Equipartition Theorem

The average energy per quadratic degree of freedom is $\frac{1}{2}kT$.

$$(p_1, \ldots p_f, q_1, \ldots q_f)$$

$$\overline{E_i} = \frac{1}{2}kT$$

1. Ideal gas monatomic

$$E = \sum_{i=1}^{N} \frac{\vec{p_i}^2}{2m} \qquad \overline{E} = \frac{3}{2}NkT$$

2. 1d harmonic oscillator in eq. with reservoir at temp T

$$E = \frac{p^2}{2m} + \frac{1}{2}k_o x^2$$

$$\text{Mean } K \cdot E = \overline{\frac{p^2}{2m}} = \frac{1}{2}kT$$

$$\text{Mean } P.E = \overline{\frac{1}{2}k_0 x^2} = \frac{1}{2}kT$$

$$\text{Mean total energy} = \frac{1}{2}kT + \frac{1}{2}kT = kT$$

vibrational degree of freedom : oscillator

3. Rotational $K \cdot E = \frac{1}{2}I\dot{\theta}^2 \longrightarrow$ quadratic degree freedom

each rotational degree of freedom contributes $\frac{1}{2}kT$

Quantum harmonic Oscillator

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad n = 0, 1, 2 \cdots \qquad \hbar = \frac{h}{2\pi}$$

$$\omega = \sqrt{\frac{k_0}{m}}.$$

$$\bar{E} = \frac{\sum\limits_{n=0}^{\infty} e^{-\beta E_n}\, E_n}{\sum\limits_{n=0}^{\infty} e^{-\beta E_n}}$$

$$\boxed{\bar{E} = -\frac{\partial}{\partial \beta} \ln Z}$$

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta \left(n + \frac{1}{2}\right)\hbar\omega}$$

$$= e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} \quad \underset{\longrightarrow}{} \text{Geometric progression}$$

$$Z = e^{-\frac{\beta\hbar\omega}{2}} \frac{1}{1 - e^{-\beta\hbar\omega}}$$

$$\boxed{\ln Z = -\frac{1}{2}\beta\hbar\omega - \ln\left(1 - e^{-\beta\hbar\omega}\right)}$$

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$$\bar{E} = -\frac{\partial}{\partial\beta}\ln Z = -\left(-\frac{1}{2}\hbar\omega - \frac{e^{-\beta\hbar\omega}\cdot\hbar\omega}{1 - e^{-\beta\hbar\omega}}\right)$$

$$\boxed{\bar{E} = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right)}$$

limit $\beta\hbar\omega = \frac{\hbar\omega}{kT} \ll 1 \longrightarrow$ classical limit

$$\bar{E} \simeq \hbar\omega\left(\frac{1}{2} + \frac{1}{\beta\hbar\omega}\right) \simeq \hbar\omega\frac{1}{\beta\hbar\omega} \simeq \frac{1}{\beta} = kT$$

$$\beta \hbar \omega \gg 1 \qquad \frac{\hbar \omega}{kT} \gg 1$$

$$\overline{E} = \left(\frac{\hbar \omega}{2} + \underbrace{\frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}}_{\text{negligible}} \right).$$

$$\overline{E} \simeq \frac{\hbar \omega}{2} \qquad \text{as } T \to 0.$$

Specific heats of solids

N_a atoms per mole of solid. Free to vibrate about their equilibrium positions : lattice vibrations.

intermolecular forces to lowest order $\simeq \frac{1}{2} k x^2$.

give energy

$$E = \sum_{i=1}^{3N_a} \left(\frac{p_i^2}{2m} + \frac{1}{2} K_i q_i^2 \right).$$

$3N_a$ independent 1d H.O s

At high temp, classical description is valid.

Equipartition works.

Total mean energy/mole $= 3 N_a \left[\left(\frac{1}{2} kT \right) \times 2 \right]$

$$= 3 N_a kT = 3 RT$$

Molar specific heat at const V

$$C_v = \left(\frac{\partial \bar{E}}{\partial T} \right) = 3R \longrightarrow \text{Dulong Petit's Law}$$

fails for $T \longrightarrow 0$.

Einstein Model

all atoms in a solid vibrate with the same angular frequency ω. Then $K_i = m\omega^2$

1 mole of solid $\equiv 3N_a$ independent 1D H·O.

From previous calculation

$$\overline{E} = 3N_a \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right).$$

$$C_v = \left(\frac{\partial \overline{E}}{\partial T} \right)_v = \left(\frac{\partial \overline{E}}{\partial \beta} \right)_v \frac{\partial \beta}{\partial T} = -\frac{1}{kT^2} \frac{\partial \overline{E}}{\partial \beta} .$$

$$C_V = -\frac{1}{kT^2} \left\{ \frac{\partial}{\partial \beta} \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1} \right] \right\} 3N_a \hbar\omega \cdot$$

$$= -\frac{3N_a \hbar\omega}{kT^2} \left[-\frac{e^{\beta\hbar\omega} \hbar\omega}{(e^{\beta\hbar\omega}-1)^2} \right]$$

Einstein temp.

$$\uparrow$$

$$\beta\hbar\omega = \frac{\hbar\omega}{kT} = \frac{\theta_E}{T}$$

$$C_V = \frac{3N_a \hbar\omega k}{k^2 T^2} \left[\frac{e^{\beta\hbar\omega} \hbar\omega}{(e^{\beta\hbar\omega}-1)^2} \right]$$

$$\boxed{C_V = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}}$$

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2}.$$

high temp $\quad \frac{\theta_E}{T} \ll 1$

$$C_V \cong 3R\left(\frac{\theta_E}{T}\right)^2 \frac{1}{\left(\frac{\theta_E}{T}\right)^2} \quad \simeq \quad 3R \quad \uparrow \begin{array}{l}\text{simplifying}\\ \text{assumption}\\ \text{of same}\\ \text{freq.}\end{array}$$

low temp $\quad \frac{\theta_E}{T} \gg 1 \quad T \to 0$

$$\boxed{\begin{array}{l}\text{Exptly } C_V \sim T^3 \\ \text{at low temp.}\end{array}}$$

$$C_V \cong 3R\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T} \quad \longrightarrow 0 \text{, as } T \to 0$$

$$\therefore \text{ 3rd Law .}$$