

CHAPTER 4

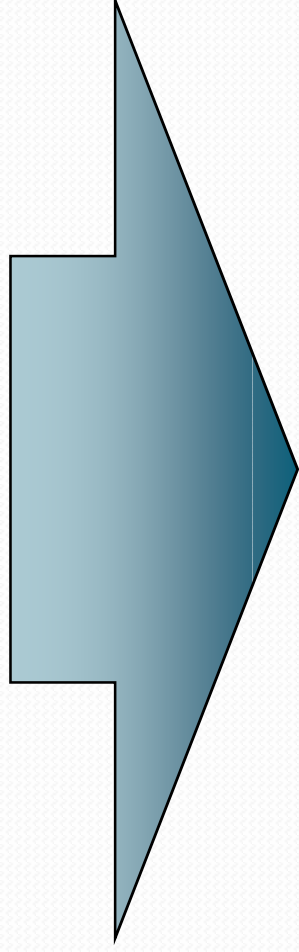
Crystal Dynamics I

- SOUND WAVES
- LATTICE VIBRATIONS OF 1D CRYSTALS
 - chain of identical atoms
 - chain of two types of atoms
- LATTICE VIBRATIONS OF 3D CRYSTALS
- PHONONS
- HEAT CAPACITY FROM LATTICE VIBRATIONS
- ANHARMONIC EFFECTS
- THERMAL CONDUCTION BY PHONONS

Crystal Dynamics

- Concern with the spectrum of characteristics vibrations of a crystalline solid.
- Leads to;
 - consideration of the conditions for wave propagation in a periodic lattice,
 - the energy content,
 - the specific heat of lattice waves,
 - the particle aspects of quantized lattice vibrations (phonons)
 - consequences of an harmonic coupling between atoms.

Crystal Dynamics



These introduces us to the concepts of

- forbidden and permitted frequency ranges, and
- electronic spectra of solids

Crystal Dynamics

- In previous chapters we have assumed that the atoms were at rest at their equilibrium position. This can not be entirely correct (against to the HUP); Atoms vibrate about their equilibrium position at absolute zero.
- The energy they possess as a result of zero point motion is known as zero point energy.
- The amplitude of the motion increases as the atoms gain more thermal energy at higher temperatures.
- In this chapter we discuss the nature of atomic motions, sometimes referred to as lattice vibrations.
- In crystal dynamics we will use the harmonic approximation , amplitude of the lattice vibration is small. At higher amplitude some unharmonic effects occur.

Crystal Dynamics

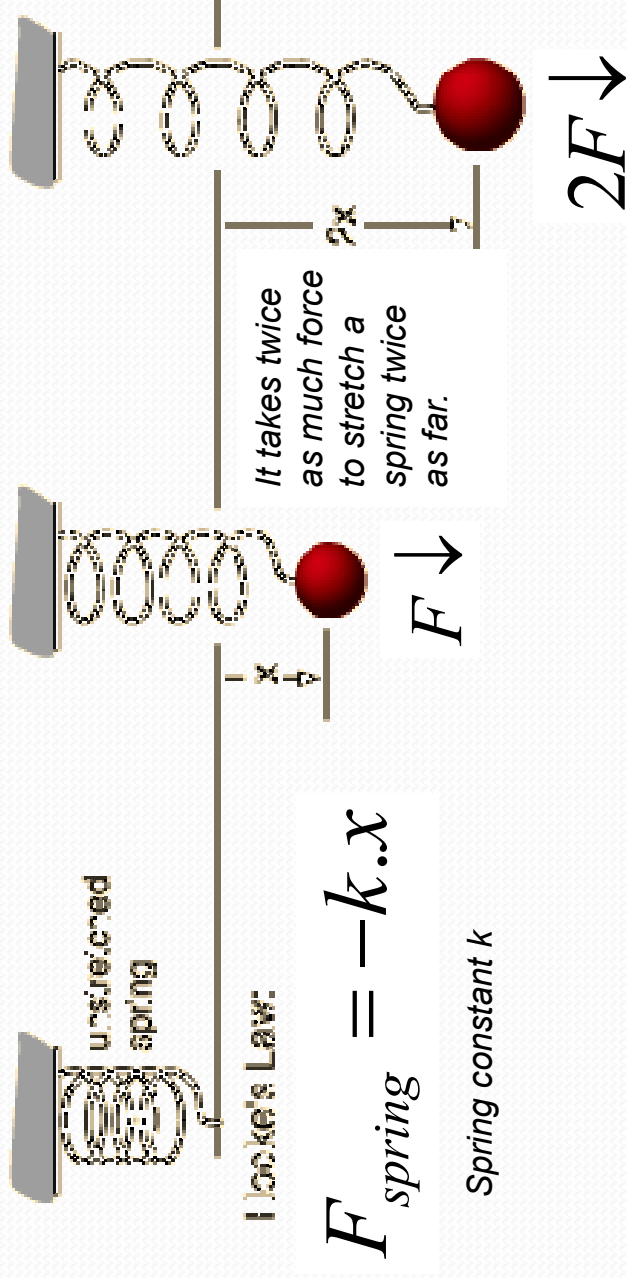
- Our calculations will be restricted to lattice vibrations of small amplitude. Since the solid is then close to a position of stable equilibrium its motion can be calculated by a generalization of the method used to analyse a simple harmonic oscillator. The small amplitude limit is known as harmonic limit.
- In the linear region (the region of elastic deformation), the restoring force on each atom is approximately proportional to its displacement (Hooke's Law).
- There are some effects of nonlinearity or 'anharmonicity' for larger atomic displacements.
- Anharmonic effects are important for interactions between phonons and photons.

Crystal Dynamics

- Atomic motions are governed by the forces exerted on atoms when they are displaced from their equilibrium positions.
- To calculate the forces it is necessary to determine the wavefunctions and energies of the electrons within the crystal. Fortunately many important properties of the atomic motions can be deduced without doing these calculations.

Hooke's Law

- One of the **properties of elasticity** is that it takes about twice as much force to stretch a spring twice as far. That linear dependence of displacement upon stretching force is called Hooke's law.

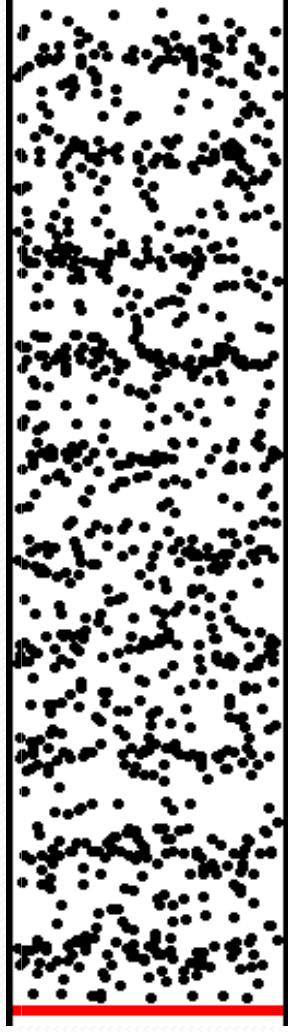


Hooke's Law

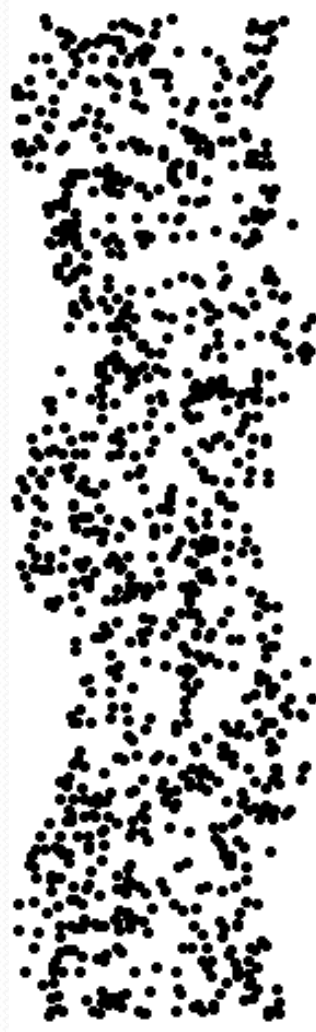
- The point at which the **Elastic Region** ends is called the **inelastic limit**, or the proportional limit. In actuality, these two points are not quite the same.
- The **inelastic Limit** is the point at which **permanent deformation occurs**, that is, after the elastic limit, if the force is taken off the sample, it will **not return to its original size** and shape, permanent deformation has occurred.
- The **Proportional Limit** is the point at which the deformation is **no longer directly proportional to the applied force** (Hooke's Law no longer holds). Although these two points are slightly different, we will treat them as the same in this course.

SOUND WAVES

- Mechanical waves are waves that propagate through a material medium (solid, liquid, or gas) at a wave speed which depends on the elastic and inertial properties of that medium. There are two basic types of wave: longitudinal mechanical waves, so called as they travel in the same direction as the wave, and transverse waves.



Longitudinal Waves



Transverse Waves

SOUND WAVES

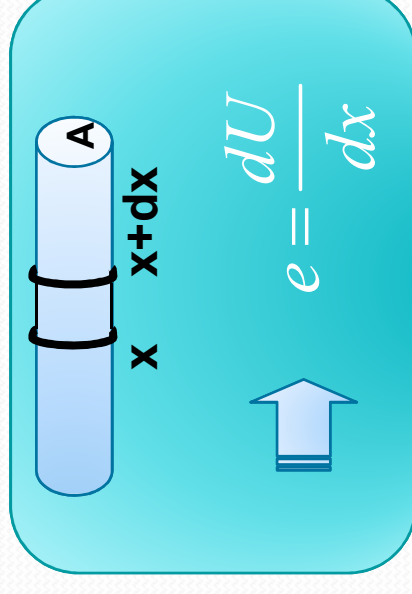
- Sound waves propagate through solids. This tells us that wavelike lattice vibrations of wavelength long compared to the interatomic spacing are possible. The detailed atomic structure is unimportant for these waves and their propagation is governed by the macroscopic elastic properties of the crystal.
- We discuss sound waves since they must correspond to the low frequency, long wavelength limit of the more general lattice vibrations considered later in this chapter.
- At a given frequency and in a given direction in a crystal it is possible to transmit three sound waves, differing in their direction of polarization and in general also in their velocity.

Elastic Waves

- A solid is composed of discrete atoms, however when the **wavelength is very long**, one may disregard the atomic nature and treat the solid as a **continuous medium**. Such vibrations are referred to as **elastic waves**.

Elastic Wave Propagation (longitudinal) in a bar

- At the point x elastic displacement is $U(x)$ and strain 'e' is defined as the change in length per unit length.

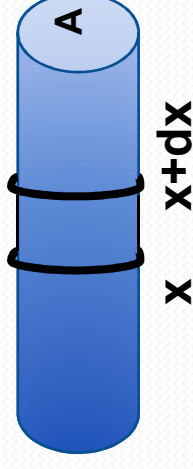


Elastic Waves

- According to **Hooke's law stress S** (force per unit area) is proportional to the **strain e** .

$$S = C.e$$

C = Young modulus



- To examine the dynamics of the bar, we choose an arbitrary segment of length dx as shown above. Using Newton's second law, we can write for the **motion of this segment**,

$$(\rho A dx) \frac{\partial^2 u}{\partial t^2} = [S(x+dx) - S(x)] A$$

Mass x Acceleration

Net Force resulting from stresses

Elastic Waves

• Equation of motion

$$(\rho A dx) \frac{\partial^2 u}{\partial t^2} = [S(x+dx) - S(x)] A$$

$$[S(x+dx) - S(x)] = \frac{\partial S}{\partial x} dx$$

$$(\rho A dx) \frac{\partial^2 u}{\partial t^2} = C \frac{\partial^2 u}{\partial x^2} A dx$$

$$\rho \frac{\partial^2 u}{\partial t^2} = C \frac{\partial^2 u}{\partial x^2}$$

$$u = A e^{i(kx - \omega t)}$$

$$S = C \cdot e$$

$$e = \frac{du}{dx}$$

$$S = C \cdot \frac{\partial u}{\partial x}$$

$$\frac{\partial S}{\partial x} = C \cdot \frac{\partial^2 u}{\partial x^2}$$

Cancelling common terms of A dx;

Which is the wave eqn. with an offered sol'n and velocity of sound waves ;

- **k = wave number** ($2\pi/\lambda$)
- **ω = frequency of the wave**
- **A = wave amplitude**

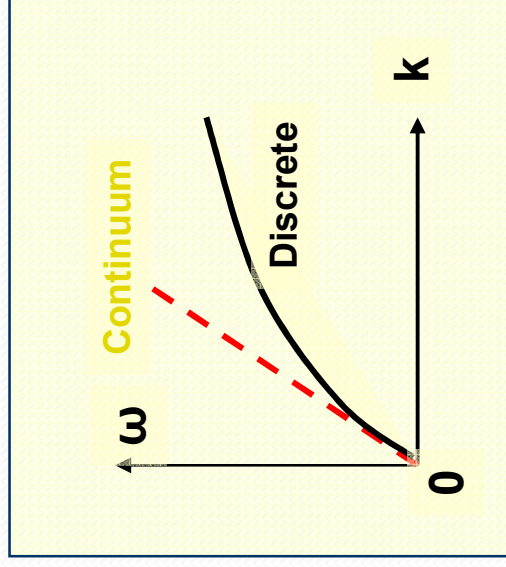
$$\omega = v_s k$$

$$v_s = \sqrt{C / \rho}$$

Dispersion Relation

- The relation connecting the frequency and wave number is known as the **dispersion relation**.

$$\omega = v_s k$$



* Slope of the curve gives the velocity of the wave.

- At small λ $k \rightarrow \infty$ (scattering occurs)
- At long λ $k \rightarrow 0$ (no scattering)
- When k increases velocity decreases. As k increases further, the scattering becomes greater since the strength of scattering increases as the wavelength decreases, and the velocity decreases even further.

Speed of Sound Wave

- The speed with which a longitudinal wave moves through a liquid of density ρ is

$$V_L = \lambda v = \sqrt{\frac{C}{\rho}}$$

C = Elastic bulk modulus
 ρ = Mass density

- The velocity of sound is in general a function of the direction of propagation in crystalline materials.
- Solids will sustain the propagation of transverse waves, which travel more slowly than longitudinal waves.
- The larger the elastic modulus and smaller the density, the more rapidly can sound waves travel.

Speed of sound for some typical solids

Solid	Structure Type	Nearest Neighbour Distance (Å)	Density ρ (kg/m ³)	Elastic bulk modulus Y (10^{10} N/m ²)	Calculated Wave Speed (m/s)	Observed speed of sound (m/s)
Sodium	B.C.C	3.71	970	0.52	2320	2250
Copper	F.C.C	2.55	8966	13.4	3880	3830
Aluminum	F.C.C	2.86	2700	7.35	5200	5110
Lead	F.C.C	3.49	11340	4.34	1960	1320
Silicon	Diamond	2.35	2330	10.1	6600	9150
Germanium	Diamond	2.44	5360	7.9	3830	5400
NaCl	Rocksalt	2.82	2170	2.5	3400	4730

- V_L values are comparable with direct observations of speed of sound.
- Sound speeds are of the order of 5000 m/s in typical metallic, covalent and ionic solids.

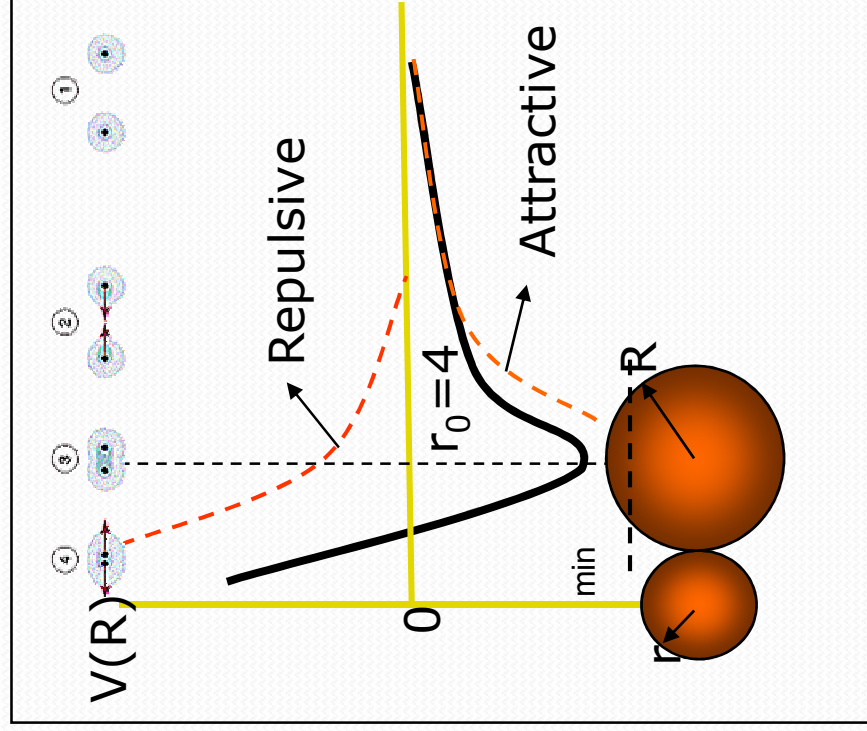
Sound Wave Speed

- A lattice vibrational wave in a crystal is a repetitive and systematic sequence of atomic displacements of
 - longitudinal,
 - transverse, or
 - some combination
- An equation of motion for any displacement can be produced by means of considering the restoring forces on displacement velocity, v
- As waves travel can create a dispersion relationship between frequency or angular frequency ω or between angular frequency and wavevector.

Lattice vibrations of 1D crystal

Chain of identical atoms

- Atoms interact with a potential $V(r)$ which can be written in Taylor's series.



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

This equation looks like as the potential energy associated of a spring with a spring constant :

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

We should relate K with elastic modulus C :

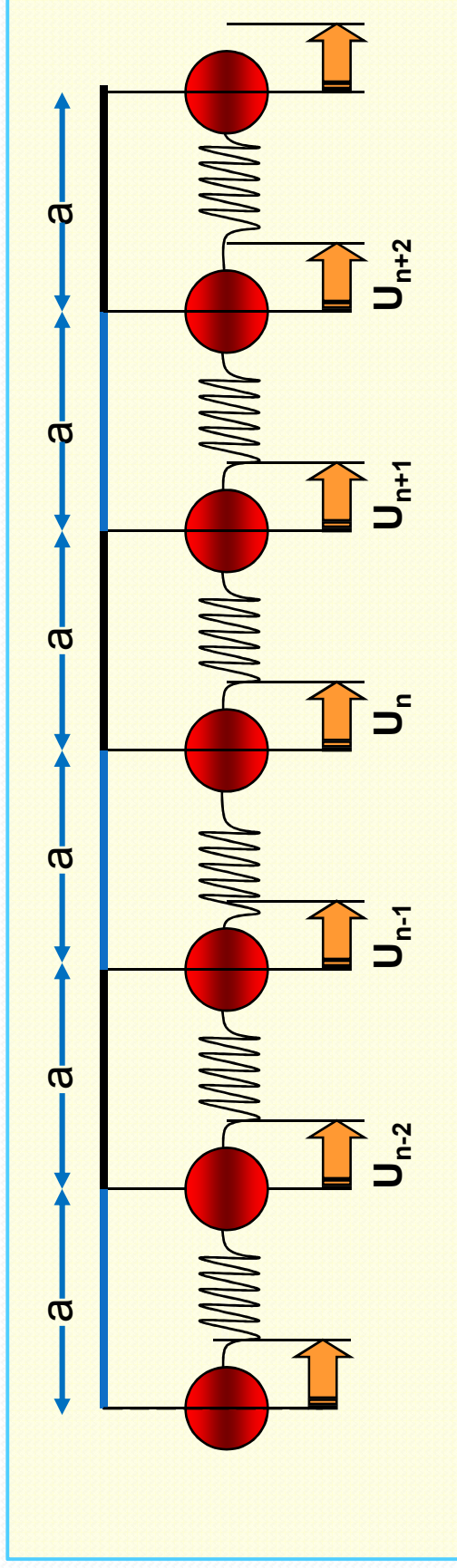
$$Force = C \times \frac{(r-a)}{a}$$

$$Force = K(r-a)$$

$$C = Ka$$

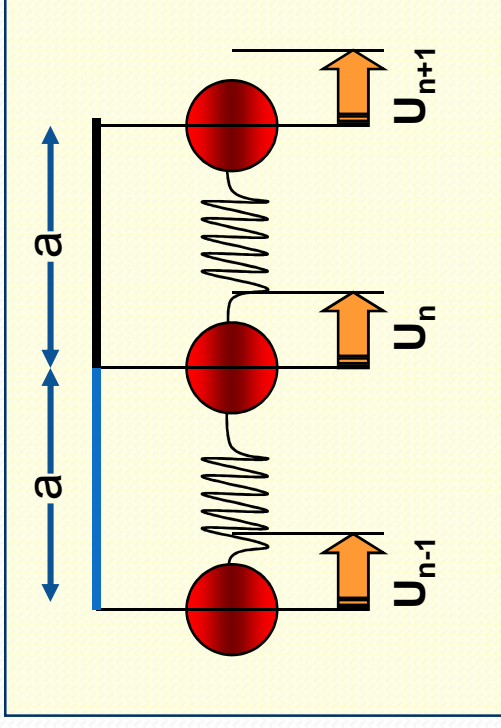
Monoatomic Chain

- The simplest crystal is the one dimensional chain of identical atoms.
- Chain consists of a very large number of identical atoms with identical masses.
- Atoms are separated by a distance of “ a ”.
- Atoms move only in a direction parallel to the chain.
- Only nearest neighbours interact (short-range forces).



Monoatomic Chain

- Start with the simplest case of monoatomic linear chain with only nearest neighbour interaction



- If one expands the energy near the equilibrium point for the n^{th} atom and use elastic approximation, Newton's equation becomes

$$m\ddot{u}_n = K(u_{n+1} - 2u_n + u_{n-1})$$

Monoatomic Chain

The force on the n^{th} atom;

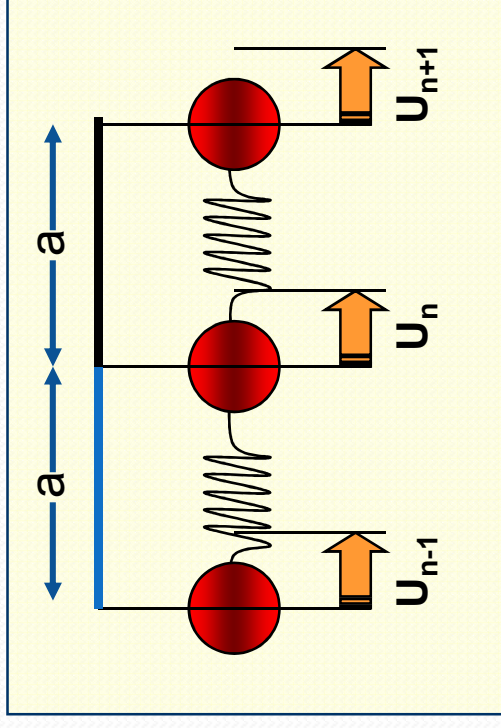
- The force to the right;

$$K(u_{n+1} - u_n)$$

- The force to the left;

$$K(u_n - u_{n-1})$$

- The total force = Force to the right – Force to the left



$$m \ddot{u}_n + K(2u_n - u_{n-1} - u_{n+1}) = 0$$

Eqn's of motion of all atoms are of this form, only the value of 'n' varies

Monoatomic Chain

- All atoms oscillate with a same amplitude A and frequency ω . Then we can offer a solution;

$$u_n = A \exp [i (kx_n^0 - \omega t)]$$

$$\dot{u}_n = \frac{du_n}{dt} = -i\omega A \exp [i (kx_n^0 - \omega t)]$$

$$\ddot{u}_n = \frac{d^2 u_n}{dt^2} = (i)^2 \omega^2 A \exp [i (kx_n^0 - \omega t)]$$

$$\ddot{u}_n = -\omega^2 u_n$$

$$x_n^0 = na$$

Undisplaced
position

$$x_n = na + u_n$$

Displaced
position

Monoatomic Chain

Equation of motion for nth atom

$$\begin{aligned}
 \ddot{m}u_n &= K(u_{n+1} - 2u_n + u_{n-1}) \\
 -m\omega^2 A e^{i(kx_n^0 - \omega t)} &= K \left(A e^{i(kx_{n+1}^0 - \omega t)} - 2A e^{i(kx_n^0 - \omega t)} + A e^{i(kx_{n-1}^0 - \omega t)} \right)
 \end{aligned}$$

kna $k(n+1)a$ kna $k(n-1)a$

$$\begin{aligned}
 -m\omega^2 A e^{i(kna - \omega t)} &= K \left(A e^{i(kna + ka - \omega t)} - 2A e^{i(kna - \omega t)} + A e^{i(kna - ka - \omega t)} \right) \\
 -m\omega^2 A e^{i(kna - \omega t)} &= K \left(A e^{i(ka)} e^{i(kna - \omega t)} - 2A e^{i(kna - \omega t)} + A e^{-i(ka)} e^{i(kna - \omega t)} \right)
 \end{aligned}$$

Cancel Common terms

$$-m\omega^2 = K(e^{ika} - 2 + e^{-ika})$$

Monoatomic Chain

$$-m\omega^2 = K(e^{ika} - 2 + e^{-ika})$$

$$-m\omega^2 = K(2\cos ka - 2)$$

$$= -2K(1 - \cos ka)$$

$$m\omega^2 = 4K \sin^2 \left(\frac{ka}{2} \right)$$

$$\omega^2 = \frac{4K}{m} \sin^2 \left(\frac{ka}{2} \right)$$

$$\omega = \sqrt{\frac{4K}{m} \sin^2 \left(\frac{ka}{2} \right)}$$

$$\omega_{\max} = \sqrt{\frac{4K}{m}}$$

$$e^{ix} + e^{-ix} = 2 \cos x$$

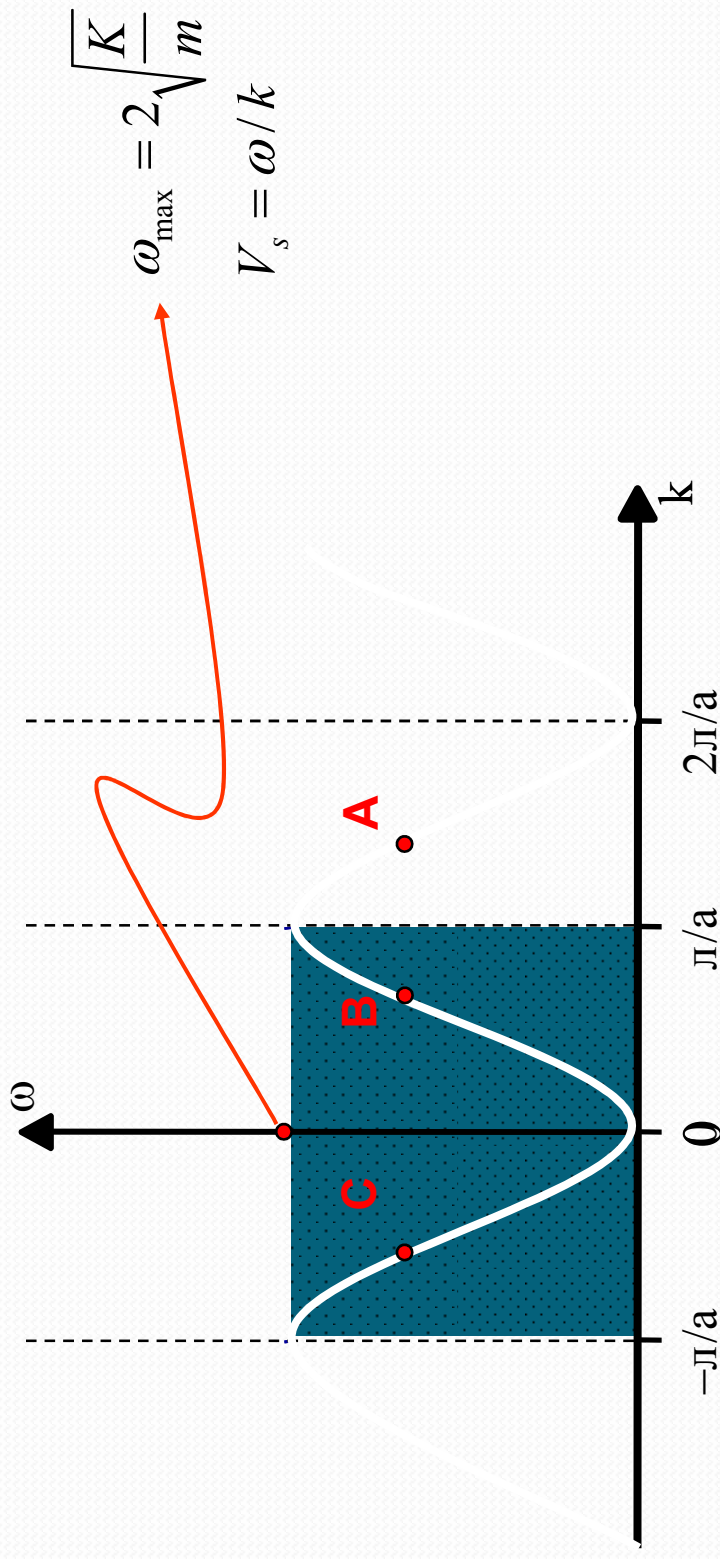
$$e^{ika} + e^{-ika} = 2 \cos ka$$

$$(1 - \cos x) = 2 \sin^2 \left(\frac{x}{2} \right)$$

Maximum value of it is 1

Monoatomic Chain

- ω versus k relation;



- Normal mode frequencies of a 1D chain
The points **A**, **B** and **C** correspond to the same frequency, therefore they all have the same instantaneous atomic displacements. The dispersion relation is periodic with a period of $2\pi/a$.

Monoatomic Chain

Note that:

$$\omega = \sqrt{\frac{4K}{m} \sin^2 \frac{ka}{2}}$$

- In above equation **n** is **cancelled out**, this means that the eqn. of motion of all atoms leads to the same algebraic eqn. This shows that our trial function U_n is indeed a solution of the eqn. of motion of n-th atom.
- We started from the eqn. of motion of **N coupled harmonic oscillators**. If one atom starts vibrating it does not continue with constant amplitude, but transfer energy to the others in a complicated way; the vibrations of individual atoms are not simple harmonic because of this **exchange energy among them**.
- Our wavelike solutions on the other hand are **uncoupled oscillations** called **normal modes**; each **k** has a **definite ω** given by above eqn. and **oscillates independently of the other modes**.
- So the **number of modes** is **expected to be the same as the number of equations N**. Let's see whether this is the case;



Establish which wavenumbers are possible for our one dimensional chain. Not all values are allowed because n th atom is the same as the $(N+n)$ th as the chain is joined on itself. This means that the wave eqn. of

$$u_n = A \exp [i (kx_n^0 - \omega t)]$$

must satisfy the periodic boundary condition

$$u_n = u_{N+n}$$

which requires that there should be an integral number of wavelengths in the length of our ring of atoms

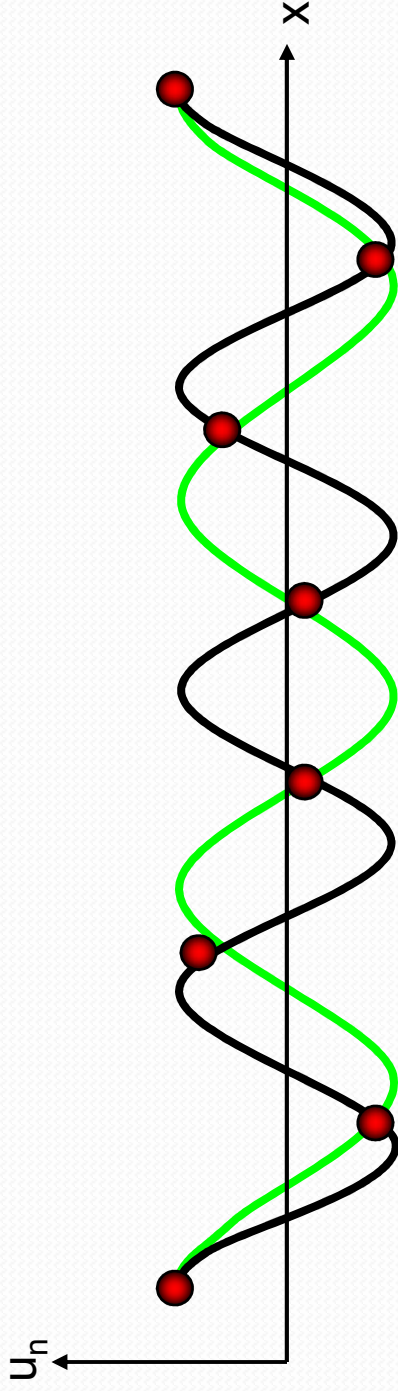
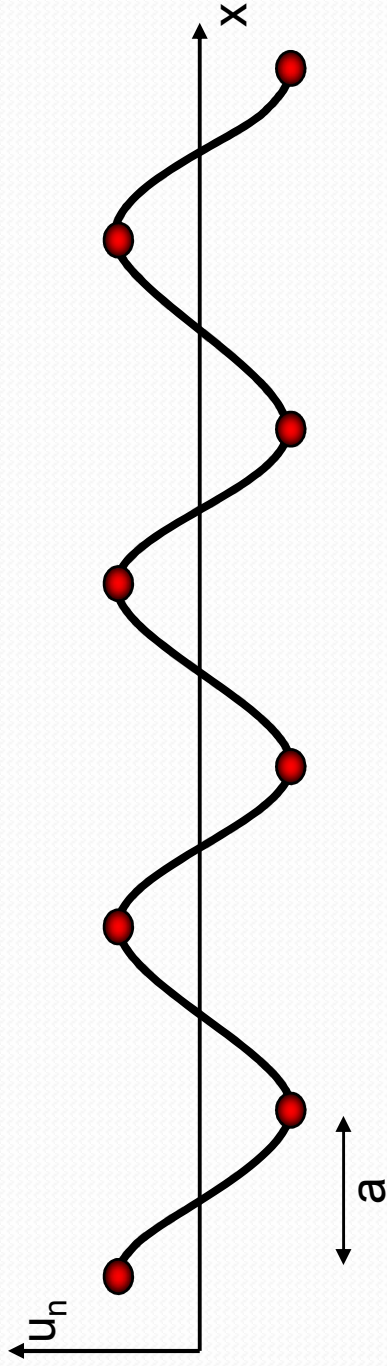
$$Na = p\lambda$$

Thus, in a range of $2\pi/a$ of k , there are N allowed values of k .

$$Na = p\lambda \Rightarrow \lambda = \frac{Na}{p} = \frac{2\pi}{k} \Rightarrow Nk = \frac{2\pi}{a} p$$

Monoatomic Chain

What is the physical significance of wave numbers outside the range of $2\pi/a$?



Monoatomic Chain

$$\lambda = 2a; k = \frac{2\pi}{\lambda} \Rightarrow k = \frac{\pi}{a}$$

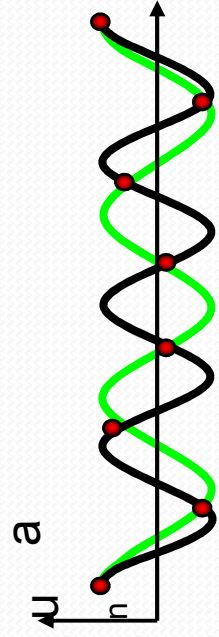
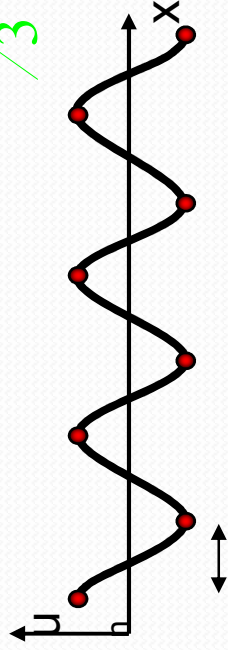
This value of k corresponds to the maximum frequency; alternate atoms oscillate in antiphase and the waves at this value of k are standing waves.

White line :

$$4\lambda = 7a \Rightarrow \lambda = \frac{7a}{4} \Rightarrow k = \frac{2\pi}{7a/4} = \frac{8\pi}{7a} = 1.14 \frac{\pi}{a}$$

Green line :

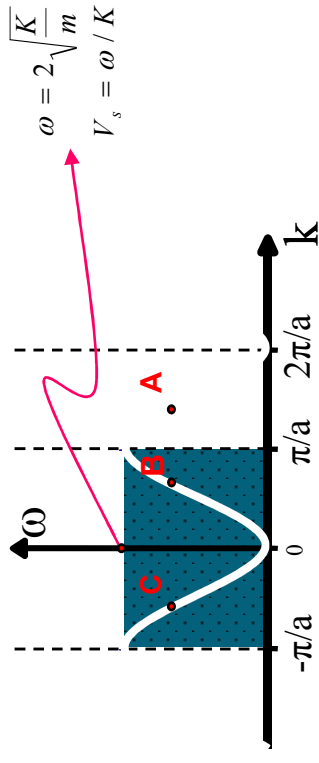
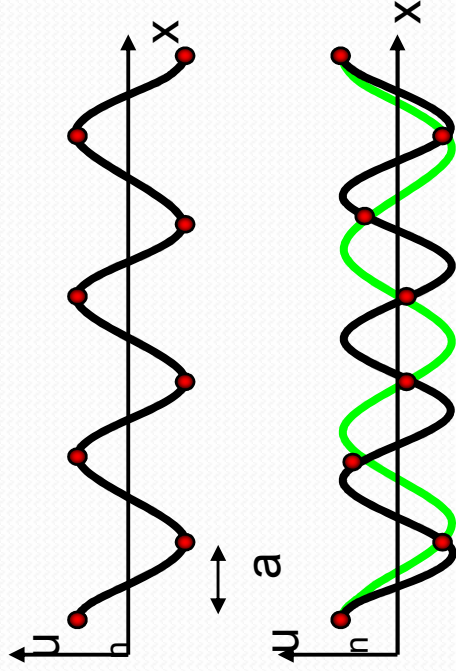
$$3\lambda = 7a \Rightarrow \lambda = \frac{7a}{3} \Rightarrow k = \frac{2\pi}{7a/3} = \frac{6\pi}{7a} = 0.85 \frac{\pi}{a}$$



ω - k relation

Monoatomic Chain

- The points **A** and **C** both have same frequency and same atomic displacements
- They are waves moving to the left.
- The **green line** corresponds to the **point B** in dispersion diagram.
- The point **B** has the same frequency and displacement with that of the points **A** and **C** with a difference.
- The **point B** represents a wave moving to the right since its group velocity $(d\omega/dk) > 0$.



ω - k relation (dispersion diagram)

- The points **A** and **C** are exactly equivalent; adding any multiple of $2\pi/a$ to k does not change the frequency and its group velocity, so point **A** has no physical significance.

• $k = \pi/a$ has special significance

• $\theta = 90^\circ$

Bragg reflection can be obtained at $\omega = 2m = 4K \sin \frac{k a}{2}$

$$k = \pm \pi/a$$

For the whole range of k ($\pm a$)

At the beginning of the chapter, in the long wavelength limit, the velocity of sound waves has been derived as

$$V_s = \sqrt{c/\rho}$$

$$\frac{c}{\rho}$$

$$\frac{Ka}{\rho}$$

Using elastic properties, let's see whether the dispersion relation leads to the same equation in the long λ limit.

$$\rho = \frac{m}{a}$$

$$\frac{K}{m}a^2$$

If λ is very long; $ka \ll 1$ so $\sin ka \approx ka$

$$\omega^2 m = 4K \frac{k^2 a^2}{4}$$



$$V_s = \frac{\omega}{k}$$

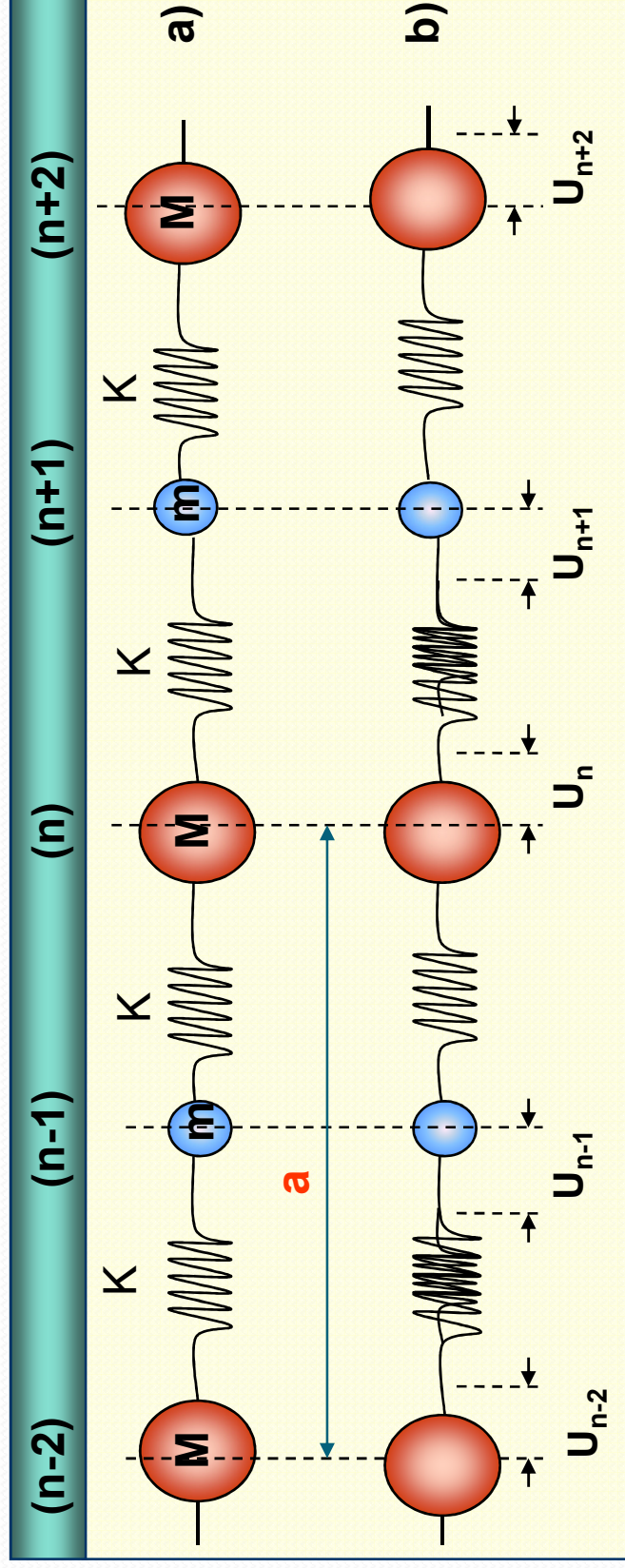
$$= \sqrt{\frac{K}{m}a}$$

Monoatomic Chain

- Since there is only one possible propagation direction and one polarization direction, the 1D crystal has only one sound velocity.
- In this calculation we only take nearest neighbor interaction although this is a good approximation for the inert-gas solids, its not a good assumption for many solids.
- If we use a model in which each atom is attached by springs of different spring constant to neighbors at different distances many of the features in above calculation are preserved.
 - Wave equation solution still satisfies.
 - The detailed form of the dispersion relation is changed but ω is still periodic function of k with period $2\pi/a$
 - Group velocity vanishes at $k=(\pm)\pi/a$
 - There are still N distinct normal modes
 - Furthermore the motion at long wavelengths corresponds to sound waves with a velocity given by (velocity formulü)

Chain of two types of atom

- Two different types of atoms of masses M and m are connected by identical springs of spring constant K ;



- This is the simplest possible model of an ionic crystal.
- Since a is the repeat distance, the nearest neighbors separations is $a/2$

Chain of two types of atom

- We will consider only the first neighbour interaction although it is a poor approximation in ionic crystals because there is a long range interaction between the ions.
- The model is complicated due to the presence of two different types of atoms which move in opposite directions.

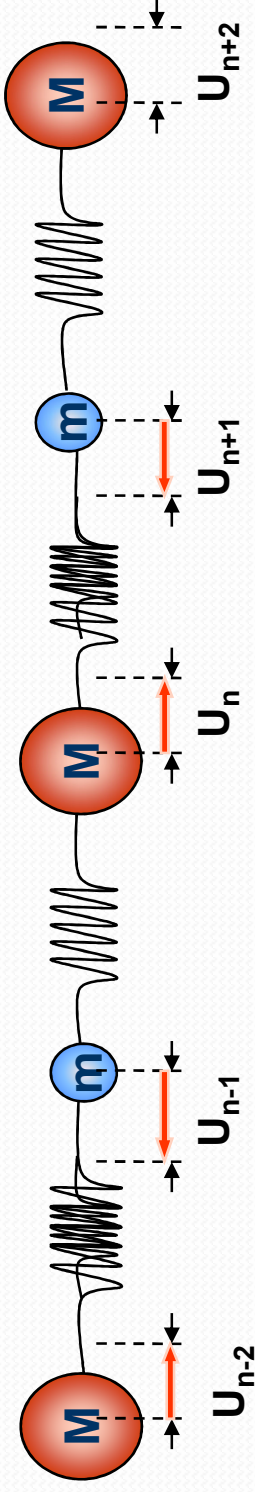
Our aim is to obtain ω - k relation for diatomic lattice



Two equations of motion must be written;

One for mass M , and
One for mass m .

Chain of two types of atom



Equation of motion for mass M (n^{th}):

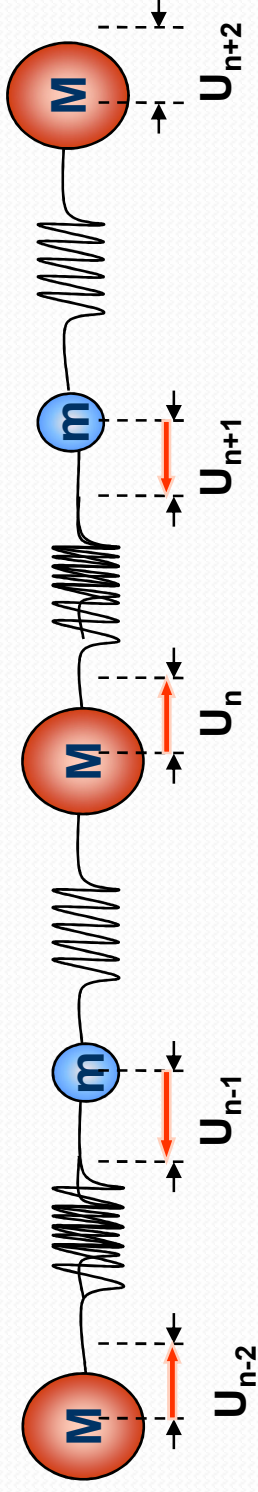
mass x acceleration = restoring force

$$\begin{aligned} M \ddot{u}_n &= K(u_{n+1} - u_n) - K(u_n - u_{n-1}) \\ &= K(u_{n+1} - 2u_n + u_{n-1}) \end{aligned}$$

Equation of motion for mass m ($(n-1)^{\text{th}}$):

$$\begin{aligned} m \ddot{u}_{n-1} &= K(u_n - u_{n-1}) - K(u_{n-1} - u_{n-2}) \\ &= K(u_n - 2u_{n-1} + u_{n-2}) \end{aligned}$$

Chain of two types of atom



Offer a solution for the mass M

$$u_n = A \exp \left[i \left(kx_n^0 - \omega t \right) \right] \quad x_n^0 = na / 2$$

For the mass m;

$$u_{n-1} = \alpha A \exp \left[i \left(kx_n^0 - \omega t \right) \right]$$

α : complex number which determines the relative amplitude and phase of the vibrational wave.

$$\ddot{u}_n = -\omega^2 A \exp \left[i \left(kx_n^0 - \omega t \right) \right]$$

Chain of two types of atom

For n^{th} atom (M):

$$M \ddot{u}_n = K(u_{n+1} - 2u_n + u_{n-1})$$

$$-\omega^2 MAe \left(i \left(\frac{kna}{2} - \omega t \right) \right) = K \left(\alpha Ae \left(i \left(\frac{k(n+1)a}{2} - \omega t \right) \right) - 2Ae \left(i \left(\frac{kna}{2} - \omega t \right) \right) + \alpha Ae \left(i \left(\frac{k(n-1)a}{2} - \omega t \right) \right) \right)$$

$$-\omega^2 MAe \left(i \left(\frac{kna}{2} - \omega t \right) \right) = K \left(\alpha Ae \left(i \left(\frac{kna}{2} - \omega t \right) \right) e^{i \frac{ka}{2}} - 2Ae \left(i \left(\frac{kna}{2} - \omega t \right) \right) + \alpha Ae \left(i \left(\frac{kna}{2} - \omega t \right) \right) e^{-i \frac{ka}{2}} \right)$$

Cancel common terms

$$-\omega^2 M = K \left(\alpha e^{i \frac{ka}{2}} - 2 + \alpha e^{-i \frac{ka}{2}} \right)$$

$$\omega^2 M = 2K \left(1 - \alpha \cos \frac{ka}{2} \right)$$

$$e^{ix} + e^{-ix} = 2 \cos x$$

Chain of two types of atom

For the $(n-1)^{\text{th}}$ atom (m)

$$mu_{n-1} = K(u_n - 2u_{n-1} + u_{n-2})$$

$$-\alpha A \omega^2 m e = K \left(A e^{i \left(\frac{kna}{2} - \omega t \right)} - 2\alpha A e^{i \left(\frac{k(n-1)a}{2} - \omega t \right)} + A e^{i \left(\frac{k(n-2)a}{2} - \omega t \right)} \right)$$

$$-\alpha \omega^2 m A e^{i \left(\frac{kna}{2} - \omega t \right)} e^{-i \frac{ka}{2}} = K \left(A e^{i \left(\frac{kna}{2} - \omega t \right)} - 2\alpha A e^{i \left(\frac{kna}{2} - \omega t \right)} e^{-i \frac{ka}{2}} + A e^{i \left(\frac{kna}{2} - \omega t \right)} e^{-i \frac{2ka}{2}} \right)$$

Cancel common terms

$$-\alpha \omega^2 m e^{-i \frac{ka}{2}} = K \left(1 - 2\alpha e^{-i \frac{ka}{2}} + e^{-ika} \right)$$

$$-\alpha \omega^2 m = K \left(e^{\frac{ka}{2}} - 2\alpha + e^{-\frac{ka}{2}} \right)$$

$$e^{ix} + e^{-ix} = 2 \cos x$$

$$-\alpha \omega^2 m = 2K \left(\cos \frac{ka}{2} - \alpha \right)$$

Chain of two types of atom

$$\omega^2 M = 2K \left(1 - \alpha \cos \frac{ka}{2} \right) \quad \text{for } M$$

$$\alpha \omega^2 m = K \left(\alpha - \cos \frac{ka}{2} \right) \quad \text{for } m$$

- Now we have a pair of algebraic equations for α and ω as a function of k . α can be found as
$$\alpha = \frac{2K \cos(ka/2)}{2K - \omega^2 M} = \frac{2K \cos(ka/2)}{2K - \omega^2 m}$$
- A quadratic equation for ω^2 can be obtained by cross-multiplication

Chain of two types of atom

$$\alpha = \frac{2K \cos(ka/2)}{2K - \omega^2 m} \neq \frac{2K - \omega^2 M}{2K \cos(ka/2)}$$

$$4K^2 \cos^2\left(\frac{ka}{2}\right) = 4K^2 - 2K\omega^2(M+m) + \omega^4 Mm$$

$$4K^2 \left(1 - \cos^2\left(\frac{ka}{2}\right)\right) - 2K\omega^2(m+M) + \omega^4 Mm = 0$$

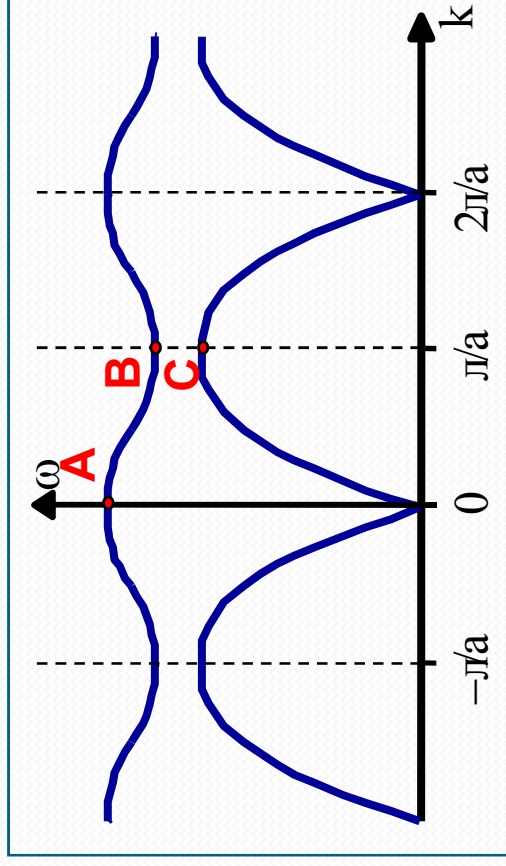
$$\omega^4 - 2K\left(\frac{m+M}{mM}\right)\omega^2 + 4K^2 \frac{\sin^2(ka/2)}{mM} = 0$$

The two roots are; $x_{1,2} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$\omega_{\mp}^2 = \frac{K(m+M)}{mM} \mp K \left[\left(\frac{m+M}{mM} \right)^2 - \frac{4 \sin^2(ka/2)}{mM} \right]^{1/2}$$

Chain of two types of atom

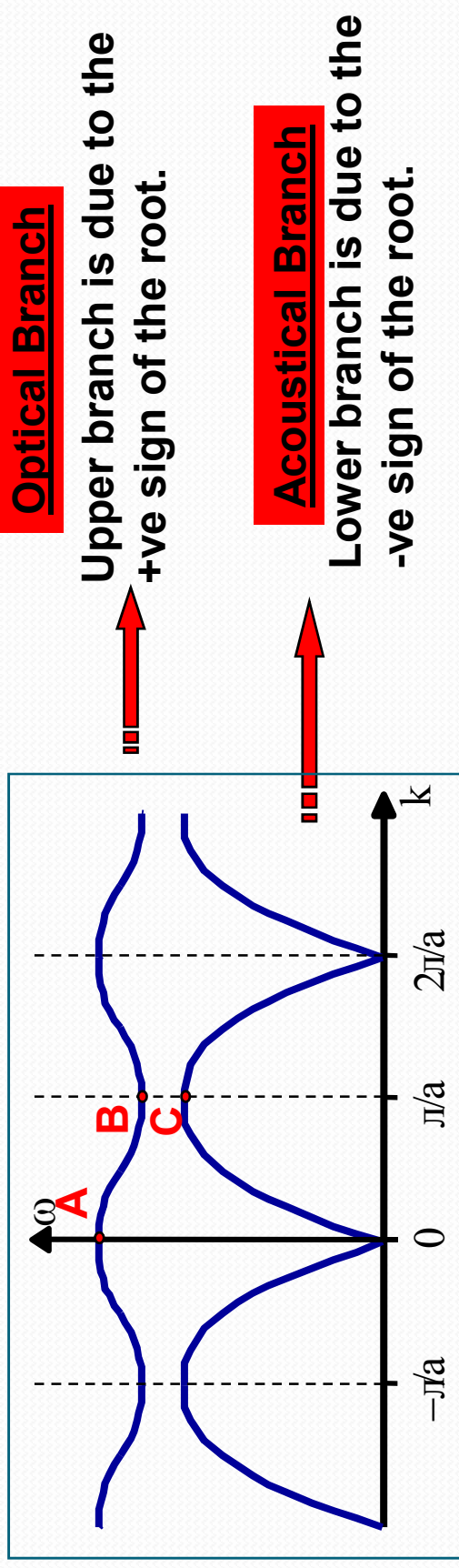
- ω versus k relation for diatomic chain;



- Normal mode frequencies of a chain of two types of atoms in the crystal contains N unit cells we would expect to find $2N$ normal modes of vibrations and this is the total number of atoms at rest.
At A, the two atoms are oscillating in antiphase with their centre of mass at rest.
At B, the lighter mass m is oscillating and M is at rest, and at C, M is oscillating and m is at rest.

Chain of two types of atom

- As there are two values of ω for each value of k , the dispersion relation is said to have two branches;



- The dispersion relation is periodic in k with a period $2\pi/a$.
- This result remains valid for a chain of containing an arbitrary number of atoms per unit cell.

Chain of two types of atom

- Let's examine the limiting solutions at 0, A, B and C.
- In long wavelength region ($ka \ll 1$); $\sin(ka/2) \approx ka/2$ in ω - k .

$$\omega_{1,2}^2 = \frac{K(m+M)}{mM} \mp K \left[\left(\frac{m+M}{mM} \right)^2 - \frac{4 \sin^2(ka/2)}{mM} \right]^{1/2}$$

$$\omega^2 \approx \frac{K(m+M)}{mM} \pm K \left[\left(\frac{m+M}{mM} \right)^2 - \frac{4k^2 a^2}{mM} \right]^{1/2}$$

$$= \frac{K(m+M)}{mM} \left[1 \pm \left(1 - \frac{mM}{(m+M)^2} k^2 a^2 \right)^{1/2} \right]$$

Use Taylor expansion: $(1-x)^{1/2} \approx 1-x/2$ for small x

$$\omega^2 \approx \frac{K(m+M)}{mM} \left[1 \pm \left(1 - \frac{mM}{2(m+M)^2} k^2 a^2 \right) \right]$$

Chain of two types of atom

Taking +ve root; $\sin ka \ll 1$ (max value of optical branch)

$$\omega_{\max opt}^2 \approx \frac{2K(m+M)}{mM}$$

Taking -ve root; (min value of acoustical branch)

$$\omega_{\min acus.}^2 \approx \frac{K(m+M)}{mM} \left[\frac{mMk^2 a^2}{2(m+M)^2} \right] \approx \frac{Kk^2 a^2}{2(m+M)}$$

By substituting these values of ω in α (relative amplitude) equation and using $\cos(ka/2) \approx 1$ for $ka \ll 1$ we find the corresponding values of α as;

$$\alpha = \frac{2K - \omega^2 M}{2K \cos(ka/2)}$$

$$\alpha \approx 1 \quad \text{OR} \quad \alpha \approx -\frac{M}{m}$$

Chain of two types of atom

Substitute

$$\omega_{\text{min ac}}^2$$

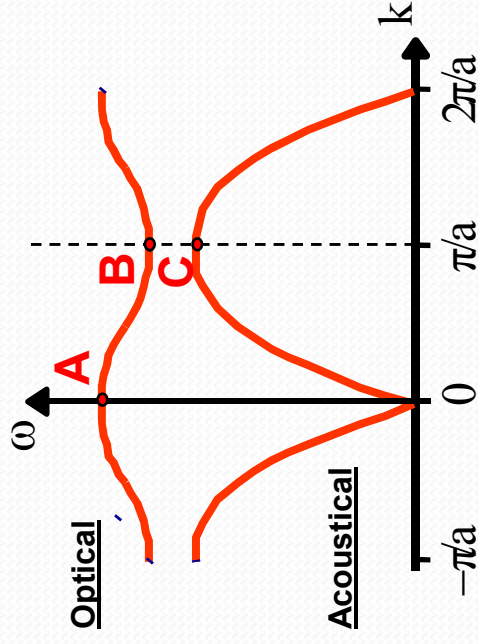
into relative amplitude α

$$\omega_{\text{min ac}}^2 \approx \frac{K(k^2 a^2)}{2(m+M)}$$

$$\alpha = \frac{2K - \omega^2 M}{2K \cos(ka/2)}$$

$$\alpha \approx 1$$

This solution represents long-wavelength sound waves in the neighborhood of point 0 in the graph; the two types of atoms oscillate with same amplitude and phase, and the velocity of sound is



$$v_s = \frac{\omega}{k} = a \left(\frac{K}{2(m+M)} \right)^{1/2}$$

Chain of two types of atom

Substitute

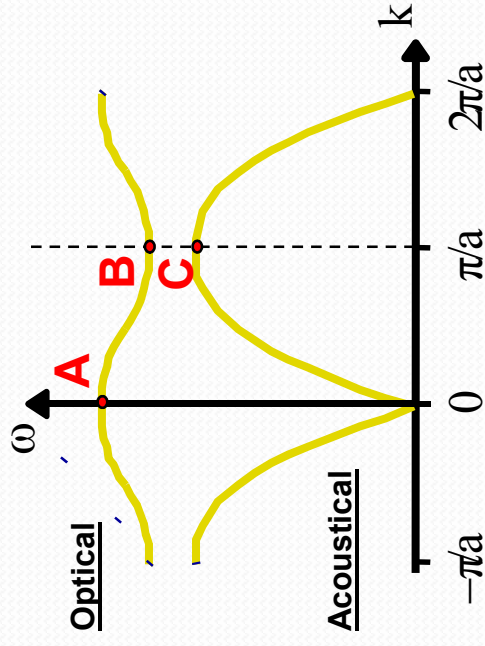
$$\omega_{\max_{\text{op}}}^2$$

into relative amplitude we obtain,

$$\omega_{\max_{\text{op}}}^2 \approx \frac{2K(m+M)}{mM}$$

$$\alpha = \frac{2K - \omega^2 M}{2K \cos(ka/2)}$$

$$\alpha \approx -\frac{M}{m}$$



This solution corresponds to point A in dispersion graph. This value of α shows that the two atoms oscillate in antiphase with their center of mass at rest.

Chain of two types of atom

- The other limiting solutions of equation ω^2 are for $ka = \pi$,
i.e. $\sin(ka/2) = 1$. In this case

$$\omega_{\max_{ac}}^2 = \frac{K(m+M)}{Mm} \mp K \left[\left(\frac{M+m}{Mm} \right)^2 - \frac{4}{Mm} \right]^{1/2}$$

$$= \frac{K(m+M) \mp K(M-m)}{Mm}$$

$$\omega_{\max_{ac}}^2 = \frac{2K}{M} \quad \text{(C)}$$

OR

$$\omega_{\min_{op}}^2 = \frac{2K}{m} \quad \text{(B)}$$

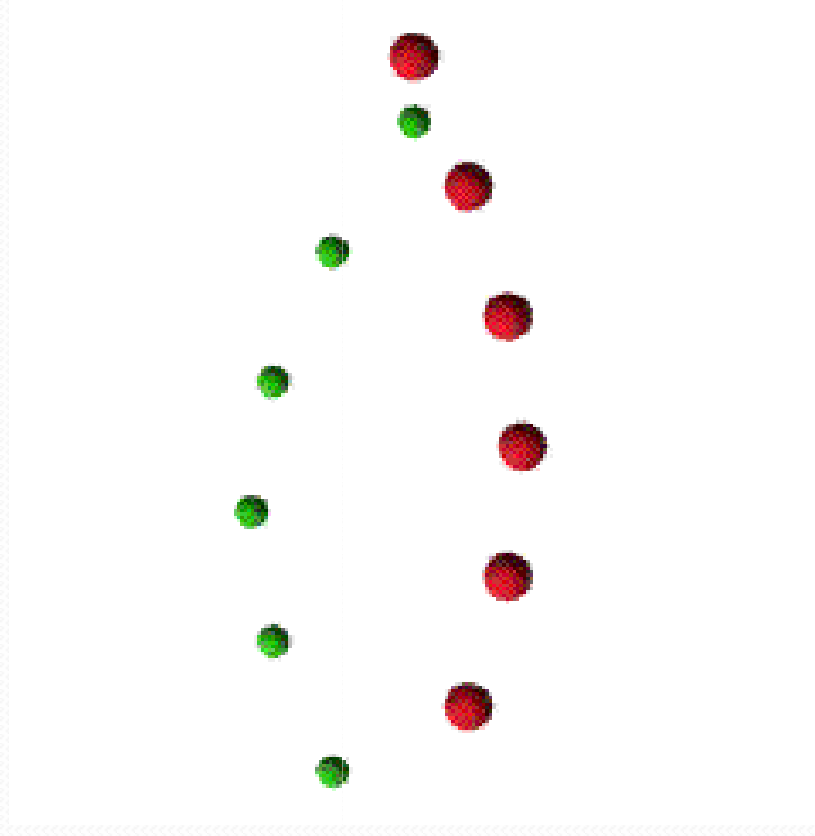
- At max.acoustical point C, M oscillates and m is at rest.
- At min.optical point B, m oscillates and M is at rest.



Acoustic/Optical Branches

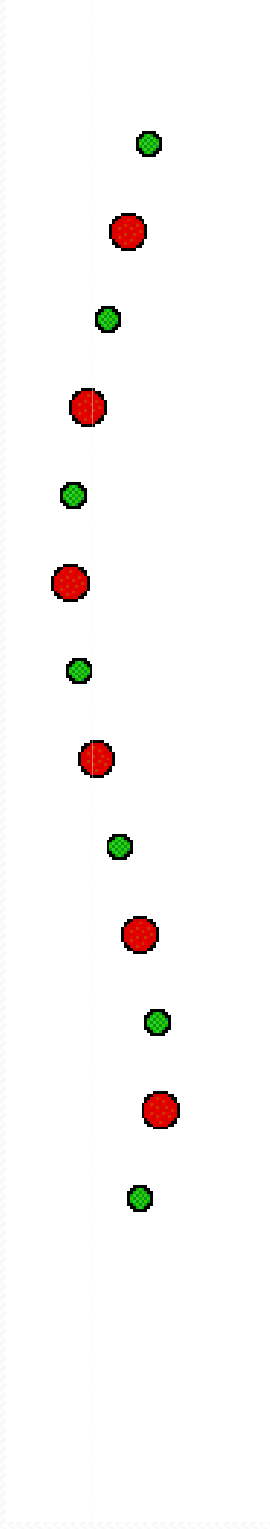
- The acoustic branch has this name because it gives rise to long wavelength vibrations - speed of sound.
- The optical branch is a higher energy vibration (the frequency is higher, and you need a certain amount of energy to excite this mode). The term “optical” comes from how these were discovered - notice that if atom 1 is +ve and atom 2 is -ve, that the charges are moving in opposite directions. You can excite these modes with electromagnetic radiation (ie. The oscillating electric fields generated by EM radiation)

Transverse optical mode for diatomic chain



Amplitude of vibration is strongly exaggerated!

Transverse acoustical mode for diatomic chain



What is phonon?

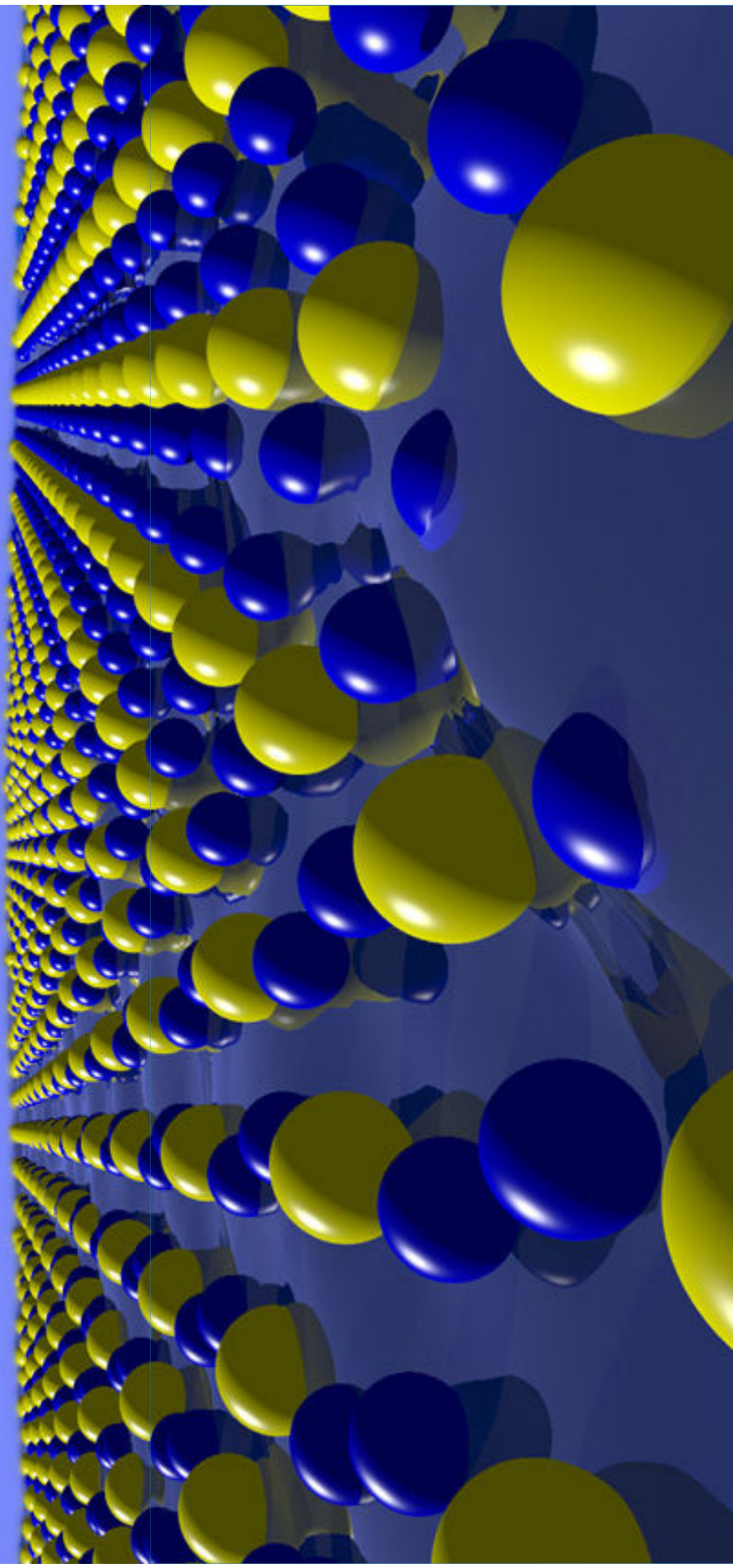
- Consider the regular lattice of atoms in a uniform solid material.
- There should be energy associated with the vibrations of these atoms.
- But they are tied together with bonds, so they can't vibrate independently.
- The vibrations take the form of collective modes which propagate through the material.
- Such propagating lattice vibrations can be considered to be sound waves.
- And their propagation speed is the **speed of sound** in the material.

Phonon

- The vibrational energies of molecules are quantized and treated as **quantum harmonic oscillators**.
- Quantum harmonic oscillators have equally spaced energy levels with separation $\Delta E = h\nu$.
- So the oscillators can accept or lose energy only in discrete units of energy $h\nu$.
- The evidence on the behaviour of vibrational energy in periodic solids is that the collective vibrational modes can accept energy only in discrete amounts, and these quanta of energy have been labelled "phonons".
- Like the photons of electromagnetic energy, they obey **Bose-Einstein statistics**.

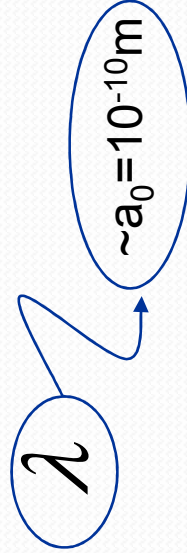
CHAPTER 4

CRYSTAL DYNAMICS II



PHONONS

- Quanta of lattice vibrations
- Energies of phonons are quantized

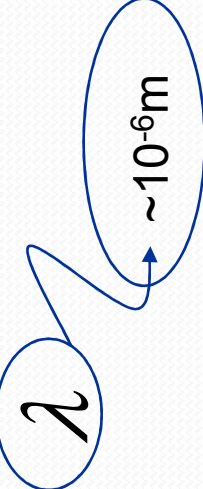
$$E_{phonon} = \frac{h v_s}{\lambda}$$


$\sim a_0 = 10^{-10} \text{m}$

$$P_{phonon} = \frac{h}{\lambda}$$

PHOTONS

- Quanta of electromagnetic radiation
- Energies of photons are quantized as well

$$E_{photon} = \frac{hc}{\lambda}$$


$\sim 10^{-6} \text{m}$

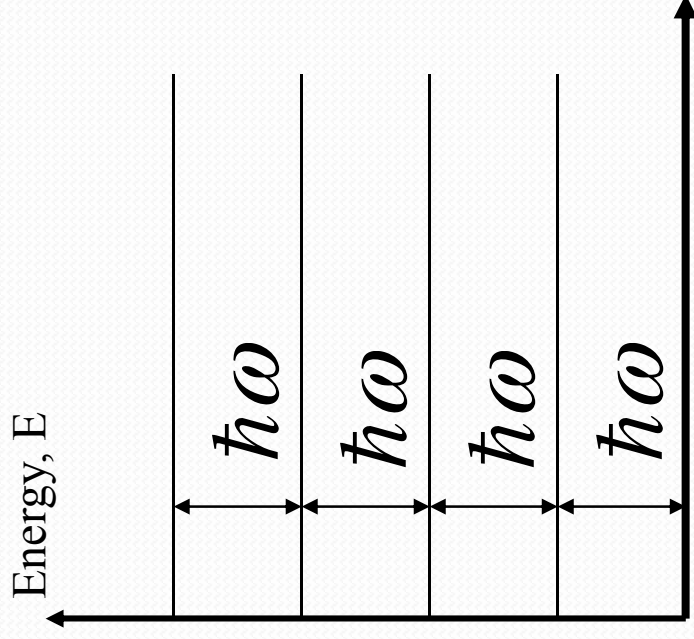
$$P_{photon} = \frac{h}{\lambda}$$

Energy of harmonic oscillator

Obtained by in a classical way of considering the normal modes that we have found are independent and harmonic.

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

- Make a transition to Q.M.
- Represents equally spaced energy levels



Energy levels of atoms vibrating at a single frequency ω

It is possible to consider ε_n as constructed by adding n excitation quanta each of energy $\hbar\omega$ to the ground state.

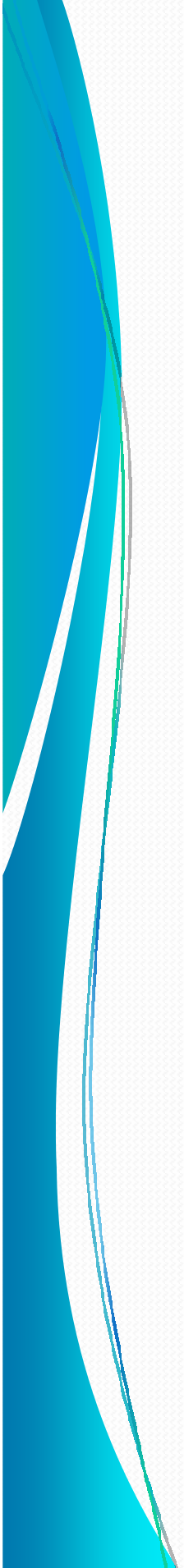
$$\varepsilon_0 = \frac{1}{2} \hbar\omega$$

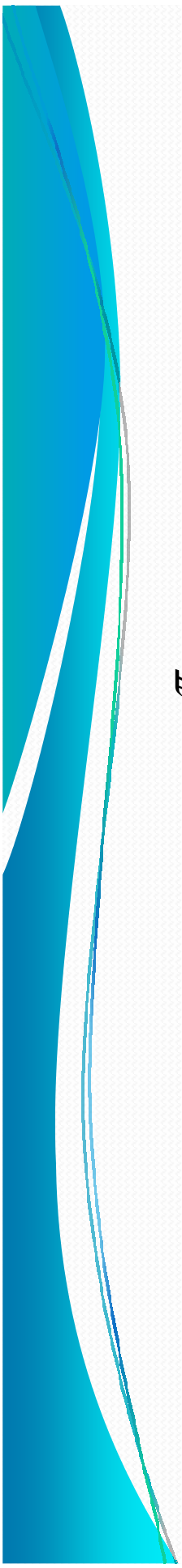
A transition from a lower energy level to a higher energy level.

$$\Delta\varepsilon = \left(n_2 + \frac{1}{2} \right) \hbar\omega - \left(n_1 + \frac{1}{2} \right) \hbar\omega$$

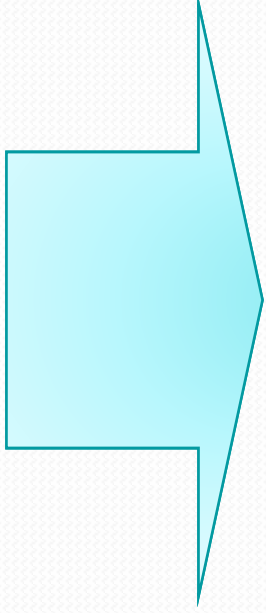
$$\Delta\varepsilon = \underbrace{(n_2 - n_1)}_{\text{unity}} \hbar\omega \Rightarrow \Delta\varepsilon = \hbar\omega$$

absorption of phonon

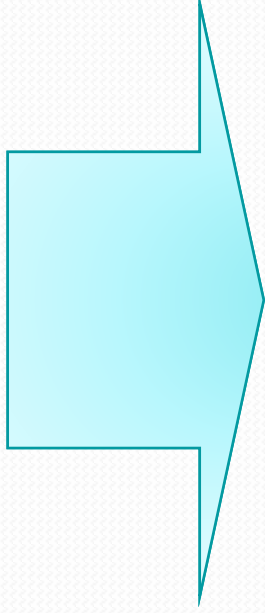
- 
- The converse transition results an emission of phonon with an energy $\hbar\omega$.
 - Phonons are quanta of lattice vibrations with an angular frequency of ω .
 - Phonons are not localized particles.
 - Its momentum is exact, but position can not be determined because of the uncertainty principle.
 - However, a slightly localized wavepacket can be considered by combining modes of slightly different λ and ω .



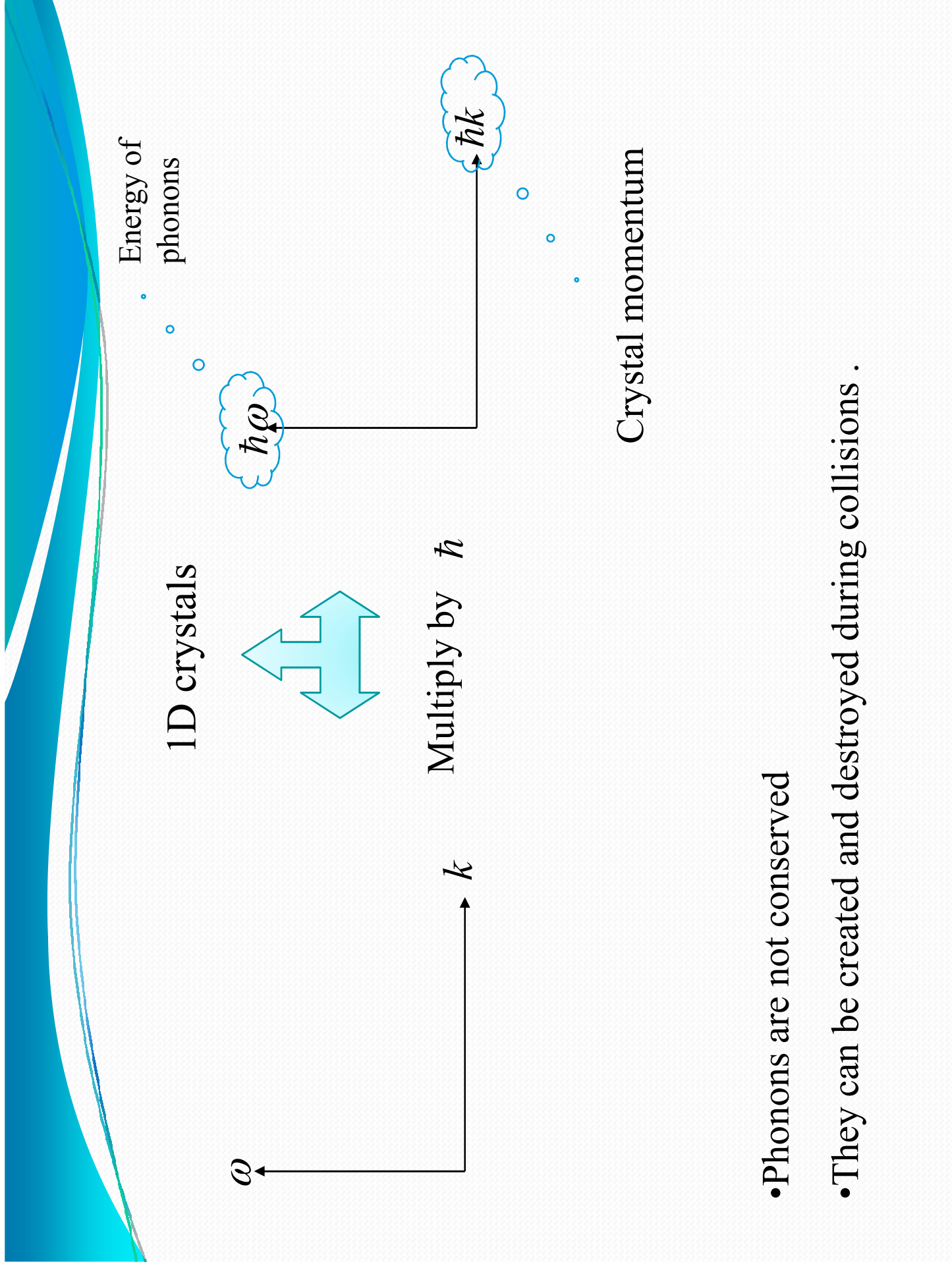
Assume waves with a spread of k of $\frac{\pi}{10a}$; so this wavepacket will be localized within 10 unit cells.



This wavepacket will represent a fairly localized phonon moving with group velocity $\frac{d\omega}{dk}$.

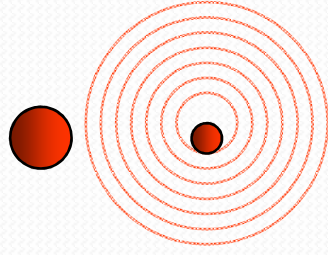


Phonons can be treated as *localized particles* within some limits.

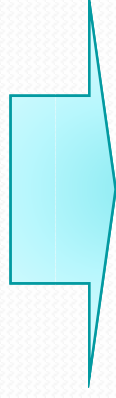


- Phonons are not conserved
- They can be created and destroyed during collisions .

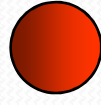
Thermal energy and lattice vibrations



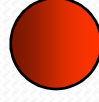
- Atoms vibrate about their equilibrium position.
- They produce vibrational waves.
- This motion is increased as the temperature is raised.

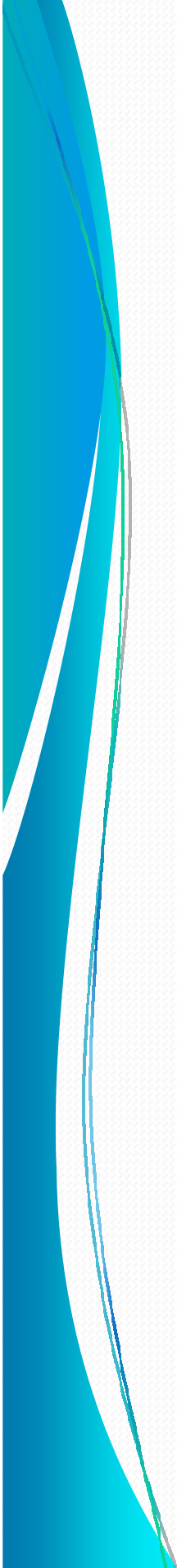


In a solid, the energy associated with this **vibration** and perhaps also with the **rotation** of atoms and molecules is called as **thermal energy**.



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





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 1 gmole 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. In non-magnetic insulators, it is the only contribution.

Other contributions;

- In metals → from the conduction electrons.
- In magnetic materials → from magnetizing 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

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

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

Energy of oscillator

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

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

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

$$\bar{\mathcal{E}} = \sum_n P_n \mathcal{E}_n$$

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

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

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

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

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

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

Eqn (*) can be written

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

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

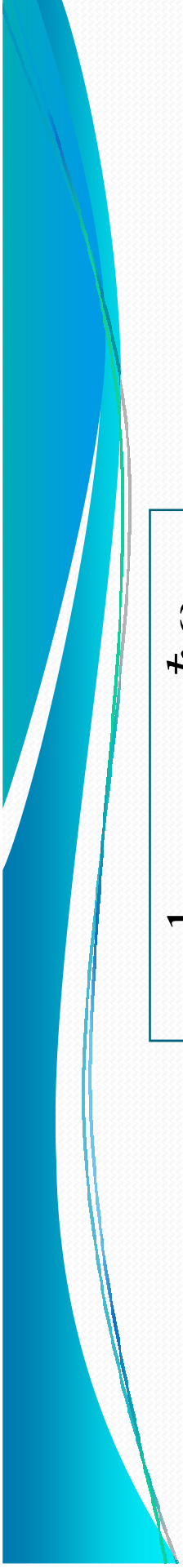
$$\bar{\varepsilon} = k_B T^2 \frac{\partial}{\partial T} \left[\ln e^{-\hbar\omega/2k_B T} - \ln(1 - e^{-\hbar\omega/k_B T}) \right]$$

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

$$\frac{\partial}{\partial x} (\ln x) = \frac{1}{x}$$

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

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


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

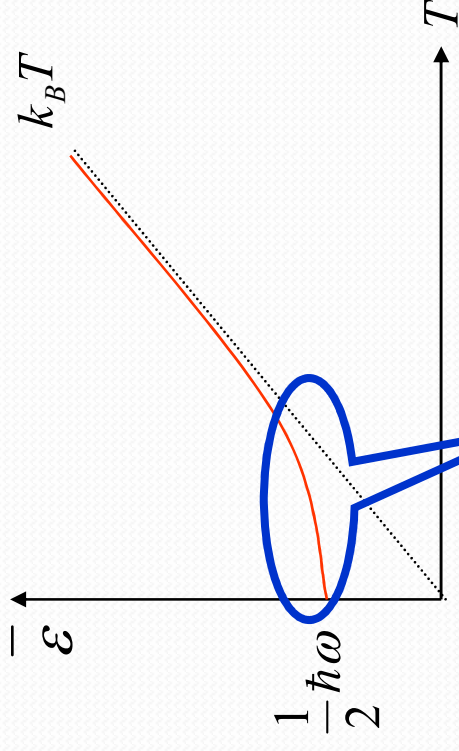
This is the mean energy of phonons. The first term in the above equation is the zero-point energy. As we have mentioned before even at 0°K atoms vibrate in the crystal and have zero-point energy. This is the minimum energy of the system.

The average number of phonons is given by Bose-Einstein distribution as

(number of phonons) x (energy of phonon) = (second term in $\bar{\varepsilon}$)

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

The second term in the mean energy is the contribution of phonons to the energy.



Mean energy of a harmonic oscillator as a function of T

low temperature limit

$$\hbar\omega \gg k_B T$$

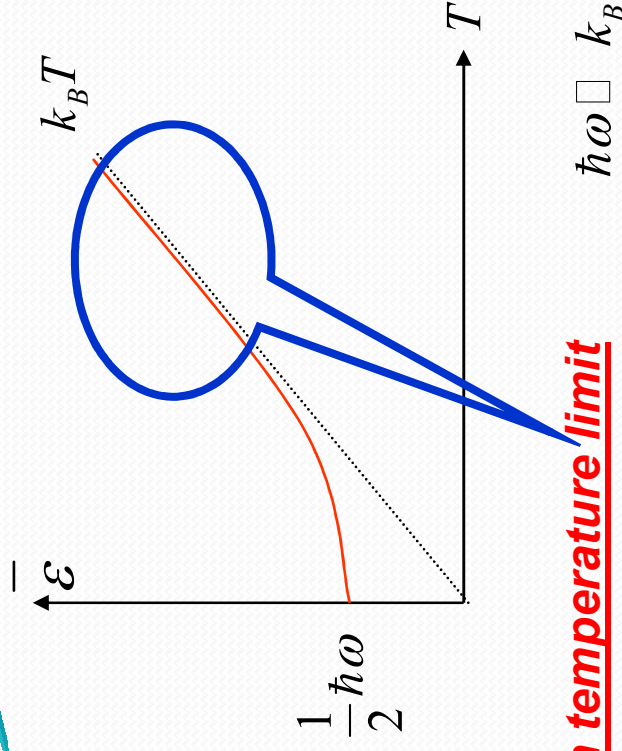
$$\bar{\varepsilon} = \frac{1}{2} \hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

Since exponential term gets bigger

$$\bar{\varepsilon} \approx \frac{1}{2} \hbar\omega$$

Zero point energy





Mean energy of a harmonic oscillator as a function of T

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

$$e^{\frac{\hbar\omega}{k_B T}} = 1 + \frac{\hbar\omega}{k_B T}$$

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

$$\bar{\varepsilon} = \frac{1}{2} \hbar\omega + k_B T$$



$$\bar{\varepsilon} \approx k_B T$$

- $\bar{\varepsilon}$ is independent of frequency of oscillation.
- This is the classical limit because the energy steps are now small compared with the energy of the harmonic oscillator.
- So that $k_B T$ is the thermal energy of the classical 1D harmonic oscillator.

Heat Capacity C

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

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

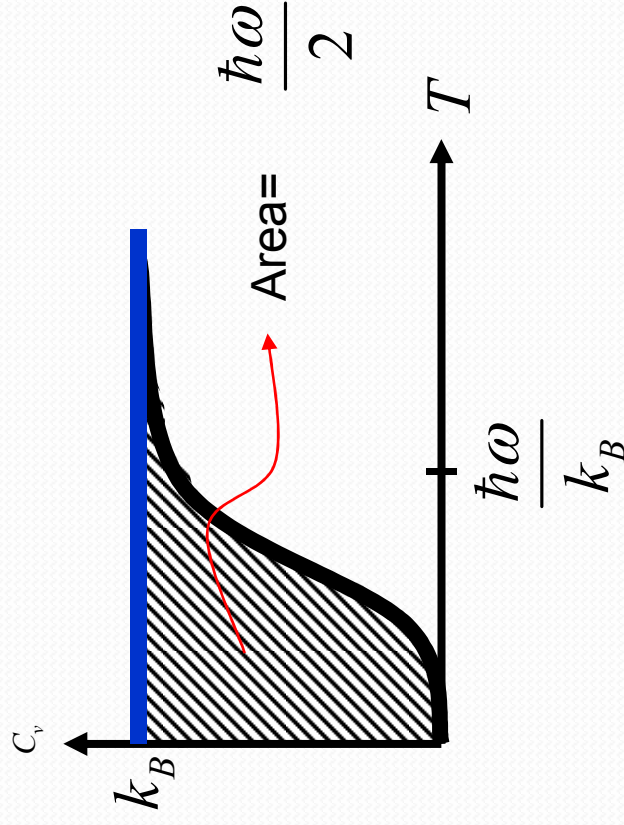
$$C_v = \frac{d\bar{\varepsilon}}{dT} = \frac{-\hbar \omega \frac{-\hbar \omega k_B}{(k_B T)^2} e^{\hbar \omega / k_B T}}{\left(e^{\hbar \omega / k_B T} - 1 \right)^2} \quad \longrightarrow \quad C_v = k_B \frac{(\hbar \omega)^2}{(k_B T)^2} \frac{e^{\hbar \omega / k_B T}}{\left(e^{\hbar \omega / k_B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

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

Plot of C_v as a function of T

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

where $\theta = \frac{\hbar\omega}{k}$

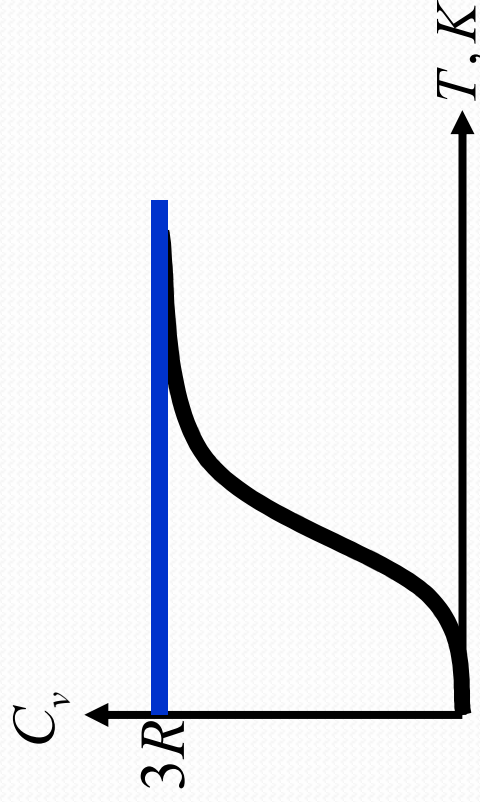


Specific heat vanishes exponentially at low T 's and tends to classical value at high temperatures.

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.

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 average energy per atom, regarded as a 3D oscillator, is $3kT$, and consequently the energy per mole is

$$\bar{\mathcal{E}} = 3Nk_B T = 3RT$$

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

$$C_v = \frac{d\bar{\mathcal{E}}}{dT} \quad \rightarrow \quad C_v = 3R = 3 \times 6.02 \times 10^{23} \text{ (atoms/mole)} \times 1.38 \times 10^{-23} \text{ (J/K)}$$

$$C_v = 24.9 \frac{J}{(K - mole)}; 1J = 0.23888 \text{ Cal} \Rightarrow C_v \approx 6 \frac{\text{Cal}}{(K - mole)}$$

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

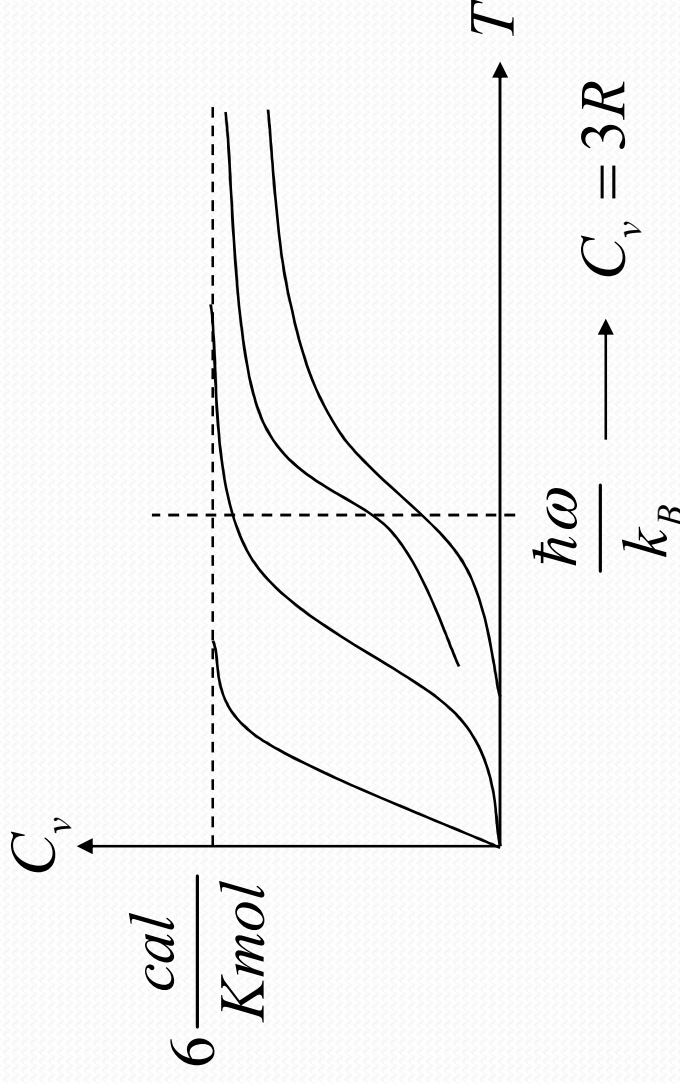
$$3Nk_B = 3R$$

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.



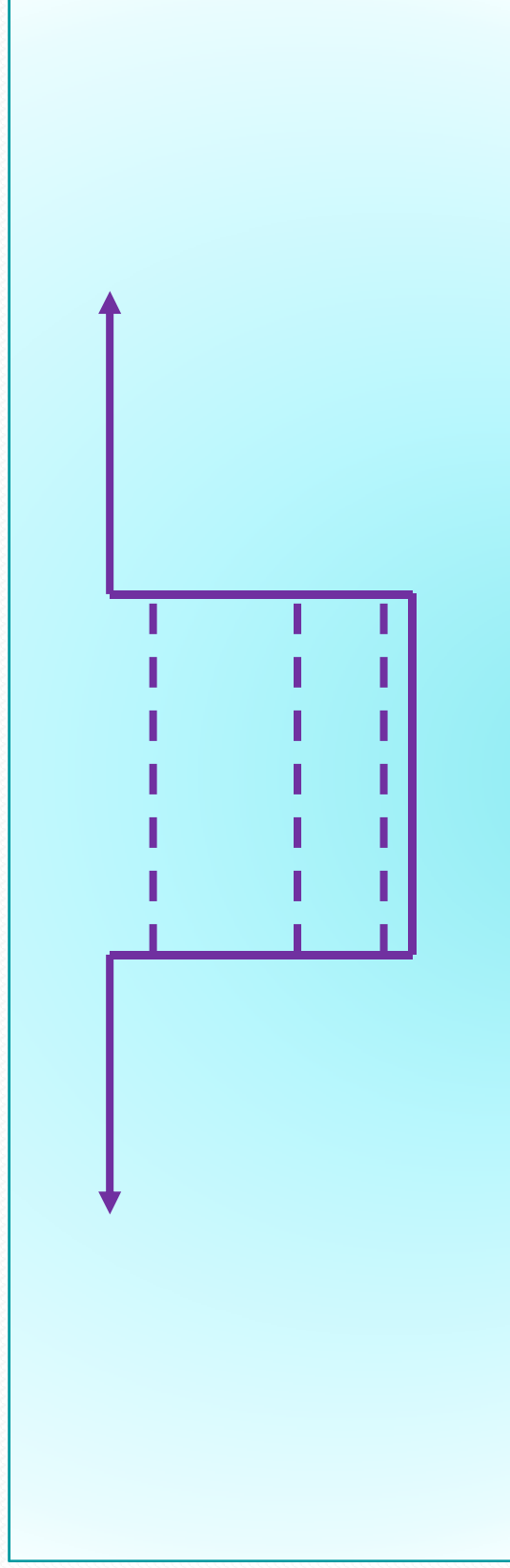
The Discrepancy of Einstein model

- 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

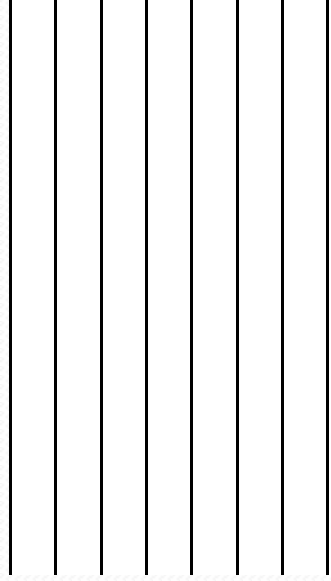
Density of States

According to Quantum Mechanics if a particle is constrained;

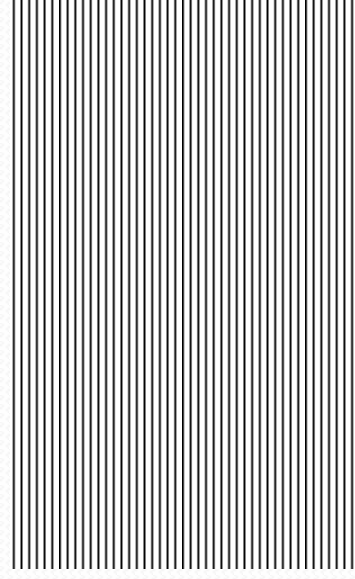
- the energy of particle can only have special discrete energy values.
- it cannot increase infinitely from one value to another.
- it has to go up in steps.



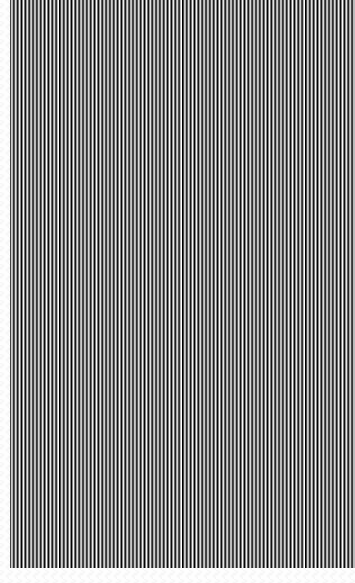
- These steps can be so small depending on the system that the energy can be considered as continuous.
- This is the case of classical mechanics.
- But on atomic scale the energy can only jump by a discrete amount from one value to another.



Definite energy levels



Steps get small



Energy is continuous

- In some cases, each particular energy level can be associated with more than one different state (or wavefunction)
- This energy level is said to be degenerate.

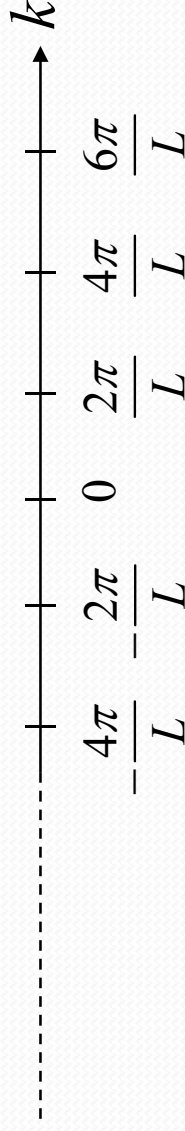


- The density of states $\rho(\varepsilon)$ is the **number of discrete states per unit energy interval**, and so that the number of states between ε and $\varepsilon + d\varepsilon$ will be $\rho(\varepsilon)d\varepsilon$.

There are two sets of waves for solution;

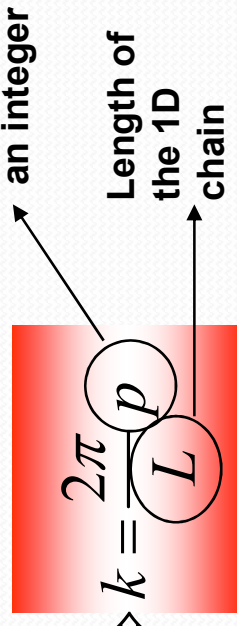
- Running waves
- Standing waves

Running waves:



These allowed k wavenumbers corresponds to the running waves; all positive and negative values of k are allowed. By means of **periodic boundary condition**

$$L = Na = p\lambda \Rightarrow \lambda = \frac{Na}{p} = \frac{2\pi}{k} \Rightarrow k = \frac{2\pi}{Na} p$$

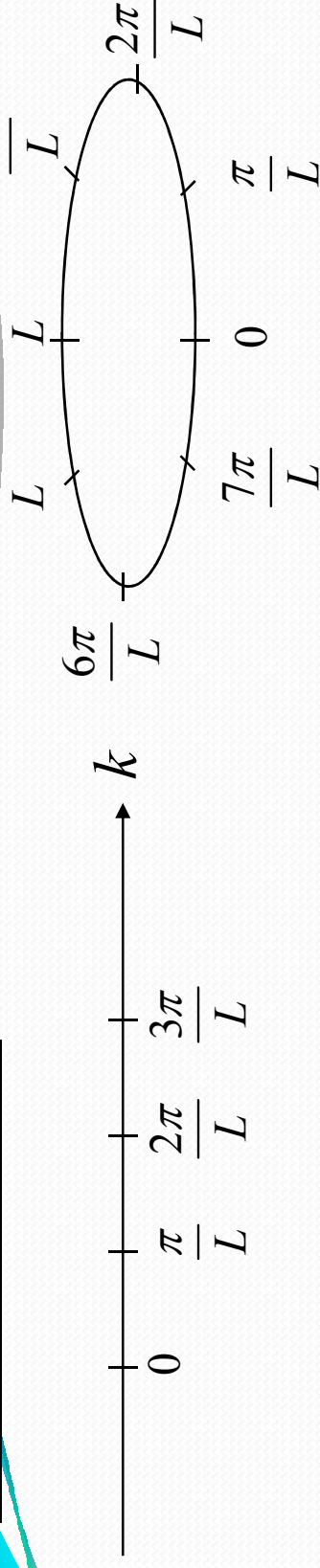


These allowed wavenumbers are uniformly distributed in k at a density of $\rho_R(k)$ between k and k+dk.

running waves

$$\rho_R(k) dk = \frac{L}{2\pi} dk$$

Standing waves:



In some cases it is more suitable to use standing waves, i.e. chain with fixed ends. Therefore we will have an integral number of half wavelngths in the chain;

$$L = \frac{n\lambda}{2}; k = \frac{2\pi}{\lambda} \Rightarrow k = \frac{2\pi n}{2L} \Rightarrow k = \frac{n\pi}{L}$$

These are the allowed wavenumbers for standing waves; only positive values are allowed.

$$k = \frac{2\pi}{L} p \longrightarrow \text{for running waves} \quad k = \frac{\pi}{L} p \longrightarrow \text{for standing waves}$$

These allowed k 's are uniformly distributed between k and $k+dk$

at a density of $\rho_S(k)$

$$\rho_S(k)dk = \frac{L}{\pi} dk$$



DOS of standing wave

$$\rho_R(k)dk = \frac{L}{2\pi} dk$$



DOS of running wave

- The *density of standing wave states is twice that of the running waves.*
- However in the case of standing waves only **positive** values are allowed
- Then the total number of states for **both running and standing waves** **will be the same** in a range dk of the magnitude k
- The **standing waves** have the same dispersion relation as **running waves**, and for a chain containing N atoms there are exactly N distinct states with k values in the range 0 to π/a .



The density of states per unit frequency range $g(\omega)$:

- The number of modes with frequencies ω and $\omega+d\omega$ will be $g(\omega)d\omega$.
- $g(\omega)$ can be written in terms of $\rho_S(k)$ and $\rho_R(k)$.

dR modes with frequency from ω to $\omega+d\omega$ corresponds

dn modes with wavenumber from k to $k+dk$

$$dn = \rho_s(k)dk = g(\omega)d\omega$$

$$dn = \rho_s(k)dk = g(\omega)d\omega$$

Choose standing waves to obtain $g(\omega)$

$$g(\omega) = \rho_s(k) \frac{dk}{d\omega}$$

Let's remember dispersion relation for 1D monoatomic lattice

$$\omega^2 = \frac{4K}{m} \sin^2 \frac{ka}{2}$$

$$\omega = 2\sqrt{\frac{K}{m}} \sin \frac{ka}{2}$$

$$\frac{d\omega}{dk} = \frac{2a\sqrt{K}}{2\sqrt{m}} \frac{ka \cos \frac{ka}{2}}{2}$$

$$g(\omega) = \rho_s(k) \frac{1}{a\sqrt{\frac{K}{m}}} \frac{1}{\cos \left(\frac{ka}{2} \right)}$$

$$g(\omega) = \rho_S(k) \frac{1}{a} \sqrt{\frac{m}{K \cos(ka/2)}}$$

$$\sin^2 x + \cos^2 x = 1 \Rightarrow \cos x = \sqrt{1 - \sin^2 x} \quad \longrightarrow \quad \cos\left(\frac{ka}{2}\right) = \sqrt{1 - \sin^2\left(\frac{ka}{2}\right)}$$

$$g(\omega) = \rho_S(k) \frac{1}{a} \sqrt{\frac{m}{K}} \frac{\sqrt{4}}{\sqrt{1 - \sin^2\left(\frac{ka}{2}\right)}} \frac{\sqrt{4}}{\sqrt{4}}$$

Multiply and divide

$$g(\omega) = \rho_S(k) \frac{1}{a} \sqrt{\frac{m}{K}} \frac{2}{\sqrt{\frac{4K}{m} - \frac{4K}{m} \sin^2\left(\frac{ka}{2}\right)}}$$

$$g(\omega) = \frac{2}{\pi a} \left(\frac{m}{K} \right)^{-1/2} \frac{1}{\sqrt{\omega_{\max}^2 - \omega^2}}$$

True density of states

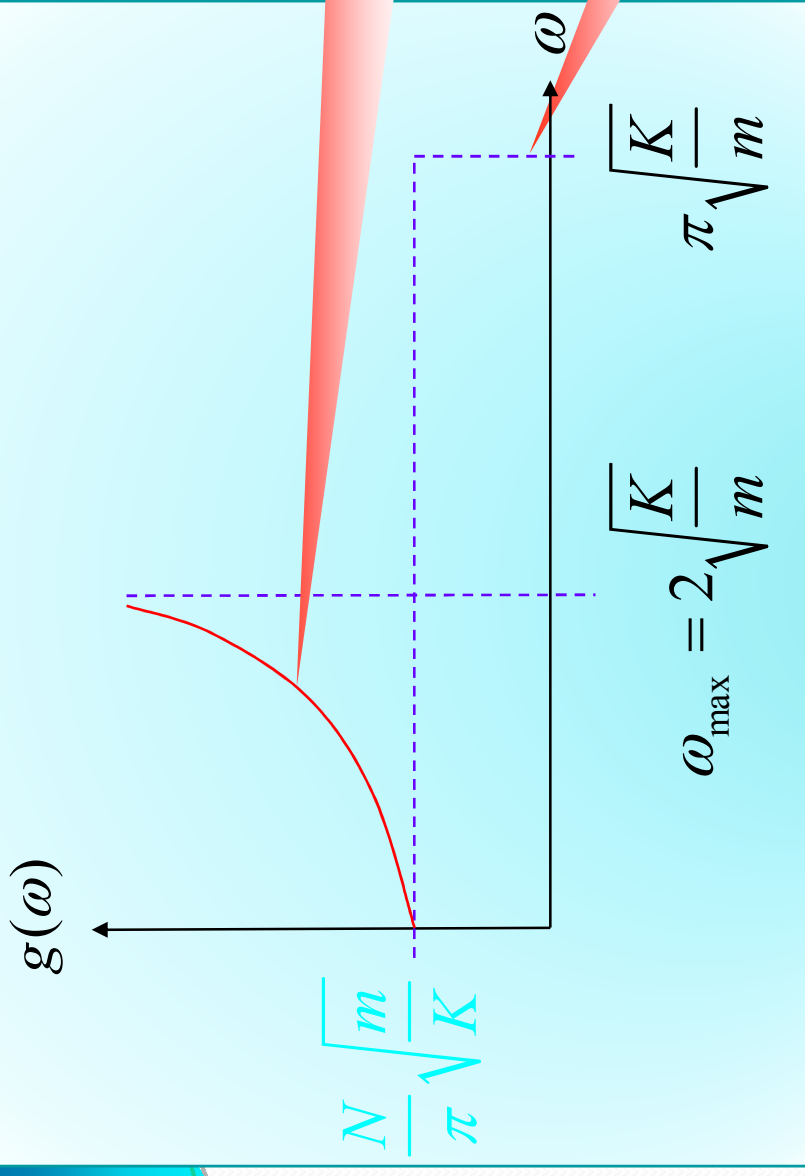
Let's remember:

$$\rho_S(k) dk = \frac{L}{\pi} dk$$

$$L = Na$$

$$\omega^2 = \frac{4K}{m} \sin^2\left(\frac{ka}{2}\right)$$

$$\omega_{\max}^2 = \frac{4K}{m}$$



$$g(\omega) = \frac{2N}{\pi} (\omega_{\max}^2 - \omega^2)^{-1/2}$$

True density of states by means of above equation

constant density of states

True DOS (density of states) tends to infinity at $\omega_{\max} = 2\sqrt{\frac{K}{m}}$

since the group velocity $d\omega/dk$ goes to zero at this value of ω .

Constant density of states can be obtained by ignoring the dispersion of sound at wavelengths comparable to atomic spacing.

The energy of lattice vibrations will then be found by integrating the energy of single oscillator over the distribution of vibration frequencies. Thus

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

Mean energy of a harmonic oscillator

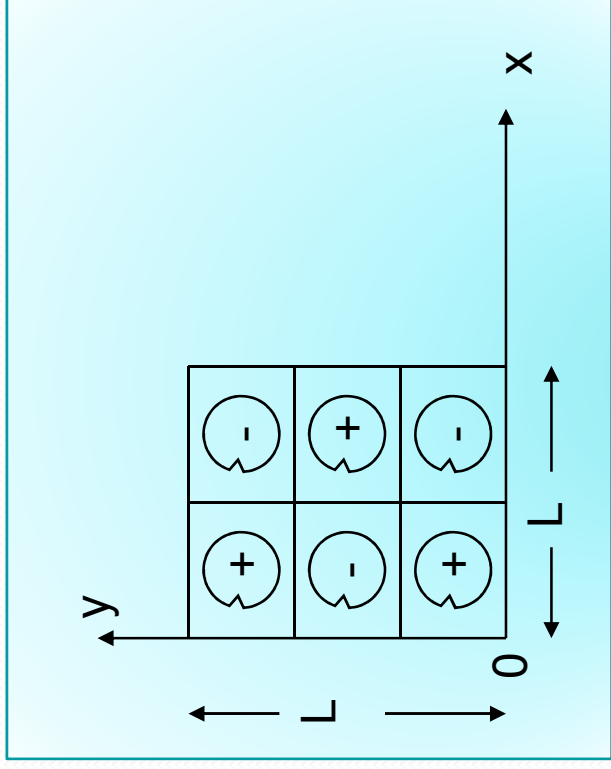
$$\frac{2N}{\pi} \left(\omega_{\max}^2 - \omega^2 \right)^{-1/2} \text{ for 1D}$$

One can obtain same expression of $g(\omega)$ by means of using running waves.

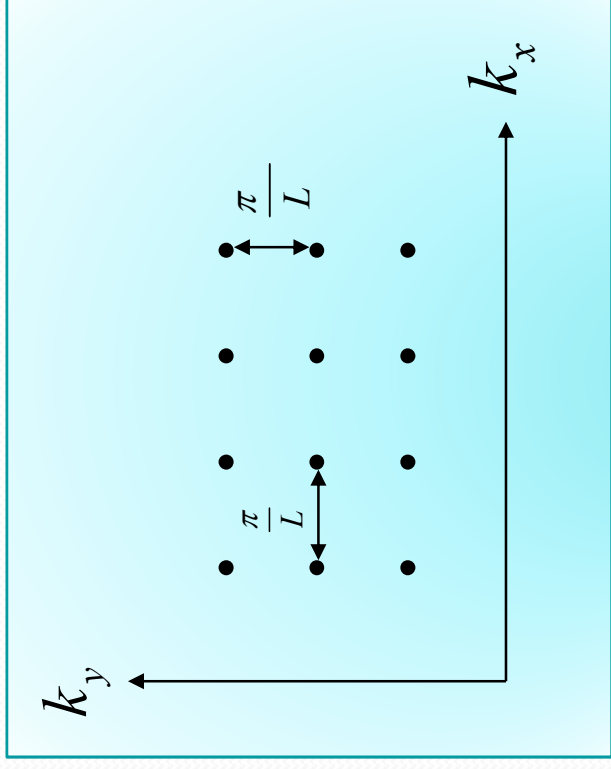
It should be better to find 3D DOS in order to compare the results with experiment.

3D DOS

- Let's do it first for 2D
- Then for 3D.
- Consider a crystal in the shape of 2D box with crystal lengths of L .



Standing wave pattern for a
2D box



Configuration in k -space

• Let's calculate the number of modes within a range of wavevector k .

• Standing waves are chosen but running waves will lead same expressions.

• Standing waves will be of the form

$$U = U_0 \sin(k_x x) \sin(k_y y)$$

• Assuming the boundary conditions of

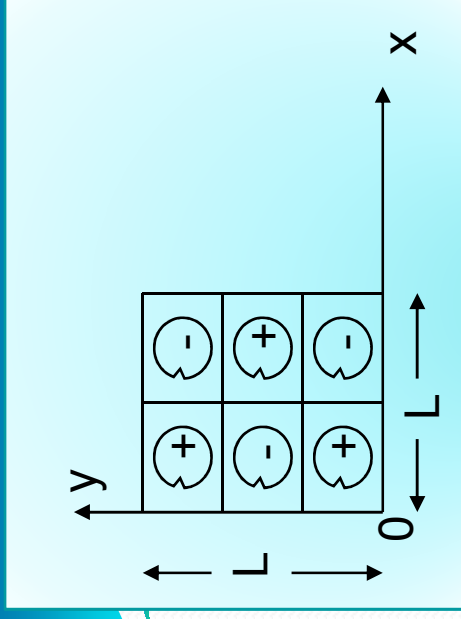
• Vibration amplitude should vanish at edges of

$$x = 0; y = 0; x = L; y = L$$

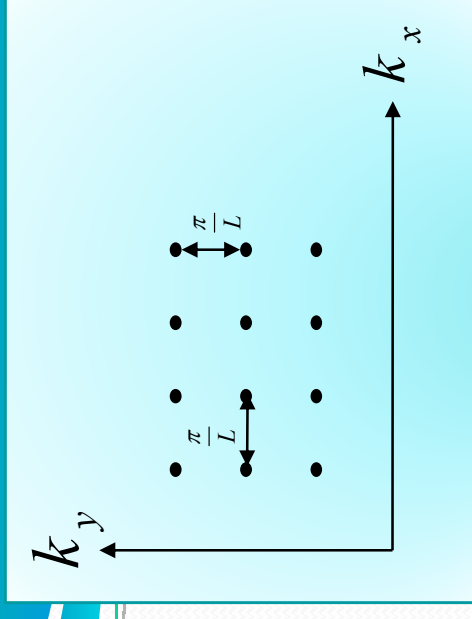
Choosing

$$k_x = \frac{p\pi}{L}; k_y = \frac{q\pi}{L}$$

positive integer



Standing wave pattern for a 2D box



Configuration in k -space

- The allowed k values lie on a square lattice of side π / L in the positive quadrant of k -space.
- These values will so be distributed uniformly with a density of $(L / \pi)^2$ per unit area.
- This result can be extended to 3D.

Octant of the crystal:

k_x, k_y, k_z (all have positive values)

The number of standing waves;

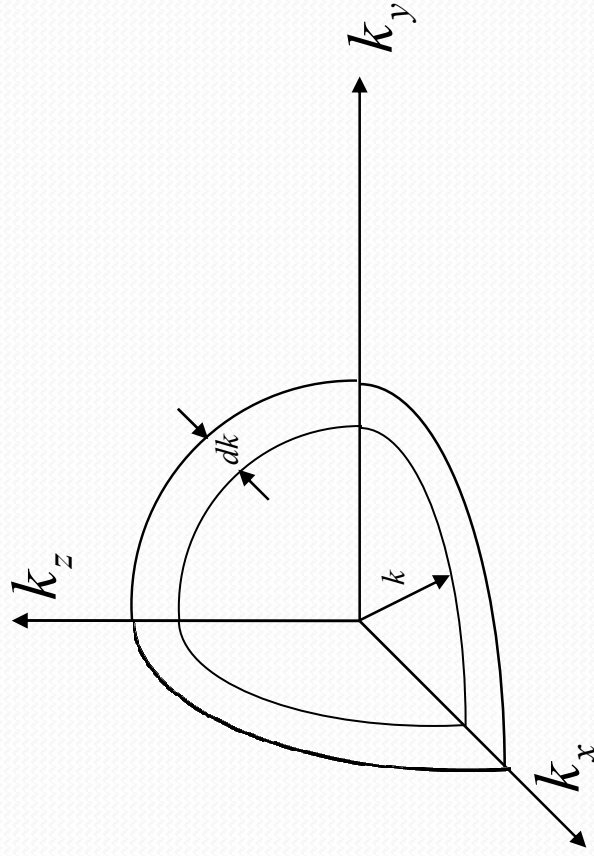
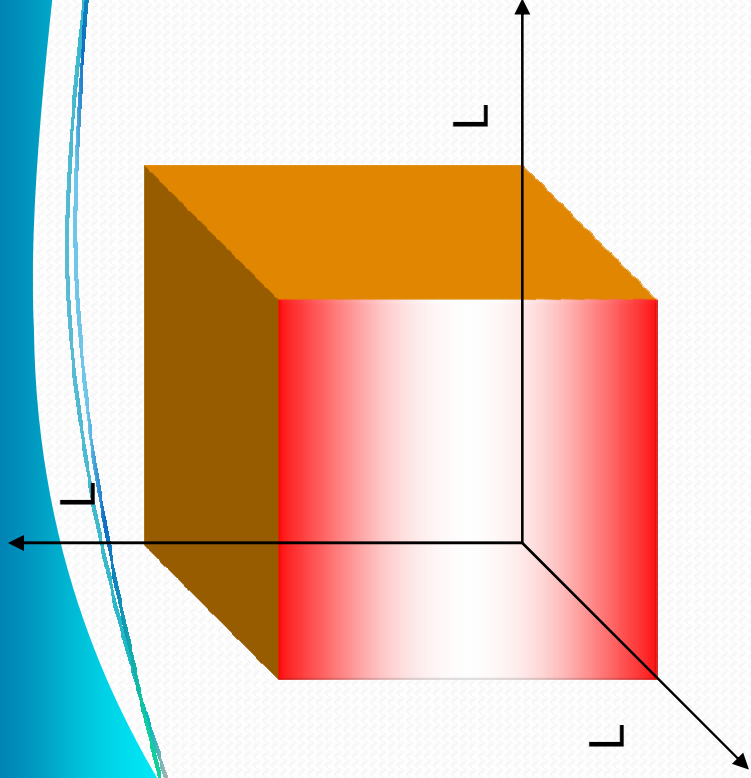
$$\rho_s(k) d^3k = \left(\frac{L}{\pi}\right)^3 d^3k = \frac{V}{\pi^3} d^3k$$

$$\frac{1}{8} \times 4\pi k^2 dk$$

$$\rho_s(k) d^3k = \frac{V}{\pi^3} \times 4\pi k^2 dk$$

$$\rho_s(k) d^3k = \frac{Vk^2}{2\pi^2} dk$$

$$\rho_s(k) = \frac{Vk^2}{2\pi^2}$$



- 
- $\rho(k) = \frac{Vk^2}{2\pi^2}$ is a new density of states defined as the

number of states per unit magnitude of k in 3D. This eqn

can be obtained by using running waves as well.

- ω (frequency) space can be related to k -space:

$$g(\omega)d\omega = \rho(k)dk \qquad g(\omega) = \rho(k)\frac{dk}{d\omega}$$

Let's find C at low and high temperature by means of

using the expression of $g(\omega)$.

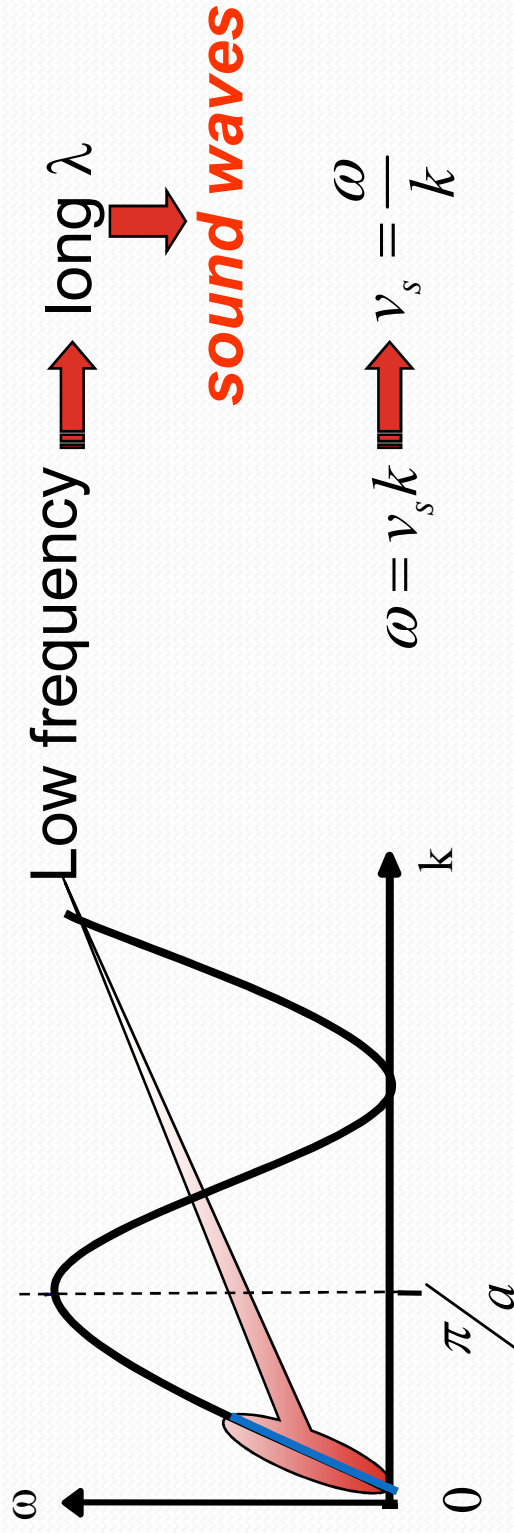
High and Low Temperature Limits

Each of the $3N$ lattice modes of a crystal containing N atoms

$$\bar{\varepsilon} = 3Nk_B T \quad \longleftrightarrow \quad C = \frac{d\bar{\varepsilon}}{dT} \quad \longleftrightarrow \quad C = 3Nk_B$$

$$T \ll \frac{\hbar\omega}{k_B} \quad \theta$$

- This result is true only if
- At low T 's only lattice modes having low frequencies can be excited from their ground states;



$$v_s = \frac{\omega}{k} \Rightarrow \frac{k}{\omega} = \frac{1}{v_s} \Rightarrow \frac{dk}{d\omega} = \frac{1}{v_s}$$

and

$$g(\omega) = \frac{Vk^2 dk}{2\pi^2 d\omega}$$

$$g(\omega) = \frac{V \left(\frac{\omega^2}{v_s^2} \right) \frac{1}{2\pi^2} \frac{1}{v_s}}{\quad} \text{ at low } T\text{'s}$$

v_s depends on the direction and there are two transverse, one longitudinal acoustic branch:

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

Velocities of sound in longitudinal and transverse direction

$$\varepsilon = \int_0^\infty \left(\frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1} \right) \times g(\omega) d\omega \quad \text{Zero point energy} = \varepsilon_z$$

$$\varepsilon = \int_0^\infty \left(\frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1} \right) \times \frac{V \omega^2}{2\pi^2} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) d\omega$$

$$\varepsilon = \left[\varepsilon_z + \frac{V}{2\pi^2} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \right] \left[\int_0^\infty \frac{\hbar \omega^3}{(e^{\hbar \omega / kT} - 1)} d\omega \right]$$

$$\int_0^\infty \frac{\hbar \omega^3}{e^{\hbar \omega / kT} - 1} d\omega = \int_0^\infty \left(\frac{k_B T}{\hbar} \right)^3 x^3 \frac{k_B T}{\hbar} dx$$

$$\varepsilon = \varepsilon_z + \frac{V}{2\pi^2} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \frac{(k_B T)^4}{\hbar^4} \pi^2 \frac{15}{4}$$

$$C_v = \frac{d\varepsilon}{dT} = \frac{2}{15} V \pi^2 k_B \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \left(\frac{k_B T}{\hbar} \right)^3$$

$$x = \frac{\hbar \omega}{k_B T}$$

$$\omega = \frac{k_B T}{\hbar} x$$

$$d\omega = \frac{k_B T}{\hbar} dx$$

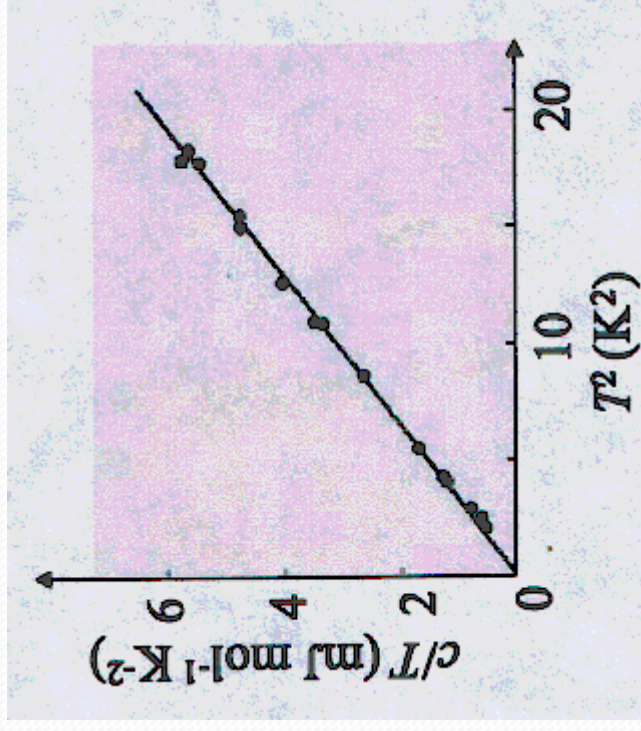
at low temperatures

How good is the Debye approximation

at low T?

$$C_v = \frac{d\varepsilon}{dT} = \frac{2}{15} V \pi^2 k_B \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \left(\frac{k_B T}{\hbar} \right)^3$$

The lattice heat capacity of solids thus varies as T^3 at low temperatures; this is referred to as the Debye T^3 law. Figure illustrates the excellent agreement of this prediction with experiment for a non-magnetic insulator. The heat capacity vanishes more slowly than the exponential behaviour of a single harmonic oscillator because the vibration spectrum extends down to zero frequency.



The Debye interpolation scheme

The calculation of $g(\omega)$ is a very heavy calculation for 3D, so it must be calculated numerically.

Debye obtained a good approximation to the resulting heat capacity by neglecting the dispersion of the acoustic waves, i.e. assuming

$$\omega = v_s k$$

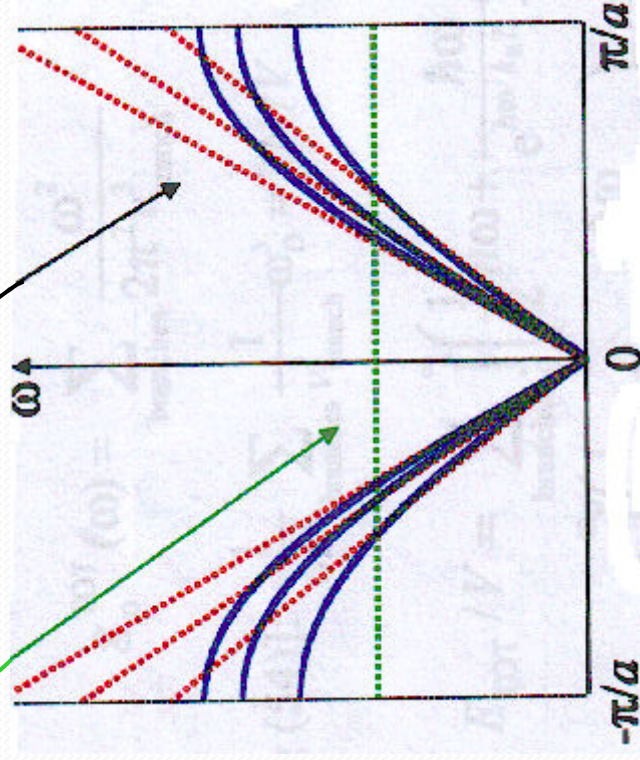
for arbitrary wavenumber. In a one dimensional crystal this is equivalent to taking $g(\omega)$ as given by the broken line of density of states figure rather than full curve. Debye's approximation gives the correct answer in either the high and low temperature limits, and the language associated with it is still widely used today.

The Debye approximation has two main steps:

1. Approximate the dispersion relation of any branch by a linear extrapolation of the small k behaviour:

Einstein approximation to the dispersion

Debye approximation to the dispersion
 $\omega = vk$



Debye cut-off frequency ω_D

2. Ensure the correct number of modes by imposing a cut-off frequency ω_D , above which there are no modes. The cut-off frequency 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

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

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

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

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

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

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

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

The lattice vibration energy of

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

becomes

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

and,

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

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 $C = \frac{dE}{dT}$

$$E = \frac{9}{8} N \hbar \omega_D + \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar \omega^3 d\omega}{e^{\hbar\omega/k_B T} - 1} \quad \rightarrow \quad C_D = \frac{dE}{dT} = \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar^2 \omega^4}{k_B T^2} \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} d\omega$$

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

$$x = \frac{\hbar\omega}{k_B T} \quad \rightarrow \quad \frac{d\omega}{dx} = \frac{k_B T}{\hbar} \quad \omega = \frac{k_B T}{\hbar} x$$

and define the Debye temperature Θ_D

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

The Debye prediction for lattice specific heat

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

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

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

How does C_{limit} at high and low temperatures?

High temperature $T \gg \Theta_D$

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

x is always small

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

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



How does C_D limit at high and low temperatures?

Low temperature $T \ll \Theta_D$

For low temperature the upper limit of the integral is infinite; the integral is then a known integral of $4\pi^4 / 15$

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

We obtain the Debye T^3 law in the form

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

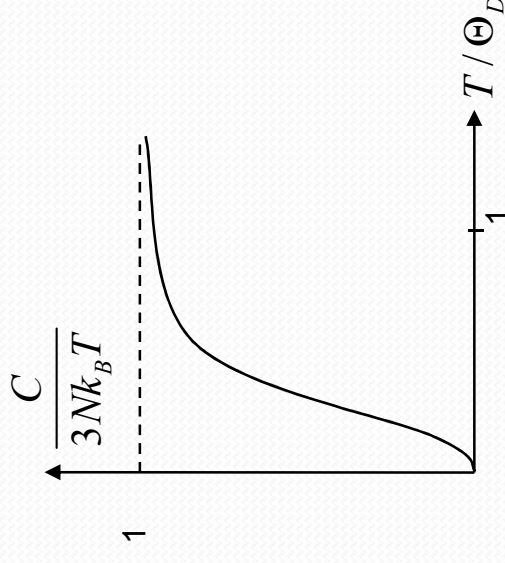
Lattice heat capacity due to Debye interpolation scheme

Figure shows the heat capacity between the two limits of high and low T as predicted by the Debye interpolation formula.

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

Because it is exact in both high and low T limits the Debye formula gives quite a good representation of the heat capacity of most solids, even though the *actual phonon-density of states curve may differ* appreciably from the Debye assumption.

Debye frequency and Debye temperature scale with the velocity of sound in the solid. So solids with low densities and large elastic moduli have high Θ_D . Values of Θ_D for various solids is given in table. Debye energy $\hbar\omega_D$ can be used to estimate the maximum phonon energy in a solid.



Lattice heat capacity of a solid as predicted by the Debye interpolation scheme

Solid	Ar	Na	Cs	Fe	Cu	Pb	C	KCl
$\Theta_D(K)$	93	158	38	457	343	105	2230	235

Anharmonic Effects

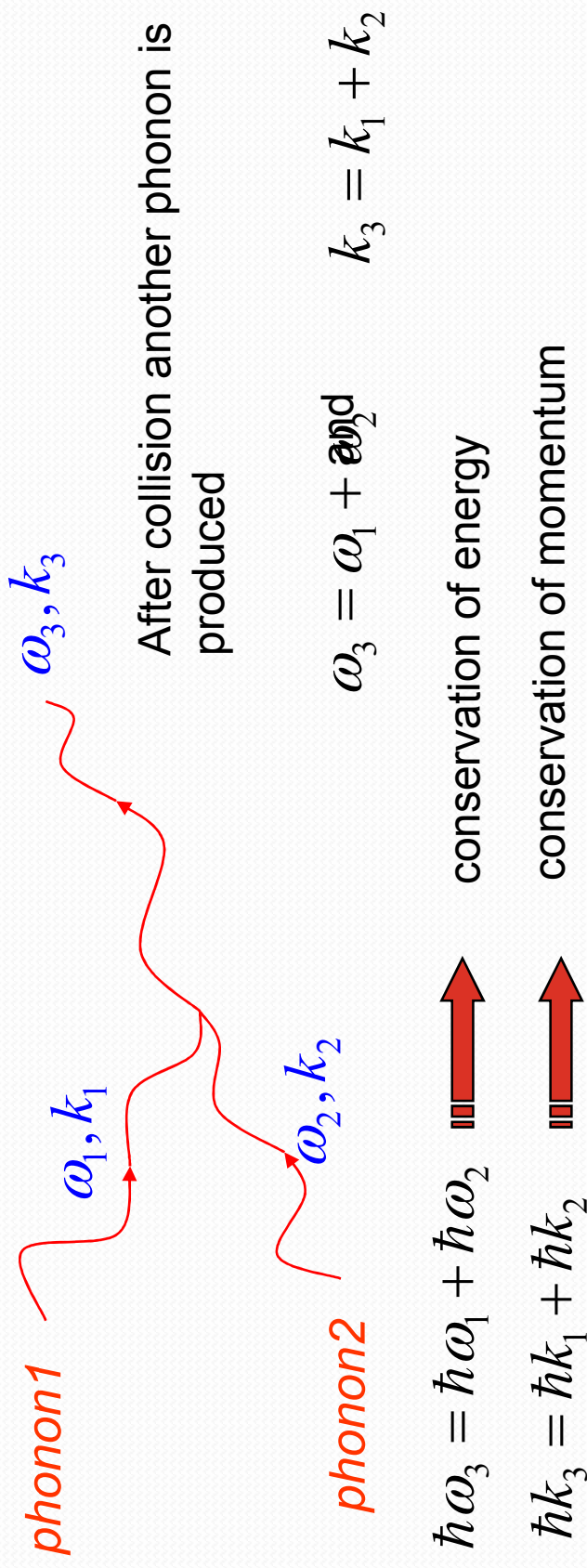
- Any real crystal resists compression to a smaller volume than its equilibrium value more strongly than expansion due to a larger volume.
- This is due to the shape of the interatomic potential curve.
- This is a departure from Hooke's law, since harmonic application does not produce this property.
- This is an anharmonic effect due to the higher order terms in potential which are ignored in harmonic approximation.

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

- 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. A typical collision process of



Phonons are represented by wavenumbers with

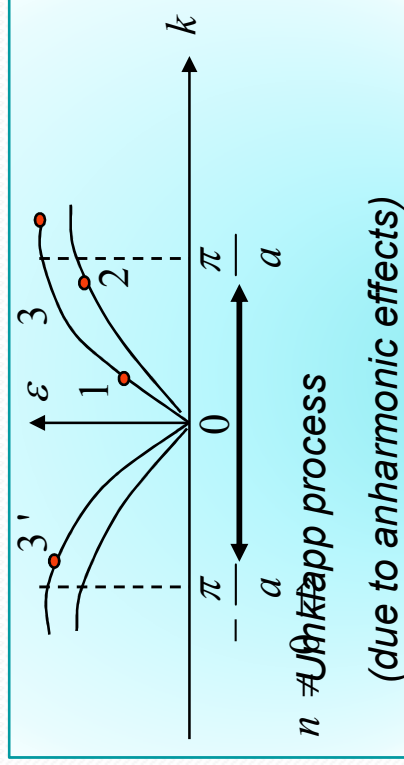
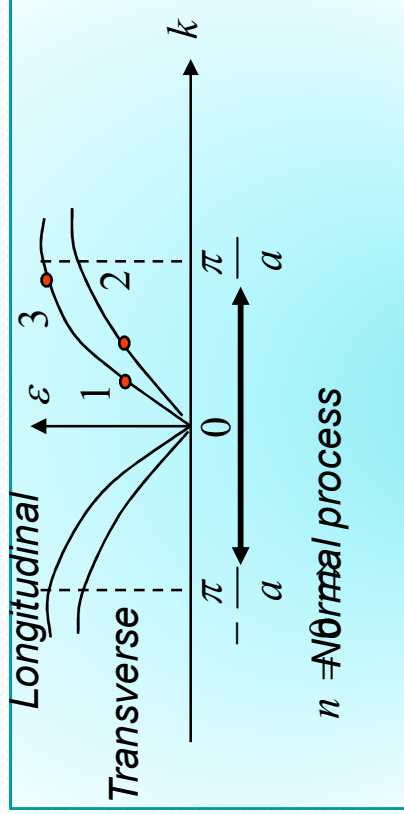
$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$$

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

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

This phonon is indistinguishable from a phonon with wavevector k_3

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



Phonon 3 has $|k| < \frac{\pi}{a}$

; Phonon 3 has $|k| > \frac{\pi}{a}$ and Phonon 3 = Phonon 3'

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.

Kinetic theory

In the elementary kinetic theory of gases, the steady state flux of a property P in the z direction is

$$flux = \frac{1}{3} \bar{v} \frac{dP}{dz}$$

Angular average

Mean free path

Constant average speed for molecules

In the simplest case where P is the number density of particles the transport coefficient obtained from above eqn. is the **diffusion coefficient** $D = \frac{1}{3} \bar{v} \lambda$.

If P is the energy density E then the flux W is the heat flow per unit area so that

$$W = \frac{1}{3} \bar{v} \frac{dE}{dz} = \frac{1}{3} \bar{v} \frac{dE}{dT} \frac{dT}{dz}$$

Now dE/dT is the specific heat C per unit volume, so that the thermal conductivity;

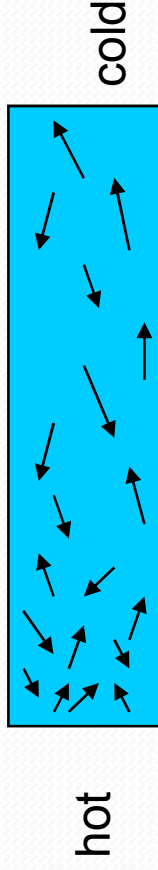
$$K = \frac{1}{3} \bar{v} \lambda C \quad \longrightarrow \quad \text{Works well for a phonon gas}$$

Heat conduction in a phonon and real gas

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

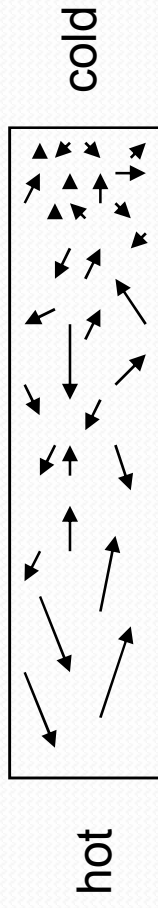
Phonon gas

- 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



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.



Temperature dependence of thermal conductivity K

$$K = \frac{1}{3} l \bar{v} C$$

Vanishes exponentially at low T 's and tends to classical value at high T 's

Approximately equal to velocity of sound and so temperature independent.

?

- Temperature dependence of phonon mean free length is determined by phonon-phonon collisions at low temperatures
- Since the heat flow is associated with a flow of phonons, the most effective collisions for limiting the flow are those in which the phonon group velocity is reversed. It is the Umklapp processes that have this property, and these are important in limiting the thermal conductivity

Conduction at high temperatures

- At temperatures much greater than the Debye temperature Θ_D the heat capacity is given by temperature-independent classical result of

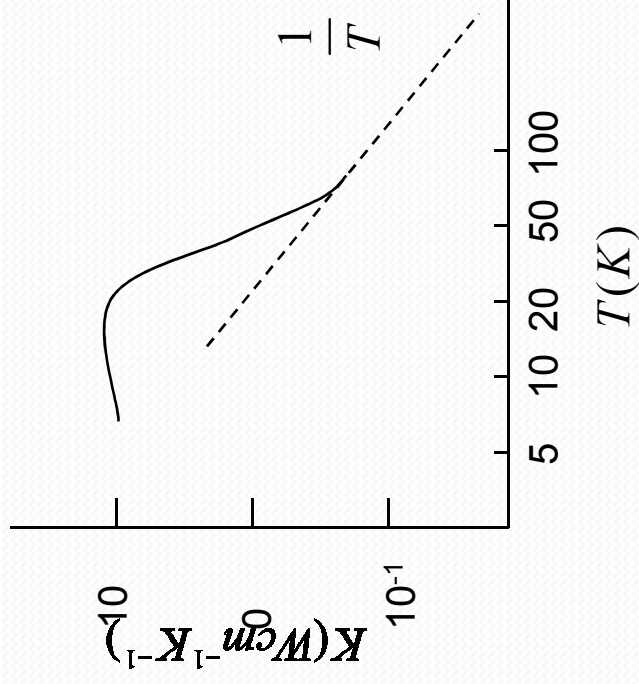
$$C = 3Nk_B$$

- The rate of collisions of two phonons \propto phonon density.
- If collisions involving larger number of phonons are important, however, then the scattering rate will increase more rapidly than this with phonon density.
- At high temperatures the average phonon density is constant and the total lattice energy $\propto T$; phonon number $\propto T$, so

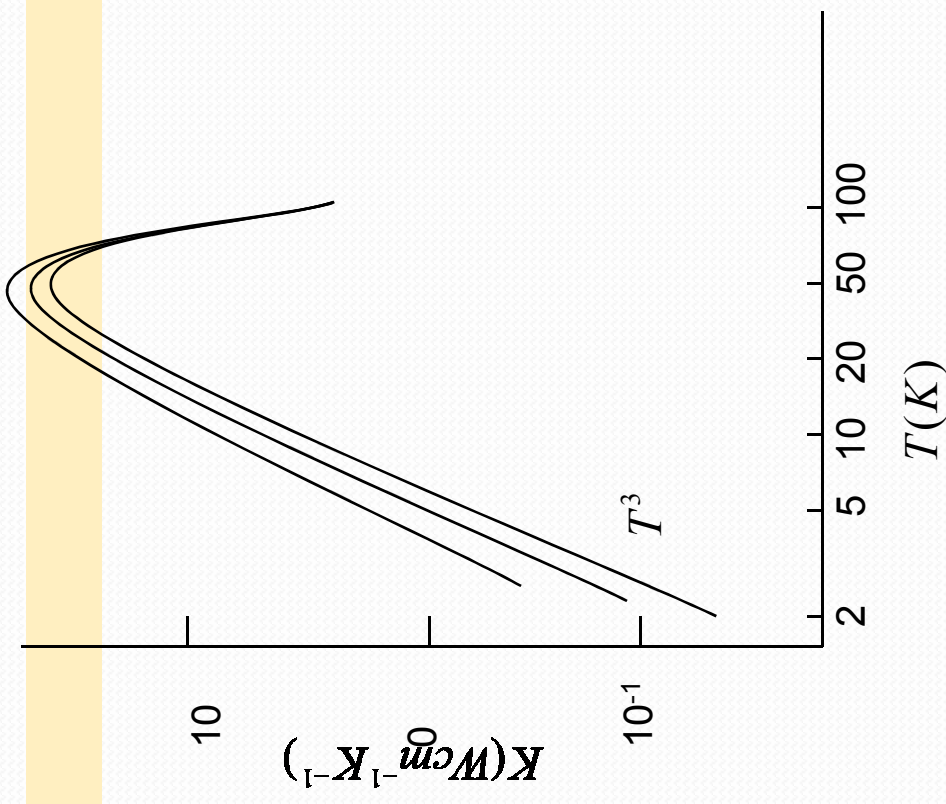
Scattering rate $\propto T$ and mean free length $\propto T^{-1}$

Then the thermal conductivity of $K = \frac{1}{3} l \bar{v} C \propto T^{-1}$.

Experimental results do tend towards this behaviour at high temperatures as shown in figure (a).



(a) Thermal conductivity of a quartz crystal



(b) Thermal conductivity of artificial sapphire rods of different diameters

Conduction at intermediate temperatures

Referring figure a

At $T < \theta_D$; the conductivity rises more steeply with falling temperature, although the heat capacity is falling in this region. Why?



This is due to the fact that Umklapp processes which will only occur if there are phonons of sufficient energy to create a phonon with $k_3 > \pi/a$. So



Energy of phonon must be \propto the Debye energy ($k\theta_D$)



The energy of relevant phonons is thus not sharply defined but their number is expected to vary roughly as

$$e^{-\theta_D/bT} \quad \text{when} \quad T \ll \theta_D,$$

where b is a number of order unity 2 or 3. Then

$$l \propto e^{\theta_D/bT}$$

This exponential factor dominates any low power of T in thermal conductivity, such as a factor of T^3 from the heat capacity.

Conduction at low temperatures

l for phonon-phonon collisions becomes very long at low T 's and eventually exceeds the size of the solid, because

number of high energy phonons necessary for Umklapp processes decay exponentially as

$$e^{-\theta_D/bT}$$

l is then limited by collisions with the specimen surface, i.e.

$$l \propto \text{Specimen diameter}$$

T dependence of K comes from C_v , which obeys T^3 law in this region

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

Temperature dependence of C_v dominates.

Size effect

- When the mean free path becomes comparable to the dimensions of the sample, transport coefficient depends on the shape and size of the crystal. This is known as a *size effect*.
- If the specimen is not a perfect crystal and contains imperfections such as dislocations, grain boundaries and impurities, then these will also scatter phonons. At the very lowest T 's the dominant phonon wavelength becomes so long that these imperfections are not effective scatterers, so;
the thermal conductivity has a T^3 dependence at these temperatures.
- The maximum conductivity between T^3 and $e^{\theta_D/bT}$ region is controlled by imperfections.
- For an impure or polycrystalline specimen the maximum can be broad and low [figure (a) on pg 59], whereas for a carefully prepared single crystal, as illustrated in figure(b) on pg 59, the maximum is quite sharp and conductivity reaches a very high value, of the order that of the metallic copper in which the conductivity is predominantly due to conduction electrons.