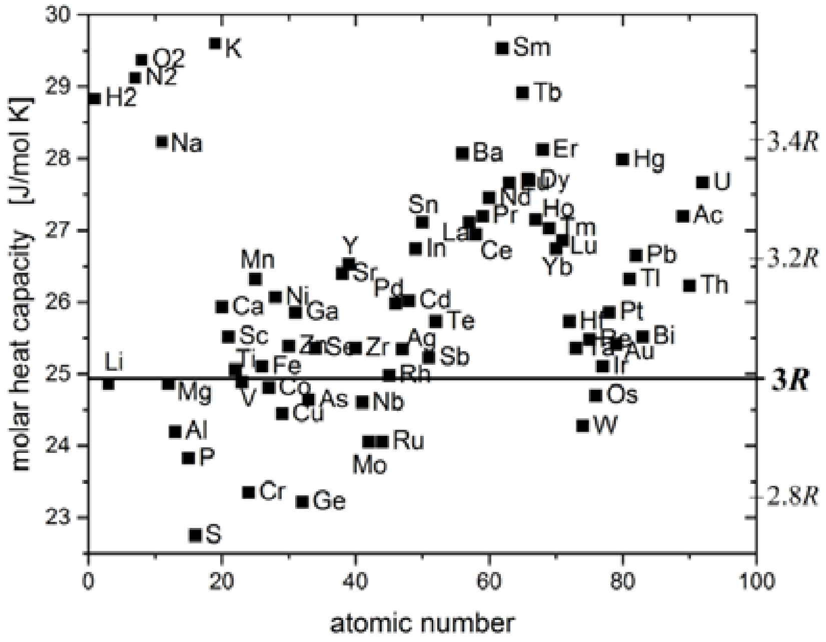
Dulong-Petit law

q Dulong-Petit law: the molar isochoric heat capacity of solids is $3R$ (25 J $K^{-1}mol^{-1}$) at sufficiently high temperatures.

Ø R: the gas constant

q Heat capacities of solids are more or less the same.



https://en.wikipedia.org/wiki/Dulong%E2%80%93Petit_law

Derivation of Dulong Petit law -1
Classical view of energy of a crystal

- Atoms in solid: oscillating and being bound by atomic bonding
  - Kinetic energy of the *i*-th atom in j-th direction: $\varepsilon_{\mathrm{K},ij} = \frac{p_{ij}^2}{2m_i}$ (3.3.1)
  - Potential energy of the *i*-th atom in j-th direction: $\varepsilon_{\mathrm{P},ij} = \frac{1}{2}k_{ij}q_{ij}^2$ (3.3.2)
    - 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
    - k_{ij}: “spring constant” for the potential energy in the *j*-th direction

Derivation of Dulong Petit law – 2
Sum of kinetic and potential energy

q Energy of a crystal = Total energy of atoms (E_{T}) = Sum of (kinetic energy in the 3 directions) + (potential energy in the 3 directions)

Ø $E_{\mathrm{T}} = \sum_{i=1}^{N}\sum_{j=1}^{3}\left(\varepsilon_{\mathrm{K},ij} + \varepsilon_{\mathrm{P},ij}\right)$

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

$$= \sum_{l=1}^{3N}\left(\frac{p_l^2}{2m_l} + \frac{1}{2}k_l q_l^2\right) \qquad (3.3.3)$$

§ *l* = 3x0+1, 3x0+2, 3x0+3, 3x1+1, 3x1+2, 3x1+3, 3x2+1, 3x2+2, 3x2+3, …., 3(*N*-1)+1, 3(*N*-1)+2, and 3(*N*-1)+3 = 1, 2, 3, 4, 5, 6, …, 3*N*-2, 3*N*-1, 3*N*

Derivation of Dulong Petit law – 3
Average kinetic energy

q The average kinetic energy of one atom in one direction using the Boltzmann distribution:

Ø $\langle \varepsilon_{K,n} \rangle = \dfrac{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} \varepsilon_{K,n} \exp[-E_{\mathrm{T}}/k_{\mathrm{B}}T]\mathrm{d}p_1\mathrm{d}q_1\cdots\mathrm{d}p_{3N}\mathrm{d}q_{3N}}{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} \exp[-E_{\mathrm{T}}/k_{\mathrm{B}}T]\mathrm{d}p_1\mathrm{d}q_1\cdots\mathrm{d}p_{3N}\mathrm{d}q_{3N}}$

$$= \frac{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} \frac{p_n^2}{2m_n} \exp\left[-\sum_{l=1}^{3N}\left(\frac{p_l^2}{2m_l}+\frac{1}{2}k_l q_l^2\right)/k_{\mathrm{B}}T\right]\mathrm{d}p_1\mathrm{d}q_1\cdots\mathrm{d}p_{3N}\mathrm{d}q_{3N}}{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} \exp\left[-\sum_{l=1}^{3N}\left(\frac{p_l^2}{2m_l}+\frac{1}{2}k_l q_l^2\right)/k_{\mathrm{B}}T\right]\mathrm{d}p_1\mathrm{d}q_1\cdots\mathrm{d}p_{3N}\mathrm{d}q_{3N}}$$

$$= \frac{\int_{-\infty}^{\infty} \frac{p_n^2}{2m_n} \exp\left[-\frac{p_n^2/2m_n}{k_{\mathrm{B}}T}\right]\mathrm{d}p_n \prod_{l=1,l\neq n}^{3N} \int_{-\infty}^{\infty} \exp\left[-\frac{p_l^2/2m_l}{k_{\mathrm{B}}T}\right]\mathrm{d}p_l \prod_{l=1}^{3N} \int_{-\infty}^{\infty} \exp\left[-\frac{k_l q_l^2/2}{k_{\mathrm{B}}T}\right]\mathrm{d}q_l}{\int_{-\infty}^{\infty} \exp\left[-\frac{p_n^2/2m_n}{k_{\mathrm{B}}T}\right]\mathrm{d}p_n \prod_{l=1,l\neq n}^{3N} \int_{-\infty}^{\infty} \exp\left[-\frac{p_l^2/2m_l}{k_{\mathrm{B}}T}\right]\mathrm{d}p_l \prod_{l=1}^{3N} \int_{-\infty}^{\infty} \exp\left[-\frac{k_l q_l^2/2}{k_{\mathrm{B}}T}\right]\mathrm{d}q_l}$$

$$= \frac{\frac{1}{2m_n}\int_{-\infty}^{\infty} p_n^2 \exp\left[-\frac{1}{2m_n k_{\mathrm{B}}T}p_n^2\right]\mathrm{d}p_n}{\int_{-\infty}^{\infty} \exp\left[-\frac{1}{2m_n k_{\mathrm{B}}T}p_n^2\right]\mathrm{d}p_n} \qquad (3.3.4)$$

Derivation of Dulong Petit law – 4
Average kinetic and potential energy

- The average kinetic energy of one atom in one direction:

Ø $$\langle \varepsilon_{\mathrm{K},n} \rangle = \frac{\frac{1}{2m_n}\int_{-\infty}^{\infty} p_n^2 \exp\left[-\frac{1}{2m_n k_\mathrm{B} T} p_n^2\right] \mathrm{d}p_n}{\int_{-\infty}^{\infty} \exp\left[-\frac{1}{2m_n k_\mathrm{B} T} p_n^2\right] \mathrm{d}p_n} = \frac{\frac{1}{2m_n}\frac{1}{2}\sqrt{\pi/\left(\frac{1}{2m_n k_\mathrm{B} T}\right)^3}}{\sqrt{\pi/(\frac{1}{2m_n k_\mathrm{B} T})}} = \frac{1}{2} k_\mathrm{B} T \qquad (3.3.5)$$

ü $x = p_n$, $a = \frac{1}{2m_n k_\mathrm{B} T}$, $\int_{-\infty}^{\infty} \exp(-ax^2)\mathrm{d}x = \sqrt{\pi/a}$, $\int_{-\infty}^{\infty} x^2 \exp(-ax^2)\mathrm{d}x = \frac{1}{2}\sqrt{\pi/a^3}$

- Similarly, the average potential energy of one atom in one direction:

Ø $$\langle \varepsilon_{\mathrm{P},n} \rangle = \frac{\frac{k_n}{2}\int_{-\infty}^{\infty} q_n^2 \exp\left[-\frac{k_n}{2k_B T} q_n^2\right] \mathrm{d}p_n}{\int_{-\infty}^{\infty} \exp\left[-\frac{k_n}{2k_B T} q_n^2\right] \mathrm{d}p_n} = \frac{\frac{k_n}{2}\frac{1}{2}\sqrt{\pi/\left(\frac{k_n}{2k_B T}\right)^3}}{\sqrt{\pi/(\frac{k_n}{2k_B T})}} = \frac{1}{2} k_\mathrm{B} T \qquad (3.3.6)$$

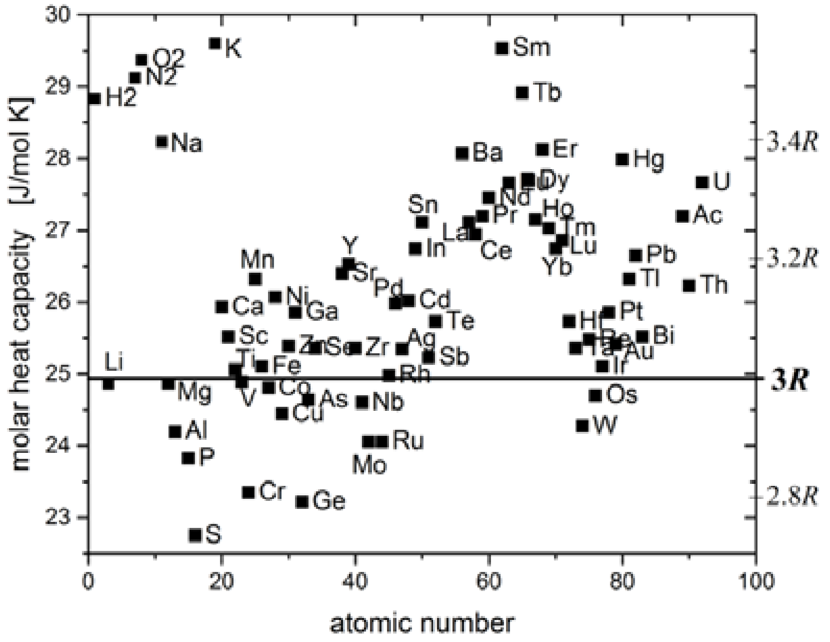
ü $x = q_n$, $a = \frac{k_n}{2k_B T}$

- One freedom of **both** kinetic and potential energy has an average value of $\frac{1}{2} k_\mathrm{B} T$

Ø energy equipartition law

Derivation of Dulong Petit law – 5

- One atom has 6 energy freedoms
  - 3 for kinetic energy, 3 for potential energy
  - the total energy of one atom at *T*:
    - $(3 + 3) \times \frac{1}{2} k_B T = 3 k_B T$
- The energy of one-mole solids at *T*:
  - $E = N_0 3 k_B T = 3RT$
- The molar isochoric heat capacity:
  - $C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3R$ (3.3.7)
  - Dulong-Petit law



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End