

Thermal Properties of Solids

(Superconductivity)

SQUID - Superconducting Quantum Interference Device

Classical Lattice heat capacity.

The major contribution to the heat capacity of solids comes from lattice vibrations. Other contributions come from conduction electrons in metals and the ordering in magnetic materials. In classical theory, the energy of a solid can be expressed as

$$E = E_s + E_v$$

$E_s \rightarrow$ energy of the static lattice

$E_v \rightarrow$ vibration energy of the solid.

The classical equipartition energy of vibration of an atom is kT at temp. T . This gives the total vibrational energy $3NkT$ if there are N atoms in the solid.

$$\therefore E = E_s + 3NkT$$

$$\text{At } T=0, E = E_s,$$

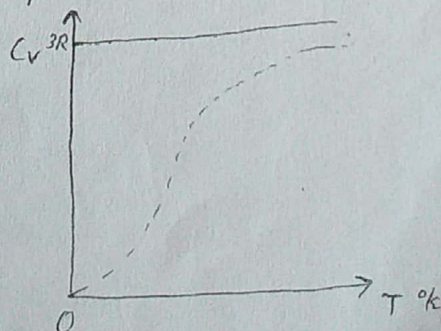
The heat capacity is defined as $C_v = \left(\frac{\partial E}{\partial T} \right)_v$

$$\therefore C_v = 3Nk = 3R$$

This is known as Dulong - Petit law.

According to this law, heat capacity is const for a solid and independent of temperature. The measured value of heat capacity approaches this value at high temp. and remains almost constant thereafter in the solid state. This is how Dulong and Petit law can be explained the behaviour of solids at high temperatures.

The Dulong - Petit law however fails to explain the variation of heat capacity with temp. Most significantly the heat capacity drops to zero as the temp approaches 0 K.



Average Thermal Energy of a harmonic oscillator.

The energy levels of a quantum harmonic oscillator is given by,

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega \quad \text{--- (1)}$$

where ' ω ' is the angular frequency of the oscillator. The average thermal energy of the oscillator E in thermal equilibrium at temp. T is written as,

$$\langle E \rangle = \sum_n P_n E_n \quad \text{--- (2)}$$

where P_n represents the probability of finding the oscillator in the energy level E_n . It is given by,

$$P_n \propto \exp\left(\frac{-E_n}{kT}\right) \quad \text{--- (3)}$$

The proportionality constant ensures that the oscillator is in one of allowed levels.

$$\therefore \sum_{n=0}^{\infty} P_n = 1 \quad \text{--- (4)}$$

$$\therefore \sum_{n=0}^{\infty} P_0 e^{\left(-E_n/kT\right)} = 1$$

$$\sum_{n=0}^{\infty} P_0 \exp\left[-\frac{\left(n + \frac{1}{2}\right) \hbar \omega}{kT}\right] = 1$$

where P_0 is the const of proportionality.

$$\therefore \sum_{n=0}^{\infty} \left(P_0 e^{-n\hbar\omega/kT} \cdot e^{-\hbar\omega/2kT} \right) = 1$$

$$P_0 e^{-\hbar\omega/2kT} \sum_{n=0}^{\infty} e^{-n\hbar\omega/kT} = 1$$

$$\text{but } \sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

$$\therefore P_0 e^{-\hbar\omega/2kT} \cdot \frac{1}{1 - e^{-\hbar\omega/kT}} = 1$$

$$P_0 = \left(1 - e^{-\hbar\omega/kT}\right) \cdot e^{-\hbar\omega/2kT} \quad \text{--- (5)}$$

Sub on (2) ; $P_n \propto e^{-E_n/kT}$

$$P_n = P_0 e^{-E_n/kT}$$

$$P_n = \left(1 - e^{-\hbar\omega/kT}\right) e^{-\hbar\omega/2kT} \cdot e^{-E_n/kT}$$

$$P_n = \left(1 - e^{-\hbar\omega/kT}\right) e^{-\hbar\omega/2kT} \cdot e^{-(n+1/2)\hbar\omega/kT}$$

$$P_n = \left(1 - e^{-\hbar\omega/kT}\right) e^{-n\hbar\omega/kT} \quad \text{--- (6)}$$

Sub (6) in (2)

$$\begin{aligned} \langle E \rangle &\leq \sum_n P_n E_n \\ &= \sum_n \left(1 - e^{-\hbar\omega/kT}\right) e^{-n\hbar\omega/kT} \cdot \left(n + \frac{1}{2}\right) \hbar\omega \\ &= \left(1 - e^{-\hbar\omega/kT}\right) \hbar\omega \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) e^{-n\hbar\omega/kT} \end{aligned}$$

put $e^{-\hbar\omega/kT} = x$

$$\begin{aligned} \therefore \langle E \rangle &= (1-x) \hbar\omega \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) x^n \\ &= (1-x) \hbar\omega \left[\sum_{n=0}^{\infty} n x^n + \frac{1}{2} \sum_{n=0}^{\infty} x^n \right] \end{aligned}$$

Again $\sum_n x^n = \frac{1}{1-x}$

$$\therefore \langle E \rangle = (1-x) \hbar\omega \left[\sum_{n=0}^{\infty} n x^n + \frac{1}{2(1-x)} \right]$$

$$\langle E \rangle = \frac{\hbar\omega}{2} + (1-x) \hbar\omega \sum_{n=0}^{\infty} n x^n$$

Also $\sum_n n x^n = \frac{x}{(1-x)^2}$

$$\therefore \langle E \rangle = \frac{1}{2} \hbar \omega + (1-x) \hbar \omega \cdot \frac{x}{(1-x)^2}$$

$$= \left(\frac{1}{2} + \frac{x}{1-x} \right) \hbar \omega$$

$$= \left(\frac{1}{2} + \frac{e^{-\hbar \omega / kT}}{1 - e^{-\hbar \omega / kT}} \right) \hbar \omega$$

$$\langle E \rangle = \left(\frac{1}{2} + \frac{1}{e^{\hbar \omega / kT} - 1} \right) \hbar \omega$$

$$\text{or } \boxed{\langle E \rangle = \left(\langle n \rangle + \frac{1}{2} \right) \hbar \omega}$$

the average ^{thermal} energy

— (7)

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

Einstein model

Einstein was the 1st person to resolve the problem of specific heat of solids by the application of Planck's quantum theory. He assumed that a crystalline solid made up of N atoms (per mole) could be regarded as an array of atomic oscillators vibrating in 3 independent directions with a constant frequency ν and that the allowed energy states of oscillators are integral multiples of $h\nu$. ($\hbar \omega$)

$$\therefore E_n = n \hbar \omega \quad (n=0, 1, 2, \dots)$$

[The factor $\frac{1}{2} \hbar \omega$ for the zero point energy was not known to Einstein and it will not affect the result].

\therefore The average thermal energy of a solid according to Einstein model is

$$\langle E \rangle = 3N \hbar \omega \langle n \rangle$$

($3N \rightarrow$ degrees of freedom)

$$\langle E \rangle = 3N\hbar\omega \left(\frac{1}{e^{\hbar\omega/kT} - 1} \right) \quad (8)$$

∴ The specific heat capacity is,

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = 3N\hbar\omega \frac{1}{\left(e^{\hbar\omega/kT} - 1 \right)^2} \cdot e^{\left(-\frac{1}{T} \right) \frac{\hbar\omega}{k}}$$

$$C_V = 3N \left(\frac{\hbar\omega}{T} \right)^2 \cdot \frac{1}{k} \cdot \frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT} - 1 \right)^2}$$

$$C_V = 3Nk \left(\frac{\hbar\omega}{kT} \right)^2 \cdot \frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT} - 1 \right)^2} \quad (9)$$

The Einstein specific heat curve is fairly close to the experimental curve except at low temps. In this region, the Einstein specific heat approaches zero more rapidly than the observed values. However, at high temperatures, it approaches the classical value.

High temp. range :-

$$\langle E \rangle = 3N\hbar\omega \left(\frac{1}{e^{\hbar\omega/kT} - 1} \right)$$

At high temp. $\hbar\omega \ll kT$

put $\hbar\omega/kT = x \Rightarrow e^x = 1 + x + \frac{x^2}{2} + \dots \approx 1 + x$

$$\therefore \langle E \rangle = 3N\hbar\omega \left(\frac{1}{1+x-1} \right)$$

$$= 3N\hbar\omega \frac{1}{x} = \frac{3N\hbar\omega kT}{\hbar\omega} = 3NkT$$

$$\therefore C_V = \frac{\partial \langle E \rangle}{\partial T} = 3Nk = \underline{\underline{3R}}$$

low temp. range :-

$$\hbar\omega \gg kT \quad \therefore e^x \gg 1$$

$$\therefore \langle E \rangle = \frac{3N \hbar\omega}{e^x} \approx \frac{3N \hbar\omega}{e^{\hbar\omega/kT}}$$

$$= 3N \hbar\omega e^{-\hbar\omega/kT}$$

$$\therefore C_V = \frac{\partial \langle E \rangle}{\partial T} = 3N \hbar\omega e^{-\hbar\omega/kT} \left(\frac{-\hbar\omega}{k} \right) \left(\frac{-1}{T^2} \right)$$

$$= 3Nk \left(\frac{\hbar\omega}{kT} \right)^2 e^{-\hbar\omega/kT}$$

Thus with decreasing temp. C_V drops exponentially.

For every solid there is a characteristic temp. above which the model works and well below this temp. the model fails. This temp. is known as Einstein characteristic temp Θ_E and defined by

$$\Theta_E = \frac{\hbar\omega_E}{k}$$

$\omega_E \rightarrow$ ^{Einstein} characteristic frequency.

The Debye model

In 1912, Debye pointed out that the source of error lies in the assumption (that all atomic oscillators vibrate independently at a const frequency) made by Einstein. According to him, the assumption is not justifiable since all atoms are elastically coupled to its neighbours. Debye therefore, simplified the problem by considering a solid as a continuously vibrating medium, which gives rise to a spectrum of frequencies instead of a single frequency as assumed in the Einstein's model.

The no. of modes whose frequencies lies b/w the interval ν and $\nu + d\nu$ is given by the density of states. (4) 2

$$g(\nu) d\nu = 4\pi V \left(\frac{1}{\nu_l^3} + \frac{2}{\nu_t^3} \right) \nu^2 d\nu \quad \text{--- (10)}$$

$V \rightarrow$ volume

$\nu_l \rightarrow$ velocity propagation in the longitudinal mode

$\nu_t \rightarrow$ velocity propagation in the transverse mode.

The function $g(\nu)$ is also known as spectral distribution function of normal modes.

Since the number of normal vibrations in a 3D crystal lattice is $3N$, the function $g(\nu)$ should satisfy the following normalization condition.

$$\int_0^{\nu_D} g(\nu) d\nu = 3N$$

where ν_D is the maximum frequency limiting the spectrum of normal modes from above and is known as Debye frequency.

$$\therefore \int_0^{\nu_D} 4\pi V \left(\frac{1}{\nu_l^3} + \frac{2}{\nu_t^3} \right) \nu^2 d\nu = 3N$$

$$4\pi V \left(\frac{1}{\nu_l^3} + \frac{2}{\nu_t^3} \right) \int_0^{\nu_D} \nu^2 d\nu = 3N$$

$$\nu_D^3 = \frac{9N}{4\pi V} \left(\frac{1}{\nu_l^3} + \frac{2}{\nu_t^3} \right) \quad \text{--- (11)}$$

Now the total energy of the oscillators in the solid is,

$$E = \int_0^{v_D} \langle E \rangle g(v) dv \quad (12)$$

$$= \int_0^{v_D} \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1} g(v) dv$$

from (8)

$$\hbar \omega = h\nu$$

$$E = 4\pi V \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \int_0^{v_D} \frac{h\nu \nu^2 d\nu}{e^{h\nu/kT} - 1}$$

from (11);

$$E = 4\pi V \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) = \frac{9N}{v_D^3}$$

$$\therefore E = \frac{9N}{v_D^3} \int_0^{v_D} \frac{h\nu \nu^2 d\nu}{e^{h\nu/kT} - 1} \quad (13)$$

To simplify (13), put $\frac{h\nu}{kT} = x$

$$\therefore d\nu = \frac{kT}{h} dx$$

Also limit is from 0 to x_D where $x_D = \frac{h\nu_D}{kT}$

$$\therefore E = \frac{9N}{v_D^3} \left(\frac{kT}{h} \right)^3 \int_0^{x_D} \frac{x^3 dx}{e^x - 1}$$

$$E = 9N \left(\frac{kT}{h\nu_D} \right)^3 \int_0^{x_D} \frac{x^3 dx}{e^x - 1}$$

Now we can define the Debye temp. as Θ_D according to the equation $h\nu_D = k\Theta_D$

$$\therefore \Theta_D = \frac{h\nu_D}{k}, \quad x_D = \frac{\Theta_D}{T}$$

$$\therefore E = 9NkT \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^3}{e^x - 1} dx \quad \text{--- (14)}$$

(a) High temp. range :-

$$x = \frac{h\nu}{kT}, \text{ at high temp. range } x \ll 1$$

$$\therefore e^x = 1 + x$$

$$\therefore E = 9NkT \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^3}{x} dx$$

$$= 9NkT \left(\frac{T}{\Theta_D} \right)^3 \frac{(x_D)^3}{3}$$

$$= 9NkT \left(\frac{T}{\Theta_D} \right)^3 \left(\frac{\Theta_D}{T} \right)^3 \cdot \frac{1}{3} = \underline{\underline{3NkT}}$$

$$\therefore C_V = \frac{\partial E}{\partial T} = \underline{\underline{3Nk}} \text{ which is the classical result.}$$

(b) Low temp range :-

At low temp $x \cdot T \ll 1 \therefore$ The upper limit of the integral can be replaced by infinity.

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

$$\therefore E = 9NkT \left(\frac{T}{\Theta_D} \right)^3 \frac{\pi^4}{15}$$

$$E = \frac{3}{5} \pi^4 N k T \left(\frac{T}{\Theta_D} \right)^3$$

$$\therefore C_V = \frac{12}{5} \pi^4 N k \left(\frac{T}{\Theta_D} \right)^3$$

This is the famous expression known as Debye T^3 law for specific heat at low temperature.

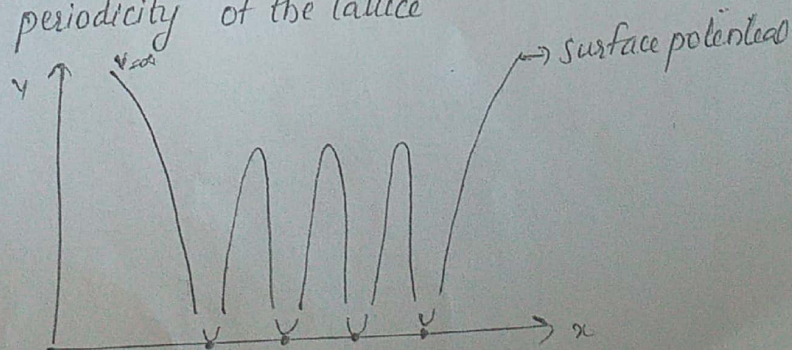
Bloch theorem

In the case of free electron theory, we assumed that the \bar{e} s move in a region of const potential inside a one or three dimensional potential well.

Although the free electron theory is able to explain the phenomena such as electrical conductivity, thermionic emission etc, it fails to explain why some materials are good electrical conductors which some are good electrical insulators.

In order to understand the difference between the conductors and insulators, it is necessary to incorporate the variation of potential inside the crystal due to the presence of +ve ion cores in the free \bar{e} model.

It is assumed that the potential inside a metallic crystal to be periodic with the periodicity of the lattice.



The potential is minimum at a +ve ion sites and maximum between the two ions. The corresponding 1D Schrodinger eqn can be written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} [E - V(x)] \psi = 0 \quad \text{--- (1)}$$

Where the periodic potential $V(x)$ may be defined by means of the lattice const 'a' as

$$V(x) = V(x+a) \quad \text{--- (2)}$$

Employing the periodic potential, Bloch has shown that the 1D soln of the Schrodinger eqn is

$$\psi(x) = e^{ikx} u_k(x) \quad \text{--- (3)}$$

In 3D $\psi(r) = e^{ik \cdot r} u_k(r) \quad \text{--- (4)}$

The above equation is known as Bloch function. They represent the free e^- wave modulated by the periodic function $u_k(x)$, where $u_k(x)$ is periodic with the periodicity of the lattice. If we have N no. of atoms in a linear chain of atoms of length L, then

$$u_k(x) = u_k(x+Na) \quad \text{--- (5)}$$

$$\psi(x) \quad \psi(x+Na) = e^{ik(x+Na)} u_k(x+Na)$$

$$\psi(x+Na) = e^{ikx} u_k(x) e^{ikNa}$$

$$\boxed{\psi(x+Na) = \psi(x) e^{ikNa}} \quad \text{--- (6)}$$

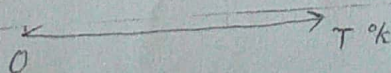
This is known as Bloch condition.

The complex conjugate of (6) is

$$\psi^*(x+Na) = \psi^*(x) e^{-ikNa} \quad \text{--- (7)}$$

$$(6) \times (7) \Rightarrow \psi(x+Na) \psi^*(x+Na) = \psi(x) \psi^*(x)$$

This shows that the probability of finding the e^- is same everywhere in the whole chain of atoms i.e., the e^- are not localised.



Kronig-Penny model

In order to know the exact $E-k$ relationship it is necessary to consider a well defined 1D periodic potential. For that we can use Kronig-Penny model. They suggested a simpler potential in the form of an array of square wells.

The corresponding Schrodinger eqns for the two regions I & II are of the form

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} E\psi = 0 \quad \text{for } 0 < x < a$$

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \quad \text{--- (1)}$$

$$\text{where } \alpha^2 = \frac{8\pi^2mE}{h^2}$$

and

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - V_0)\psi = 0 \quad \text{for } -b < x < 0$$

$$\frac{d^2\psi}{dx^2} + \beta^2\psi = 0 \quad \text{--- (2)}$$

$$\text{where } \beta^2 = \frac{8\pi^2m}{h^2} (V_0 - E)$$

The expected soln should have the form of Bloch functions. Let us suppose the general soln of (1) & (2) as

$$\psi_1(x) = Ae^{i\alpha x} + Be^{-i\alpha x}$$

$$\psi_2(x) = Ce^{\beta x} + De^{-\beta x} \quad \text{for } E < V_0$$