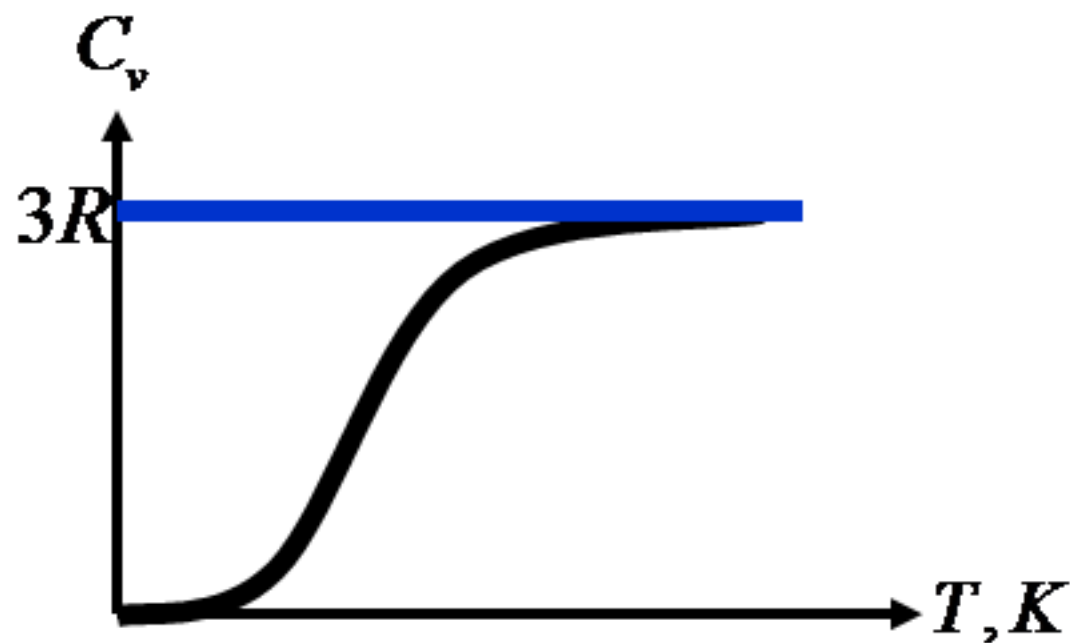# THERMAL PROPERTIES OF CRYSTAL

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Plot of C_v as a function of T

Specific heat at constant volume depends on temperature as shown in figure below. At high temperatures the value of C_v is close to 3R, where R is the universal gas constant. Since R is approximately 2 cal/K-mole, at high temperatures C_v is app. 6 cal/K-mole.

This range usually includes RT. From the figure it is seen that C_v is equal to 3R at high temperatures regardless of the substance. This fact is known as Dulong-Petit law. This law states that specific heat of a given number of atoms of any solid is independent of temperature and is the same for all materials!

Classical theory of heat capacity of solids

The solid is one in which each atom is bound to its side by a harmonic force. When the solid is heated, the atoms vibrate around their sites like a set of harmonic oscillators. The average energy for a 1D oscillator is kT. Therefore, the averaga energy per atom, regarded as a 3D oscillator, is 3kT, and consequently the energy per mole is

$$\overline{\varepsilon} \;=\; 3Nk_BT = 3RT$$

where N is Avagadro's number, k_B is Boltzmann constant and R is the gas constant. The differentiation wrt temperature gives;

$$C_v = \frac{d\overline{\varepsilon}}{dT} \implies C_v = 3R = 3 \times 6.02 \times 10^{23}\,(atoms/mole) \times 1.38 \times 10^{-23}\,(J/K)$$

$$Cv = 24.9\,\frac{J}{(K-mole)}; 1J = 0.2388Cal \Rightarrow Cv \simeq 6\,\frac{Cal}{(K-mole)}$$

Einstein heat capacity of solids

- The theory explained by Einstein is the first quantum theory of solids. He made the simplifying assumption that all 3N vibrational modes of a 3D solid of N atoms had the same frequency, so that the whole solid had a heat capacity 3N times

$$C_v = k_B \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2}$$

- In this model, the atoms are treated as independent oscillators, but the energy of the oscillators are taken quantum mechanically as

$$\hbar \omega$$

This refers to an isolated oscillator, but the atomic oscillators in a solid are not isolated. They are continually exchanging their energy with their surrounding atoms.

- Even this crude model gave the correct limit at high temperatures, a heat capacity of

$$3Nk_B = 3R$$

Dulong-Petit law where R is universal gas constant.

• *At high temperatures*, all crystalline solids have a specific heat of 6 cal/K per mole; they require 6 calories per mole to raise their temperature 1 K.

•This arrangement between observation and classical theory break down if the temperature is not high.

•Observations show that *at room temperatures and below* the specific heat of crystalline solids is not a universal constant.
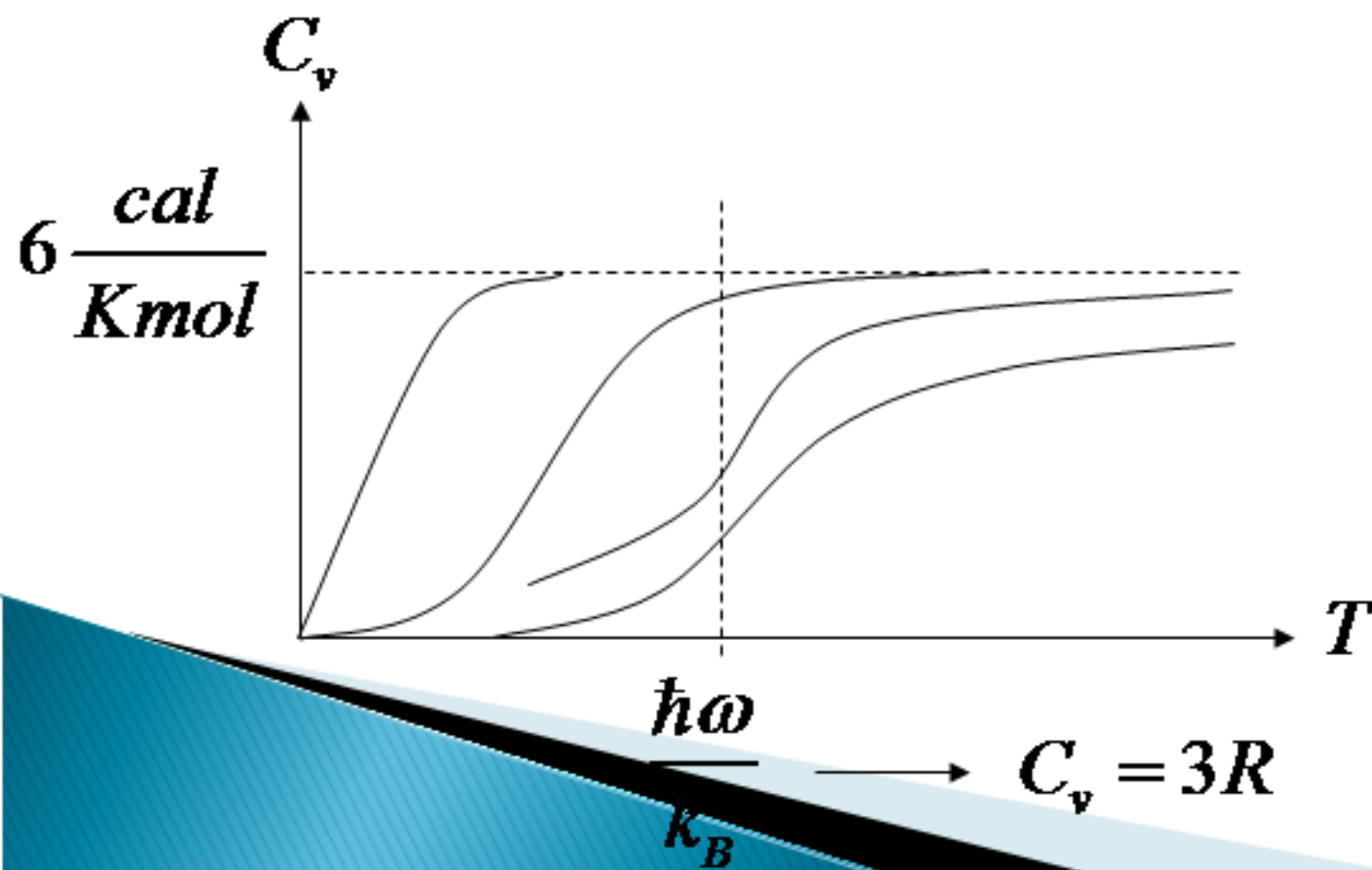
In all of these materials (Pb, Al, Si, and Diamond) specific heat approaches constant value asymptotically at high T's. But at low T's, the specific heat decreases towards zero which is in a complete contradiction with the above classical result.

$$\frac{\hbar\omega}{K_B} \longrightarrow \quad C_v = 3R$$

The Discrepancy of Einstein model

▸ Einstein model also gave correctly a specific heat tending to zero at absolute zero, but the temperature dependence near T=0 did not agree with experiment.

▸ Taking into account the actual distribution of vibration frequencies in a solid this discrepancy can be accounted using one dimensional model of monoatomic lattice

Debye cut-off frequency ω_D

The cut-off freqency is chosen to make the total number of lattice modes correct. Since there are 3N lattice vibration modes in a crystal having N atoms, we choose ω_D so that

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

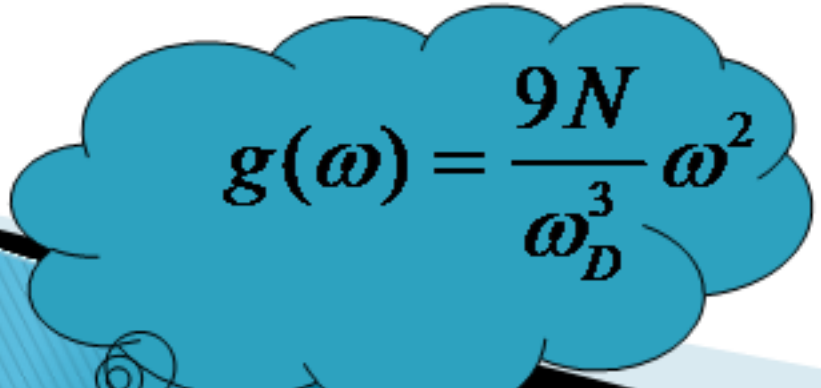$$g(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)$$

$$\frac{V}{2\pi^2}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)\int_0^{\omega_D} \omega^2 d\omega = 3N$$

$$\frac{V}{6\pi^2}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)\omega_D^3 = 3N \implies \boxed{\frac{V}{2\pi^2}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right) = \frac{3N}{\omega_D^3}3 = \frac{9N}{\omega_D^3}}$$

$$g(\omega)/\omega^2$$

$$g(\omega) = \frac{9N}{\omega_D^3}\omega^2$$

The lattice vibration energy of

$$E = \int_0^\infty \left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1} \right) g(\omega) d\omega$$

becomes

$$E = \frac{9N}{\omega_D^3}\int_0^{\omega_D}\left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}\right)\omega^2 d\omega = \frac{9N}{\omega_D^3}\left[\int_0^{\omega_D}\frac{\hbar\omega^3}{2}d\omega + \int_0^{\omega_D}\frac{\hbar\omega^3}{e^{\hbar\omega/k_BT}-1}d\omega\right]$$

and,

$$E = \frac{9}{8}N\hbar\omega_D + \frac{9N}{\omega_D^3}\int_0^{\omega_D}\frac{\hbar\omega^3 d\omega}{e^{\hbar\omega/k_BT}-1}$$

First term is the estimate of the zero point energy, and all T dependence is in the second term. The heat capacity is obtained by differentiating above eqn wrt temperature.

The heat capacity is $C = \dfrac{dE}{dT}$

$$E = \frac{9}{8}N\hbar\omega_D + \frac{9N}{\omega_D^3}\int_0^{\omega_D}\frac{\hbar\omega^3 d\omega}{e^{\hbar\omega/k_BT}-1} \implies C_D = \frac{dE}{dT} = \frac{9N}{\omega_D^3}\int_0^{\omega_D}\frac{\hbar^2\omega^4}{k_BT^2}\frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT}-1\right)^2}d\omega$$

Let's convert this complicated integral into an expression for the specific heat changing variables to

$$x = \frac{\hbar\omega}{k_BT} \implies \frac{d\omega}{dx} = \frac{kT}{\hbar} \qquad \omega = \frac{kT}{\hbar}x$$

and define the Debye temperature Θ_D

$$\Theta_D = \frac{\hbar\omega_D}{k_B}$$

The Debye prediction for lattice specific heat

$$C_D = \frac{dE}{dT} = \frac{9N}{\omega_D^3} \frac{k_B T}{\hbar} \left(\frac{k_B T}{\hbar}\right)^4 \left(\frac{\hbar^2}{k_B T^2}\right) \int_0^{\Theta_D/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx$$

$$C_D = 9 N k_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx$$

where

$$\Theta_D = \frac{\hbar \omega_D}{k_B}$$

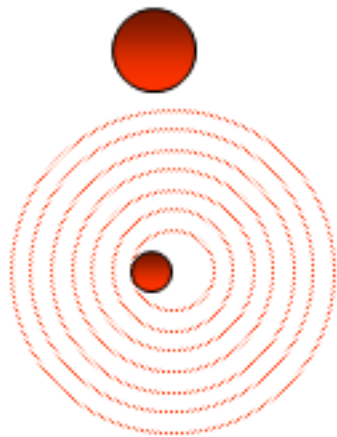How does C_D limit at high and low temperatures?

High temperature

X is always small

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} +$$

$$\frac{x^4 e^x}{\left(e^x - 1\right)^2} = \frac{x^4(1+x)}{\left(1+x-1\right)^2} = \frac{x^4(1+x)}{x^2} = x^2$$

$$T \gg \Theta_D \Rightarrow C_D \cong 9Nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} x^2 dx = 3Nk_B$$

Thermal energy and lattice vibrations

- Atoms vibrate about their equilibrium position.

- They produce vibrational waves.

- This motion is increased as the temperature is raised.

In a solid, the energy associated with this **vibration** and perhaps also with the **rotation** of atoms and molecules is called as *thermal energy.*

Note: In a gas, the translational motion of atoms and molecules contribute to this energy.

Low temperature

For low temperature the upper limit of the integral is infinite; the integral is then a known integral of

$$\cdot 4\pi^4/15$$

$$T \ll \Theta_D \Rightarrow C_D \cong 9Nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx$$

We obtain the Debye T^3 law in the form

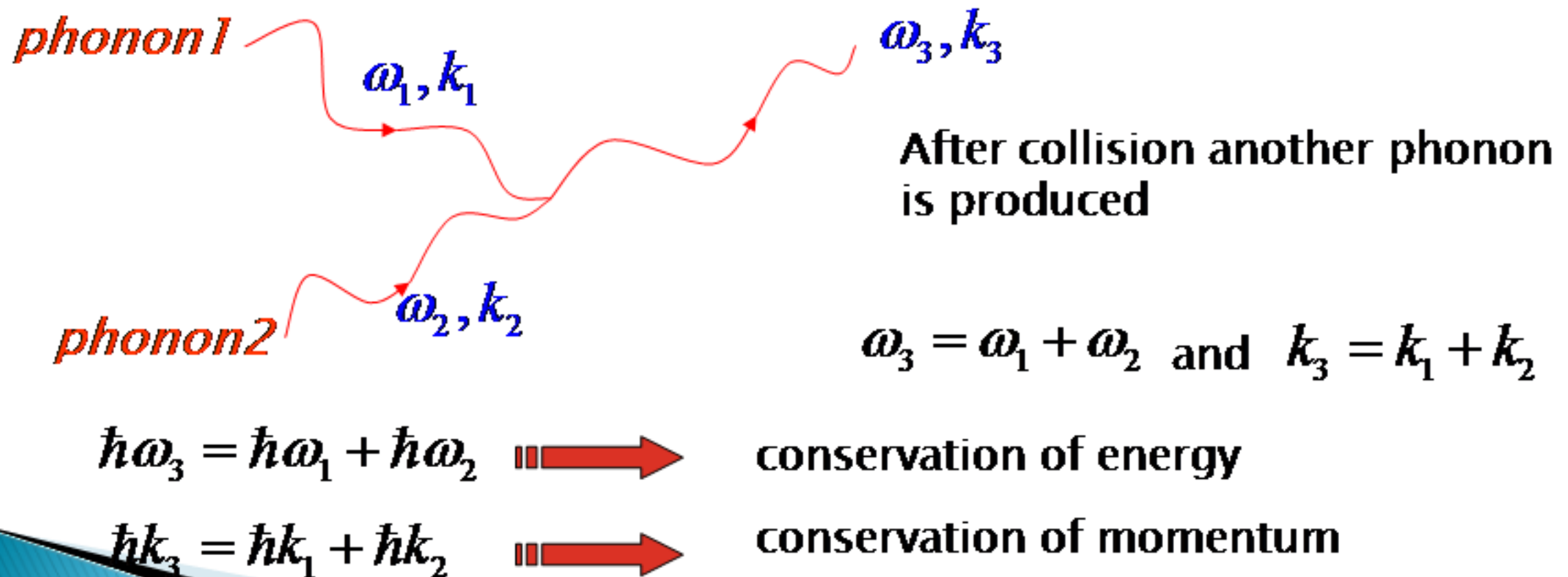$$C_D \cong \frac{12Nk_B\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^3$$

Anharmonic Effects

▷ This is an anharmonic effect due to the higher order terms in potential which are ignored in harmonic approximation.

$$V(r) = V(a) + \frac{(r-a)^2}{2}\left(\frac{d^2V}{dr^2}\right)_{r=a} + \text{-----------------}$$

▷ Thermal expansion is an example to the anharmonic effect.

▷ In harmonic approximation phonons do not interact with each other, in the absence of boundaries, lattice defects and impurities (which also scatter the phonons), the thermal conductivity is infinite.

▷ In anharmonic effect phonons collide with each other and these collisions limit thermal conductivity which is due to the flow of phonons.

Phonon–phonon collisions

The coupling of normal modes by the unharmonic terms in the interatomic forces can be pictured as collisions between the phonons associated with the modes.

phonon1

ω_1, k_1

ω_3, k_3

After collision another phonon is produced

phonon2

ω_2, k_2

$\omega_3 = \omega_1 + \omega_2$ and $k_3 = k_1 + k_2$

$\hbar\omega_3 = \hbar\omega_1 + \hbar\omega_2$ ⟹ conservation of energy

$\hbar k_3 = \hbar k_1 + \hbar k_2$ ⟹ conservation of momentum
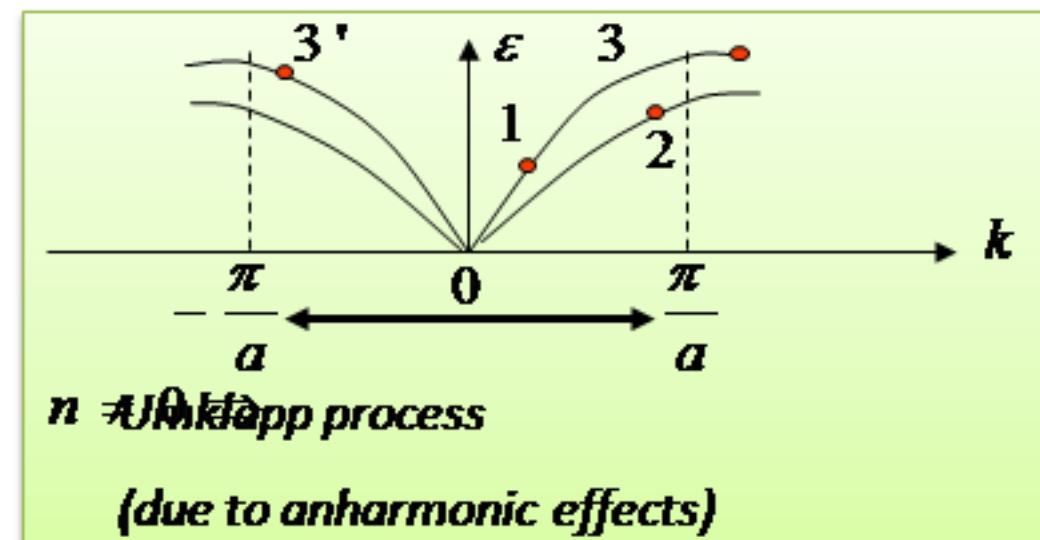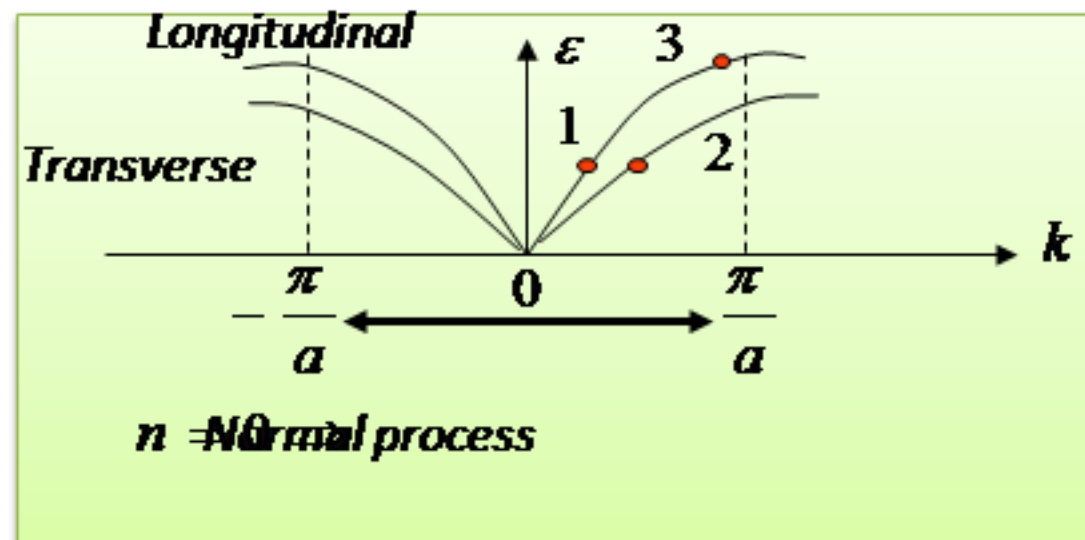
Phonons are represented by wavenumbers with

$$-\frac{\pi}{a} \le k \le \frac{\pi}{a}$$

If k_3 lies outside this range add a suitable multible of $\frac{2\pi}{a}$ to bring it back within the range of $-\frac{\pi}{a} \le k \le \frac{\pi}{a}$. Then, $k_3 = k_1 + k_2$ becomes

This phonon is indistinguishable from a phonon with wavevector k_3

$$k_3 \pm \frac{n2\pi}{a} = k_1 + k_2$$

where k_1, k_2, and k_3 are all in the above range.

Phonon3 has $|k| \prec \frac{\pi}{a}$; *Phonon3 has* $|k| \succ \frac{\pi}{a}$ *and Phonon3=Phonon3'*

Thermal conduction by phonons

- A flow of heat takes place from a hotter region to a cooler region when there is a temperature gradient in a solid.
- The most important contribution to thermal conduction comes from the flow of phonons in an electrically insulating solid.
- *Transport property* is an example of thermal conduction.
- *Transport property is* the process in which the flow of some quantity occurs.
- *Thermal conductivity* is a transport coefficient and it describes the flow.
- The thermal conductivity of a phonon gas in a solid will be calculated by means of the elementary kinetic theory of the transport coefficients of gases.

Heat conduction in a phonon and real gas
## The essential differences between the processes of heat conduction in a phonon and real gas;

Phonon gas

• Speed is approximately constant.

• Both the number density and energy density is greater at the hot end.

• Heat flow is primarily due to phonon flow with phonons being *created* at the hot end and *destroyed* at the cold end

hot   cold
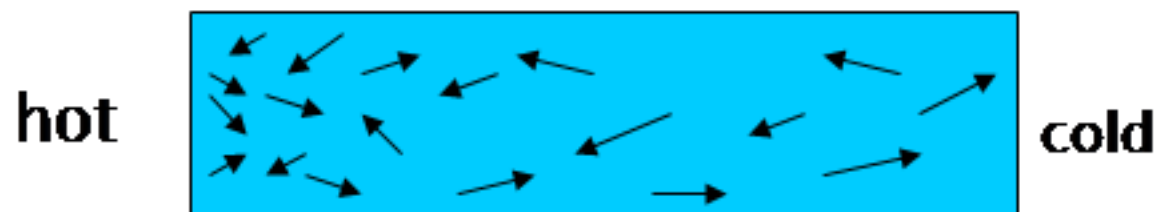
Real gas

• No flow of particles

• Average velocity and kinetic energy per particle are greater at the hot end, but the number density is greater at the cold end, and the energy density is uniform due to the uniform pressure.

• Heat flow is solely by transfer of kinetic energy from one particle to another in collisions which is a minor effect in phonon case.

hot   cold
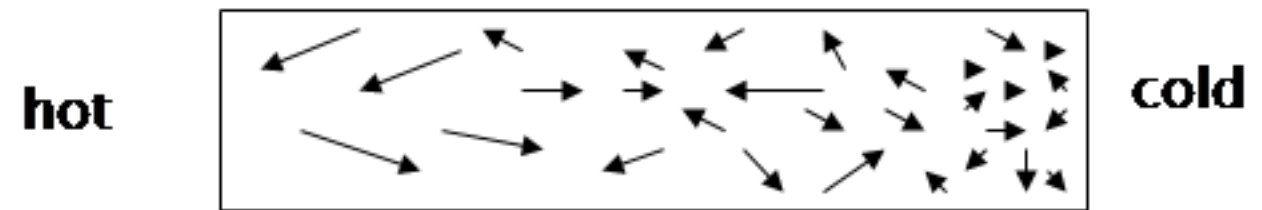
Therefore, the concept of thermal energy is fundamental to an understanding many of the basic properties of solids. We would like to know:

- What is the value of this thermal energy?

- How much is available to scatter a conduction electron in a metal; since this scattering gives rise to electrical resistance.

- The energy can be used to activate a crystallographic or a magnetic transition.

- How the vibrational energy changes with temperature since this gives a measure of the heat energy which is necessary to raise the temperature of the material.

- Recall that the specific heat or heat capacity is the thermal energy which is required to raise the temperature of unit mass or 1gmole by one Kelvin.

Heat capacity from Lattice vibrations

The energy given to lattice vibrations is the dominant contribution to the heat capacity in most solids.

Other contributions;

- In metals→ from the conduction electrons.

- In magnetic materials→ from magneting ordering.

Atomic vibrations leads to band of normal mode frequencies from zero up to some maximum value.

Calculation of the lattice energy and heat capacity of a solid therefore falls into two parts:

 i) the evaluation of the contribution of a single mode, and

ii) the summation over the frequency distribution of the modes.

Energy and heat capacity of a harmonic oscillator, Einstein Model

$$\bar{\varepsilon} = \sum_n P_n \varepsilon_n$$

Avarage energy of a harmonic oscillator and hence of a lattice mode of angular frequency at temperature T

Energy of oscillator

The probability of the oscillator being in this level as given by the Boltzman factor

$$\exp(-\varepsilon_n / k_B T)$$

$$\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar \omega$$

$$\bar{\varepsilon} = \sum_n P_n \varepsilon_n$$

$$\bar{\varepsilon} = \frac{\sum_{n=0}^{\infty} \left(n+\frac{1}{2}\right)\hbar\omega \exp\left[-\left(n+\frac{1}{2}\right)\hbar\omega/k_B T\right]}{\sum_{n=0}^{\infty} \exp\left[-\left(n+\frac{1}{2}\right)\hbar\omega/k_B T\right]} \quad (*)$$

$$z = \sum_{n=0}^{\infty} \exp[-(n+\frac{1}{2})\frac{\hbar\omega}{k_B T}]$$

$$z = e^{-\hbar\omega/2k_B T} + e^{-3\hbar\omega/2k_B T} + e^{-5\hbar\omega/2k_B T} + \ldots$$

$$z = e^{-\hbar\omega/2k_B T}(1 + e^{-\hbar\omega/k_B T} + e^{-2\hbar\omega/k_B T} + \ldots$$

$$z = e^{-\hbar\omega/2k_B T}(1 - e^{-\hbar\omega/k_B T})^{-1}$$

According to the Binomial expansion for x«1 $\quad x = -\hbar\omega/k_B T$
where

Eqn (*) can be written

$$\bar{\varepsilon} = k_B T^2 \frac{1}{z} \frac{\partial z}{\partial T} = k_B T^2 \frac{\partial}{\partial T}(\ln z)$$

$$\bar{\varepsilon} = k_B T^2 \frac{\partial}{\partial T} \ln\left(\frac{e^{-\hbar\omega/2k_B T}}{1 - e^{-\hbar\omega/k_B T}}\right)$$

$$\bar{\varepsilon} = k_B T^2 \frac{\partial}{\partial T}\left[\ln e^{-\hbar\omega/2k_B T} - \ln\left(1 - e^{-\hbar\omega/k_B T}\right)\right]$$

$$\bar{\varepsilon} = k_B T^2 \left[\frac{\partial}{\partial T}\left(-\frac{\hbar\omega}{2k_B T}\right) - \frac{\partial}{\partial T}\ln\left(1 - e^{-\hbar\omega/k_B T}\right)\right] \longrightarrow \boxed{\frac{\partial}{\partial x}(\ln x) = \frac{x'}{x}}$$

$$\bar{\varepsilon} = k_B T^2 \left[\frac{2k_B\hbar\omega}{4k_B^2 T^2} + \frac{\dfrac{\hbar\omega k_B}{k_B^2 T^2} e^{-\hbar\omega/k_B T}}{\left(1 - e^{-\hbar\omega/k_B T}\right)}\right] = \frac{1}{2}\hbar\omega + \frac{\hbar\omega e^{-\hbar\omega/k_B T}}{\left(1 - e^{-\hbar\omega/k_B T}\right)}$$

$$\boxed{\bar{\varepsilon} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}}$$

Heat Capacity C

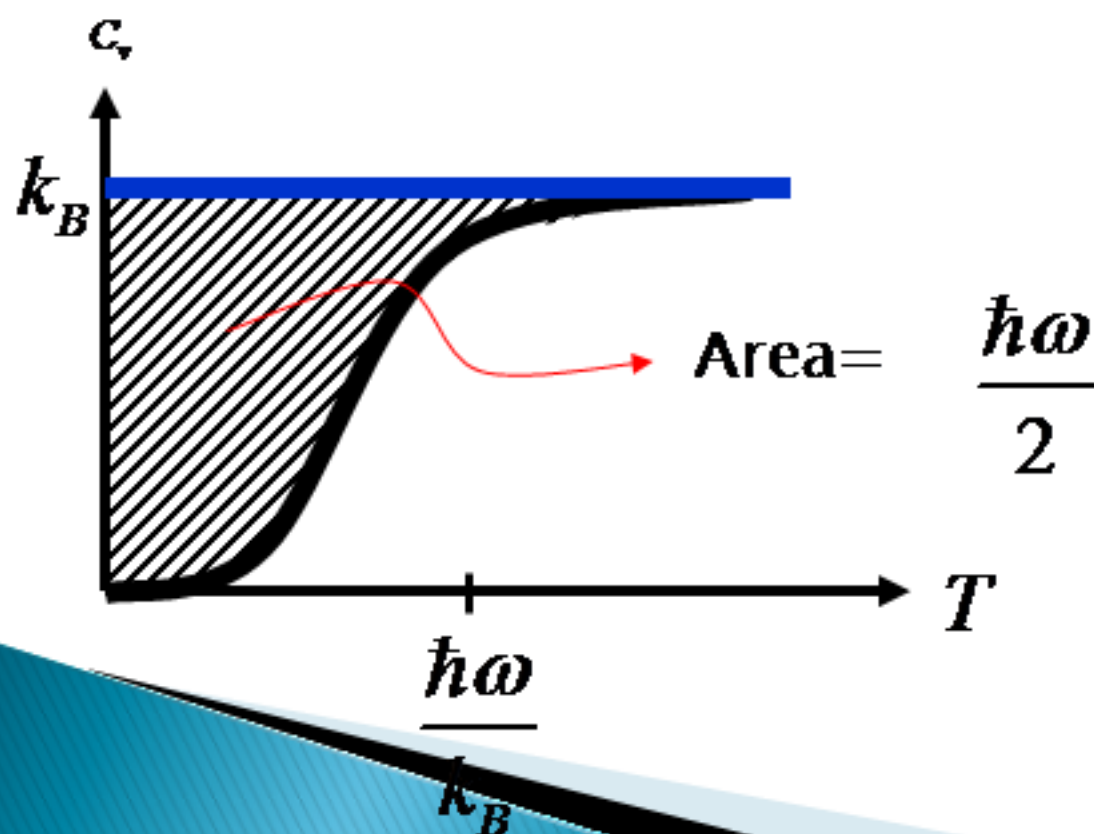▷ Heat capacity C can be found by differentiating the average energy of phonons of

$$\bar{\varepsilon} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

$$C_v = \frac{d\bar{\varepsilon}}{dT} = \frac{-\hbar\omega \dfrac{-\hbar\omega k_B}{(k_B T)^2} e^{\hbar\omega/k_B T}}{\left(e^{\hbar\omega/k_B T} - 1\right)^2} \quad \Longrightarrow \quad C_v = k_B \frac{(\hbar\omega)^2}{(k_B T)^2} \frac{e^{\hbar\omega/k_B T}}{\left(e^{\hbar\omega/k_B T} - 1\right)^2}$$

Let $\quad \theta = \dfrac{\hbar\omega}{k} \quad \Longrightarrow \quad C_v = k_B \left(\dfrac{\theta}{T}\right)^2 \dfrac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2}$

Plot of C_v as a function of T

$$C_v = k_B \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2} \quad \text{where} \quad \theta = \frac{\hbar\omega}{k}$$

c_v

k_B

Area$= \dfrac{\hbar\omega}{2}$

T

$\dfrac{\hbar\omega}{k_B}$

Specific heat vanishes exponentially at low T's and tends to classical value at high temperatures.

The features are common to all quantum systems; the energy tends to the zero-point-energy at low T's and to the classical value of Boltzmann constant at high T's.