

SPECIFIC HEAT FROM LATTICE VIBRATION

We have seen that the dilute gases can be regarded as ideal gases and their thermodynamic properties can be successfully discussed by the methods of statistical mechanics. Liquids and dense gases are difficult to handle because of the intermolecular forces which play an important role. In a crystalline solid, the atoms are very close; but such a system is well ordered.

We will show in this section how the properties of the simplest of these systems, the monatomic solids, can be discussed using the techniques of statistical mechanics.

A monatomic solid consists of a large number of atoms in regular array, a lattice. Because of thermal agitation each atom vibrates about its equilibrium position.

Consider a solid containing N non-interacting particles harmonically bound to centres of forces. The Hamiltonian of each atom is

$$H = \sum_{i=1}^3 \frac{p_i^2}{2m} + \sum_{i=1}^3 \frac{1}{2} k q_i^2$$

By the theorem of equipartition of energy

$$\text{Energy/atom} = 6 \times \frac{1}{2} kT = 3kT$$

and the total energy for N atoms $E = 3NkT$, where N is Avogadro's number.

Therefore

$$C_v = 3Nk = 3R \cong 5.96 \text{ cal/mole} \\ \cong 24.93 \text{ J/mole.}$$

This result asserts that all simple solids have the same molar specific heat equal to $24.93 \text{ J/mole}^\circ\text{K}$. This is known as the law ofulong and Petit.

The specific heat of most materials decreases as the temp is lowered. Diamond, for example, has as low a value of c_p as 1.1 even at 300 K. classical statistical mechanics could not explain this variation of the specific heat with temp.

Einstein was the first to apply quantum concept to the theory of specific heat of solids. For calculation of specific heat Einstein assumed

- The crystal consists of atoms which may be regarded as identical and independent harmonic oscillators.
- A crystalline solid having N atoms can be represented by $3N$ harmonic oscillator vibrating with same frequency.

The energy of the oscillator is given by

$$E_n = (n + \frac{1}{2}) h\nu$$

The partition function Z is

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})h\nu} = e^{-\beta h\nu/2} \sum_{n=0}^{\infty} e^{-n\beta h\nu} \\ &= e^{-\beta h\nu/2} (1 + e^{-\beta h\nu} + e^{-2\beta h\nu} + \dots) \\ &= e^{-\beta h\nu/2} (1 - e^{-\beta h\nu})^{-1} = e^{-\beta h\nu/2} \frac{1}{(1 - e^{-\beta h\nu})} \end{aligned}$$

$$\text{or, } \ln Z = -\frac{\beta}{2} h\nu - \ln(1 - e^{-\beta h\nu})$$

$$\text{Mean energy } \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{2} h\nu + \frac{e^{-\beta h\nu} h\nu}{1 - e^{-\beta h\nu}}$$

Thus, the total mean energy is

$$\langle E \rangle = 3N \langle E \rangle = 3N h\nu \left(\frac{1}{2} + \frac{1}{e^{h\nu/kT} - 1} \right)$$

and

$$\begin{aligned} C_v &= \frac{\partial \langle E \rangle}{\partial T} \bigg|_V = \frac{3N h\nu e^{h\nu/kT} (h\nu/kT^2)}{(e^{h\nu/kT} - 1)^2} \\ &= \frac{3N h^2 \nu^2 e^{h\nu/kT}}{kT^2 (e^{h\nu/kT} - 1)^2} = 3Nk \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \end{aligned} \quad \text{--- (1)}$$

where $\theta_E = \frac{h\nu}{k}$ is called Einstein characteristic temp

Now if

$$T \gg \theta_E \text{ i.e. } \frac{\theta_E}{T} \ll 1$$

We can write

$$e^{\theta_E/T} = 1 + \frac{\theta_E}{T} + \frac{1}{2} \left(\frac{\theta_E}{T} \right)^2 + \dots$$

Therefore, from eqn (1)

$$C_v = 3Nk \left(\frac{\theta_E}{T} \right)^2 \frac{(1 + \theta_E/T)}{\left(\frac{\theta_E}{T} \right)^2} = 3Nk + 3Nk \left(\frac{\theta_E}{T} \right)$$

$$\text{or, } C_v \approx 3R$$

thus, at high temp^r, the result tends towards the classical one,
 on the other hand, if $T \ll \theta_E$, i.e. $\frac{\theta_E}{T} \gg 1$

$$U = 3NK \left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T} \quad \text{< from eqn (1) >}$$

The specific heat, therefore, falls at an exponentially fast rate and tends to zero at $T \rightarrow 0$. Einstein's theory, thus explained for the first time why the molar specific heat decreases with temp^r. The specific heat tends to zero at absolute zero and rises to the classical value at high temp^r. The rate of fall, however, ~~turns out to be~~ turns out to be too fast in comparison with the observed rate. In fact, it has been observed experimentally that $U \propto T^3$ as $T \rightarrow 0$, we have to account for this discrepancy.

This discrepancy arise due to the assumption that all atoms vibrate with same frequency. In reality, if a solid has N atoms, it has $3N$ normal modes of vibrations and, hence $3N$ different frequencies. To remove the deficiencies of the Einstein model, we need a more realistic appraisal of the actual distribution of frequencies.

• DEBYE'S MODEL OF SOLIDS: PHONON GAS

In the improved model suggested by Debye, the discreteness of the atoms in the solid is neglected and the solid is treated as if it were a continuous elastic medium, each normal mode of vibrations of the elastic continuum being characterised by a frequency ω .

The number of normal modes with frequency betⁿ ω and $\omega + d\omega$ is given by

$$\sigma'(\omega) d\omega = \frac{v\omega^2 d\omega}{2\pi^2 v_s^3}$$

where v_s is the velocity of the concerned wave. Since there are two transverse and one longitudinal type of vibrations and the transverse mode is doubly degenerate, the total number of modes of vibrations in the frequency interval ω and $\omega + d\omega$ will be

$$\sigma(\omega) d\omega = \frac{v\omega^3}{2\pi^2} \left(\frac{1}{v_l^3} + \frac{1}{v_t^3} \right) d\omega \quad \text{--- (1)}$$

Debye assumed that the spectrum of frequencies is cut off at an upper limit ω_D , such that the total number of normal modes is equal to $3N$,

i.e.

$$\int_0^{\omega_D} \sigma(\omega) d\omega = 3N$$

$\omega_D \rightarrow$ maximum frequency of phonons in a crystal.

$$\text{or, } \int_0^{\omega_D} \frac{v\omega^3}{2\pi^2} \left(\frac{1}{v_l^3} + \frac{1}{v_t^3} \right) d\omega = 3N$$

$$\text{or, } \frac{V \omega_D^3}{6\pi^2} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) = 3N$$

$$\text{or, } \omega_D^3 = \frac{18N\pi^2}{V} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right)^{-1} \quad \text{--- (2)}$$

The number of phonons is not conserved, the chemical potential for phonons, $\mu = 0$. Therefore, the distribution law for phonons will be

$$\langle n_s \rangle = \frac{1}{e^{\hbar\omega/kT} - 1}$$

The internal energy of the phonon gas

$$E = \int_0^{\omega_D} \hbar\omega \langle n_s \rangle \sigma(\omega) d\omega$$

$$= \int_0^{\omega_D} \hbar\omega \frac{1}{e^{\hbar\omega/kT} - 1} \cdot \frac{9N}{\omega_D^3} \omega^2 d\omega \quad \left(\begin{array}{l} \text{using eqn} \\ \text{(1) and (2)} \\ \sigma(\omega) d\omega = \frac{9N\omega^2}{\omega_D^3} d\omega \end{array} \right)$$

$$= \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\hbar\omega/kT} - 1} d\omega$$

$$= \frac{9N\hbar}{\omega_D^3} \left(\frac{kT}{\hbar} \right)^4 \int_0^{\hbar\omega_D/kT} \frac{x^3}{e^x - 1} dx \quad \left(x = \hbar\omega/kT \right)$$

Let $\theta_D = \frac{\hbar\omega_D}{k}$; θ_D is called Debye characteristic temp.

$$\text{Therefore } E = \frac{9NkT^4}{\theta_D^3} \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx$$

Now, if $T \gg \theta_D$, $\frac{\theta_D}{T}$ is small and $\frac{x^3}{e^x - 1} = \frac{x^3}{1 + x + \frac{x^2}{2} + \dots - 1}$

$$\begin{aligned} \text{Therefore } E &= \frac{9NkT^4}{\theta_D^3} \left[\frac{x^3}{3} \right]_0^{\theta_D/T} = \frac{x^3}{1+x} \quad \left(\text{neglecting the higher power} \right) \\ &= \frac{9NkT^4}{\theta_D^3} \cdot \frac{\theta_D^3}{3T^3} = 3NkT \end{aligned}$$

This leads to the Dulong-Petit law

$$C_V = \frac{\partial E}{\partial T} = 3Nk = 3R$$

Thus, for temp greater than the Debye temp, the lattice behaves classically.

If, on the other hand, $T \ll \theta_D$, $x \rightarrow \infty$ then

$$\int_0^{\infty} \frac{x^3}{e^x - 1} dx = \int_0^{\infty} x^3 dx = \frac{\pi^4}{15}$$

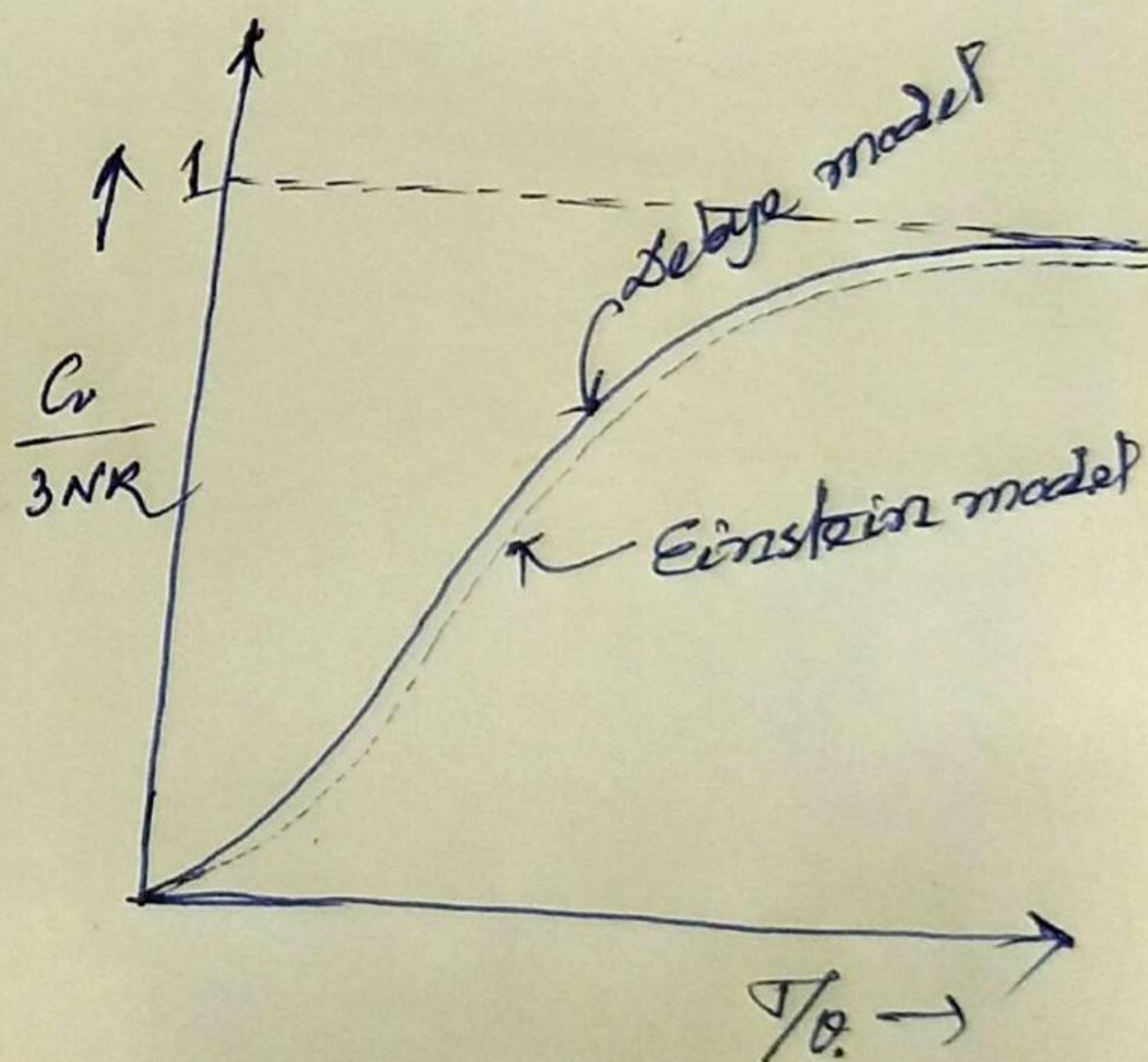
Hence $E = \frac{9NK\theta_D^3}{\theta_D^3} \frac{\pi^4}{15} = \frac{3\pi^4 NK}{5 \theta_D^3} T^4$ — (3)

and the specific heat

$$C_v = \frac{12}{5} \pi^4 NK \left(\frac{T}{\theta_D}\right)^3$$
 — (4)

Therefore $C_v \propto T^3$

The specific heat as defined by eqn (4) shows a very good agreement with experimental results.



A question that arises here is that, since sound waves can also exist in liquids, will the quantum effects, discussed above for solids, be manifest in liquids at low temperatures? Two points of importance to be noted in this respect are: (i) liquids can have only longitudinal modes of vibration; they cannot sustain transverse modes as they cannot withstand sheer stress; and (ii) normal modes in liquids may not be purely harmonic. There may also be other excitations in addition to those by phonons, such as vortex flow, turbulence or roton excitation.

Experimentation with liquids is difficult because most liquids freeze long before the temperature is low enough to exhibit the T^3 behaviour. The only exception is liquid helium, ${}^4\text{He}$, which remains liquid at very low temperatures. Since liquids can have only longitudinal modes of vibration, the formula (4) for C_v and Eq. (2) for ω_D reduces to

(4)

$$C_v = \frac{4\pi^4}{5} Nk \left(\frac{kT}{h\omega_D} \right)^3$$

$$\omega_D = \left(\frac{6\pi^2 N}{V} \right)^{1/3} v$$

and

where v is the velocity of sound in the liquid.

Therefore

$$C_v = \frac{2\pi^2 k^4 V}{15h^3 v^3} T^3$$

Hence, specific heat per gram of the liquid is

$$C_v = \frac{2\pi^2 k^4}{15\rho h^3 v^3} T^3$$

where ρ is the density of the liquid.

Substituting the value of the density of liquid helium $\rho = 145.5 \text{ kg/m}^3$ and the velocity of sound $v = 238 \text{ m/sec}$, we get

$$C_v = 20.7 T^3 \text{ J/kg/K}$$

which agrees fairly well with the experimental value

$$= (20.4 \pm 0.4) T^3 \text{ J/kg/K}$$

observed for temperatures $0 < T < 0.6 \text{ K}$.