

## Classical Theory of Specific heat of solids (Dulong and Petit law)

The classical theory is based on following assumptions:

- ① Each solid consist of large no. of atomic particles executing simple harmonic motion about their eqbm sites. They are known as simple harmonic oscillators. (SHO)
- ② These oscillators vibrates with same frequency ( $\omega_0$ ), but their energies are different because of different amplitudes.  $\omega_0$  = natural frequency of SHO.
- ③ The internal energy is largely contributed to the vibrational energy of SHO.
- ④ These oscillators can take up continuum of energy values from zero to infinity.
- ⑤ The total energy of the crystal at a given temperature is  $N$  times the average energy  $E$  of the oscillator.

further, A system of  $N$  vibrating 3D, SHO's can be considered equivalent

to  $3N$  independent vibrating 1-D harmonic oscillators.

The energy of a 1-D H.O of mass  $m$  and angular frequency  $\omega_0$  is given by

$$E = KE + PE$$

$$E = \frac{P^2}{2m} + V(x)$$

$$E = \frac{P^2}{2m} + \frac{1}{2} m \omega_0^2 x^2$$

Assuming the energy distribution in harmonic oscillators obey's Maxwell-Boltzmann distribution law.

The average energy of each H.O is given by

$$\bar{E} = \frac{\int E \cdot \exp\left(-\frac{E}{k_B T}\right) dE}{\int \exp\left(-\frac{E}{k_B T}\right) dE}$$

Putting the value of  $E$  in above integral

$$\bar{E} = \frac{\int \int \left(\frac{P^2}{2m} + \frac{1}{2} m \omega_0^2 x^2\right) \exp\left(-\frac{P^2}{2mk_B T}\right) \exp\left(-\frac{m \omega_0^2 x^2}{2k_B T}\right) dP dx}{\int \int \exp\left(-\frac{P^2}{2mk_B T}\right) \exp\left(-\frac{m \omega_0^2 x^2}{2k_B T}\right) dP dx}$$

$$\int \int \exp\left(-\frac{P^2}{2mk_B T}\right) \exp\left(-\frac{m \omega_0^2 x^2}{2k_B T}\right) dP dx$$

~~separating the integral & x integral~~  
~~dividing~~

$$\Rightarrow \frac{\iint_{p, x} \left( \frac{p^2}{2m} \right) \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}{\iint_{p, x} \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx} +$$

$$\frac{\iint_{p, x} \left( \frac{m\omega_0^2 x^2}{2} \right) \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}{\iint_{p, x} \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}$$

$$\frac{\iint_{p, x} \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}{\iint_{p, x} \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}$$

$$\Rightarrow \frac{\int_p \left( \frac{p^2}{2m} \right) \exp\left(-\frac{p^2}{2mk_B T}\right) dp}{\int_p \exp\left(-\frac{p^2}{2mk_B T}\right) dp} + \frac{\int_x \left( \frac{m\omega_0^2 x^2}{2} \right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dx}{\int_x \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dx}$$

Using,  $\int_0^{\infty} t^2 \exp(-at^2) dt = \frac{1}{4} \sqrt{\frac{\pi}{a^3}}$

and  $\int_0^{\infty} \exp(-at^2) dt = \frac{1}{2} \sqrt{\frac{\pi}{a}}$

$$\bar{E} = \frac{1}{2m} \frac{\frac{1}{4} \left[ \pi (2mk_B T)^3 \right]^{1/2}}{\frac{1}{2} \left[ \pi (2mk_B T) \right]^{1/2}} + \frac{1}{2} \frac{m\omega_0^2 \frac{1}{4} \left[ \pi \left( \frac{2k_B T}{m\omega_0^2} \right)^3 \right]^{1/2}}{\frac{1}{2} \left[ \pi \left( \frac{2k_B T}{m\omega_0^2} \right) \right]^{1/2}}$$

$$\bar{E} = \frac{1}{2} k_B T + \frac{1}{2} k_B T = k_B T$$

Thus, the total vibrational energy of a crystal containing  $N$  identical atoms or  $3N - 10^2$  H.O becomes

$$E = 3N \bar{E} = 3Nk_B T$$

The energy  $E$  depends only on the temperature provided the volume remains constant.

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = 3Nk_B$$

Here, it can be noticed that,  $C_V$  is independent of temperature, and also independent of natural freq ( $\omega_0$ ) of atoms.

Molar specific heat is, therefore, given by

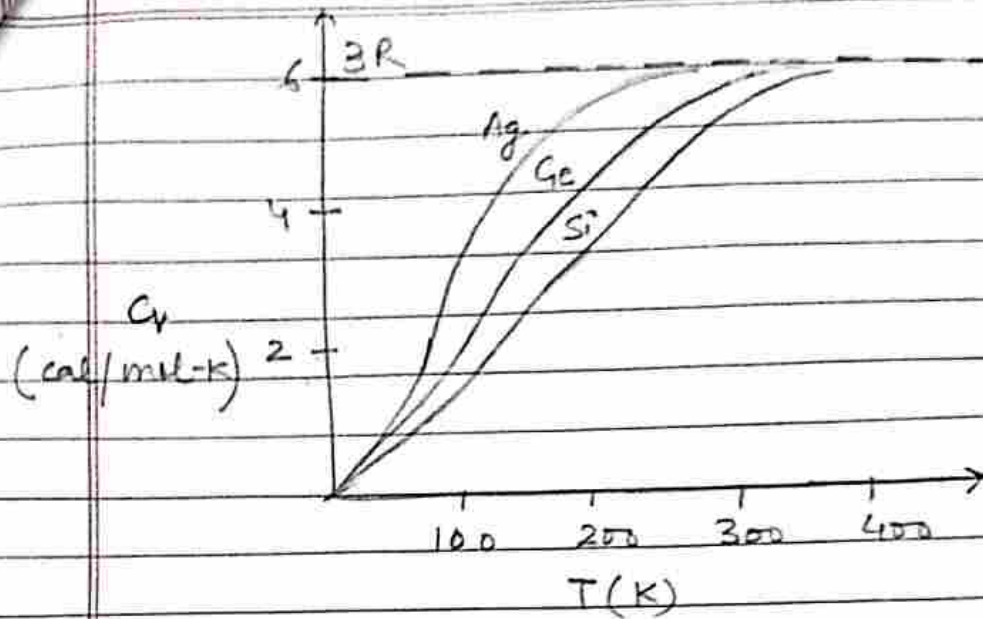
$$C_V = 3N_A k_B = 3R$$

$R =$  Gas constant &  $R = 1.987 \text{ cal/mol-K}$

$$C_V = 5.961 \text{ cal/mol-K}$$

$\Rightarrow$  According to classical theory, the molar sp. heat capacity of all the solids is constant and is independent of temperature and frequency.

This is called as Dulong & Petit's law.



Experimentally observed heat capacity curve of silver, germanium & silicon as a function of temperature has been shown in the above figure.

It can be seen that high temp and often at room temp. as well, heat capacity curve of all the above solids approaches to  $3R$  i.e. a constant value.

However, this theory fails at low temperature, as  $C_v \rightarrow 0$  as  $T \rightarrow 0$ . This discrepancy was resolved <sup>first</sup> by Einstein & then by Debye using quantum theory.