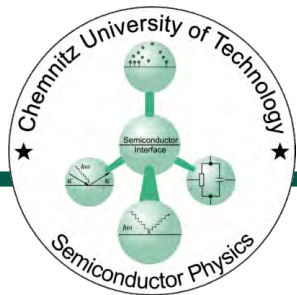


# Lattice Vibrations & Phonons

## Dispersion Relations & Density of States (DOS)



**Lattice Vibrations** are the oscillations of atoms in a solid about the equilibrium position.

- For a crystal, the equilibrium positions form a regular lattice, due to the fact that the atoms are bound to neighboring atoms.
- The **vibration** of these neighbouring atoms is **not independent** of each other.
- A regular lattice with harmonic forces between atoms and normal modes of vibrations are called **lattice waves**.
- Lattice waves range from low frequencies to high.
- The **wavelengths** at extremely high frequencies are of the order of **inter atomic spacing**.
- Lattice vibrations can also interact with free electrons in a conducting solid which gives rise to electrical resistance.



Lattice dynamics extends the concept of crystal lattice to an array of atoms with finite masses capable of motion.

The motion of these masses is a **superposition of vibrations** of atoms around the **equilibrium sites** induced by the **interaction with neighbouring atoms**.

The collective vibration of the atoms within the crystal forms a wave of allowed **wavelength** and **amplitude**.

The same way light is said to be a wave motion composed of photons, we can also think of the normal modes of vibration in a solid as being a particle!: **The Phonon**

(...)



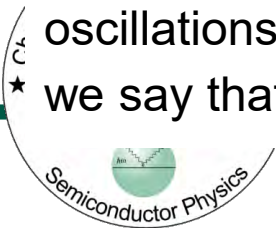
## The Phonon

The existence of the **periodic crystal lattice** in solid materials provides a medium for **characteristic vibrations**.

Between the lattice spacing, there are quantized vibrational modes which are called **phonons**.

Due to the to the wave-particle duality of quantum mechanics, the phonon can be understood as a wave and a particle. In this sense, **the phonon is a quantum of vibrational excitation in a crystal lattice**.

Note: the phonon is not actually a fundamental particle - it is a "quasiparticle". When a lattice vibrates, the nuclei oscillate about their equilibrium positions. These oscillations carry no angular momentum, only linear momentum. For this reason, we say that the phonon is a spin 0 quasiparticle.



## What is a phonon?

A phonon is the **quantum mechanical description of an elementary vibrational motion** in which a lattice of atoms or molecules uniformly oscillates at a single frequency.

In classical mechanics this designates a **normal mode of vibration**.

Normal modes are important because any arbitrary lattice vibration can be considered to be a superposition of these *elementary* vibration modes (Fourier analysis).

While normal modes are **wave-like phenomena** in classical mechanics, phonons have **particle-like properties** too, in a way related to the wave–particle duality of quantum mechanics.

# Optical Properties of Lattice Vibrations



## Dispersion Relations

Finding the **normal modes of vibration of a crystal** is not a simple easy task ... Lattice dynamic, offers two different approaches to find the **dispersion relation** within the lattice:

### Quantum Mechanics

The Schrodinger equation for the lattice vibrations must be solved.



### Semi-Classic

Classical mechanics combined with the quantum mechanics notion that the energy of lattice vibrations is quantized.

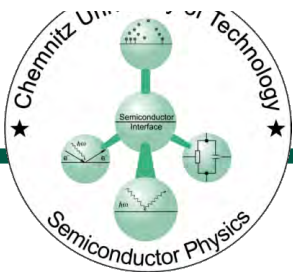


## What are dispersion relations?

In science and engineering, the **dispersion relations** describe the effect of dispersion in a medium on the properties of a wave traveling within that medium.

A dispersion relation relates the wavelength ( $\lambda$ ) or wavenumber ( $k$ ) of a wave to its frequency ( $\omega$ ).

From this relation the **phase velocity** and **group velocity** of the wave have convenient expressions which then determine the **refractive index** of the medium.)





# Extra material: physics basics to understand this chapter

Dispersion occurs when pure plane waves of different wavelengths have different propagation velocities, so that a **wave packet** of mixed wavelengths tends to spread out in space. The speed of a plane wave,  $v$ , is a function of the wave's wavelength  $\lambda$ :

$$v = v(\lambda).$$

The wave's speed, wavelength, and frequency,  $f$ , are related by the identity

$$v(\lambda) = \lambda f(\lambda).$$

The function  $f(\lambda)$  expresses the dispersion relation of the given medium. Dispersion relations are more commonly expressed in terms of the **angular frequency**  $\omega = 2\pi f$  and **wavenumber**  $k = 2\pi/\lambda$ . Rewriting the relation above in these variables gives

$$\omega(k) = v(k) k.$$

where we now view  $f$  as a function of  $k$ . The use of  $\omega(k)$  to describe the dispersion relation has become standard because both the **phase velocity**  $\omega/k$  and the **group velocity**  $d\omega/dk$  have convenient representations via this function.

The plane waves being considered can be described by

$$A(x, t) = A_0 e^{2\pi i \frac{x - vt}{\lambda}} = A_0 e^{i(kx - \omega t)},$$

where

$A$  is the amplitude of the wave,

$$A_0 = A(0, 0),$$

$x$  is a position along the wave's direction of travel, and

$t$  is the time at which the wave is described.

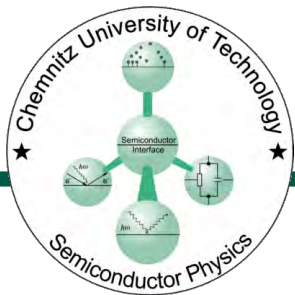
## Relation of simple harmonic motion and circular motion Mathematical description of harmonic motion

<https://www.youtube.com/watch?v=JSBw-JyFgZk>

<https://www.youtube.com/watch?v=Lv3T0zoJYzs>

<https://www.youtube.com/watch?v=k2FvSzWeVxQ>

<https://www.youtube.com/watch?v=0eBC244di5Y>





## Semi-classical treatment of lattice vibrations

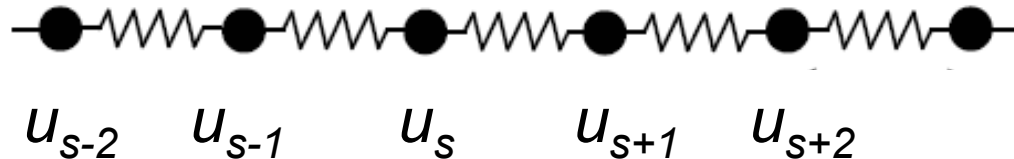
### Assumption 1

**Lattice vibrations**

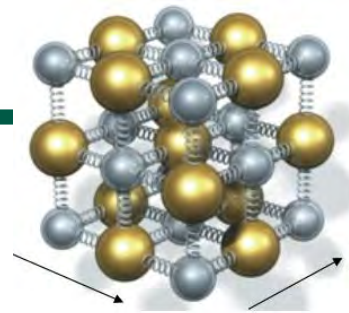


**Simple Harmonic oscillations of  
bodies connected by springs**

When an atom is displaced from its equilibrium site by a small amount a force acting on this atom, it will tend to return to its equilibrium position.



# Debye's Model for crystals

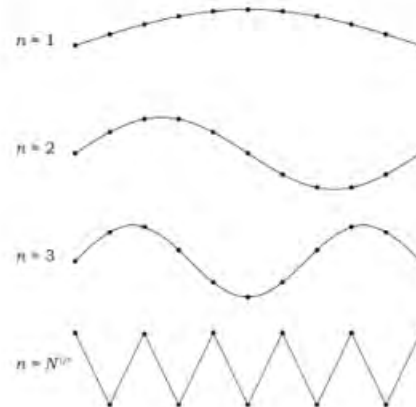


Peter Debye

Born	March 24, 1884 Maastricht, Netherlands
Died	November 2, 1966 (aged 82) Ithaca, New York, US
Citizenship	Netherlands / United States
Alma mater	RWTH Aachen University of Munich
Known for	Debye model Debye relaxation Debye frequency
Awards	Rumford Medal (1930) Faraday Lectureship Prize (1933) Lorentz Medal (1935) Nobel Prize in Chemistry (1936) Willard Gibbs Award (1949) Max Planck Medal (1950) Priestley Medal (1963) National Medal of Science (1965) <b>Scientific career</b>
Fields	Physics, Chemistry
Institutions	University of Zurich (1911–12) University of Utrecht (1912–14) University of Göttingen (1914–20) ETH Zurich (1920–27) University of Leipzig (1927–34) University of Berlin (1934–39) Cornell University (1940–50) Arnold Sommerfeld
Doctoral advisor	Lars Onsager Paul Scherrer
Doctoral students	George K. Fraenkel Fritz Zwicky

In Debye's model, we think of the atoms in a solid as connected by springs. They vibrate in 3D in a complicated way.

The problem can be simplified by treating the vibration as a superposition of waves of different frequencies.



If we suppose that the atoms are fixed at the edge of the solid, the frequency would be quantised. A quantum of this vibration energy is called a phonon.



## 1D atom chain with finite length and fixed ends



$a$  – atom spacing

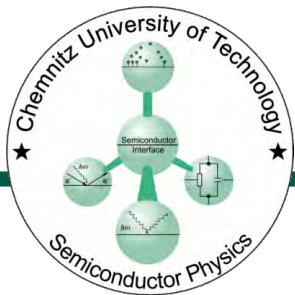
$N+1$  – number of atoms  
(but only  $N-1$  can vibrate)

$n$  – integer atom index

$L = Na$  – chain length

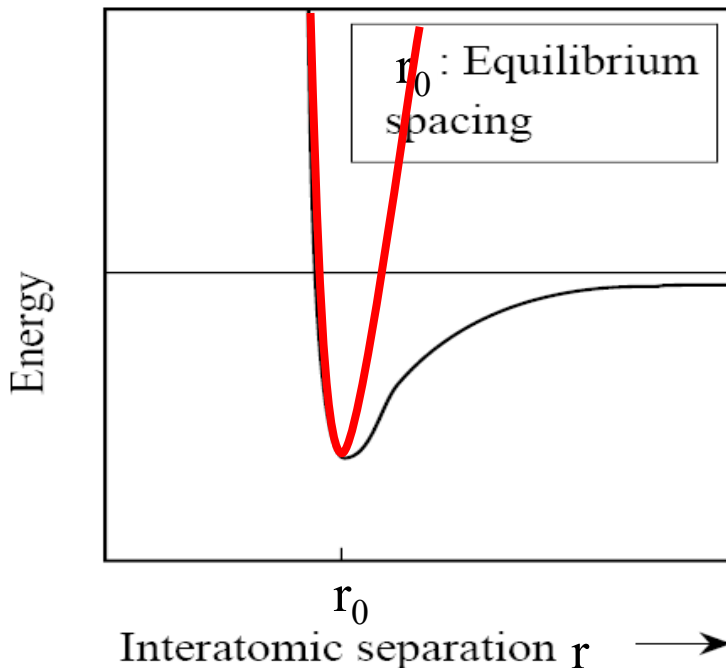
Only a limited number of vibration patterns are possible  
 $\Rightarrow$  only a discrete number of wavevectors are allowed

$$q = \frac{2\pi}{\lambda} = n \frac{2\pi}{L} \quad \text{with} \quad n = 1, 2, \dots, N-1$$



## Assumption 2

The forces acting on the bodies are related to the instantaneous potential energy of the atom. This potential energy is the interaction of the atom with the other atoms within the crystal.



## Taylor series

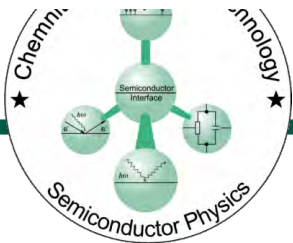
~~$$E(r) = E_0 + \left( \frac{dE}{dr} \right)_{r_0} (r - r_0) + \frac{1}{2} \left( \frac{d^2E}{dr^2} \right)_{r_0} (r - r_0)^2 + \dots$$~~

~~$$E(r) = E_0 + fr^2 + c_3r^3 + c_4r^4 + c_5r^5 \dots$$~~

Potential of interatomic forces in the vicinity of  $r_0$  is proportional to  $r^2$  !

**Harmonic approximation!!!**

**If the displacements are really small (around  $r_0$ )**



### Assumption 3

The classical motions of any atom are determined by Newton's law of mechanics:  $\vec{F} = m\vec{a}$ , in this case governed by Hook's Law: the **force** required to compress or extend a **spring** is directly proportional to the distance it is stretched  $F = -kx$ .

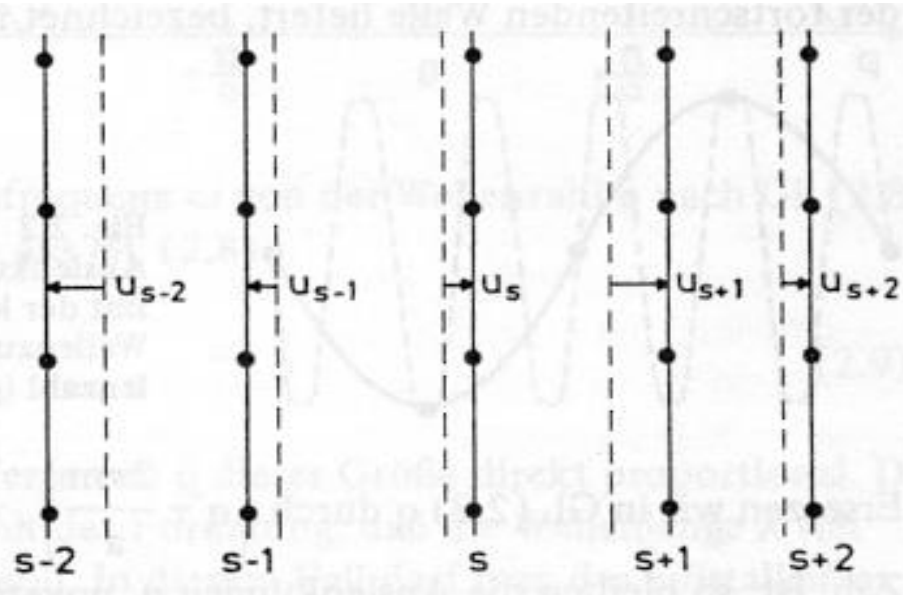
**Writing the Eq. of Motion for our harmonic oscillator**

$$E(x) = \frac{1}{2} fx^2$$

$$F(x) = -\frac{dE}{dx} = -fx \quad , \quad F(x) \text{ force exerted by the spring}$$

$$\frac{d^2 E}{dx^2} = f \quad \leftarrow \quad \text{Spring constant (force constant)}$$

# Crystal with **one atom** in the basis



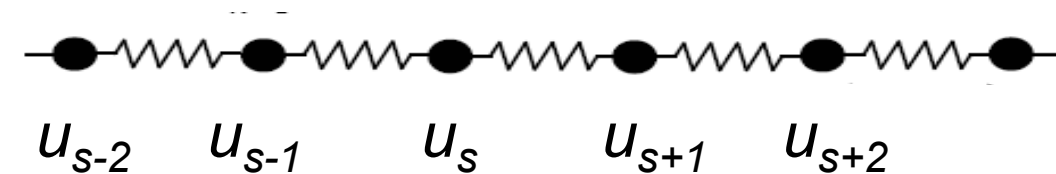
$$F_s = \sum_n f_n (u_{s+n} - u_s)$$

$$M_s \frac{d^2 u_s}{dt^2} = \sum_n f_n (u_{s+n} - u_s)$$

$f$  – force constant (spring constant)

$M = M_s$  – the mass of the atom  $s$

$U_s, U_{s+n}, \text{ etc.}$  = instantaneous potential energies of the atoms; is related to the interaction of the atom with the other atoms within the crystal.



$$F_s = f_1 (u_{s+1} - u_s) + f_1 (u_{s-1} - u_s)$$

$$M \frac{d^2 u_s}{dt^2} = f_1 (u_{s+1} - u_s) + f_1 (u_{s-1} - u_s)$$

**Considering only interaction  
between nearest neighbours**

**Crystal with one atom in the basis - analytical solution of equations**

$$u_s = A \exp i(-\omega t) \qquad u_{s+n} = A \exp i(qna - \omega t)$$

$a$  : interatomic distance

$\omega$  : frequency of the propagating wave

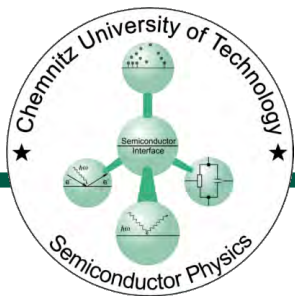
$q = \frac{2\pi}{\lambda}$  : wavenumber or spatial frequency of a wave

$A$  : amplitude

$$-\omega^2 M = \sum_{n=1}^{\infty} f_n (\exp(iqna) + \exp(-iqna) - 2) = 2 \sum_{n=1}^{\infty} f_n (\cos(qna) - 1)$$

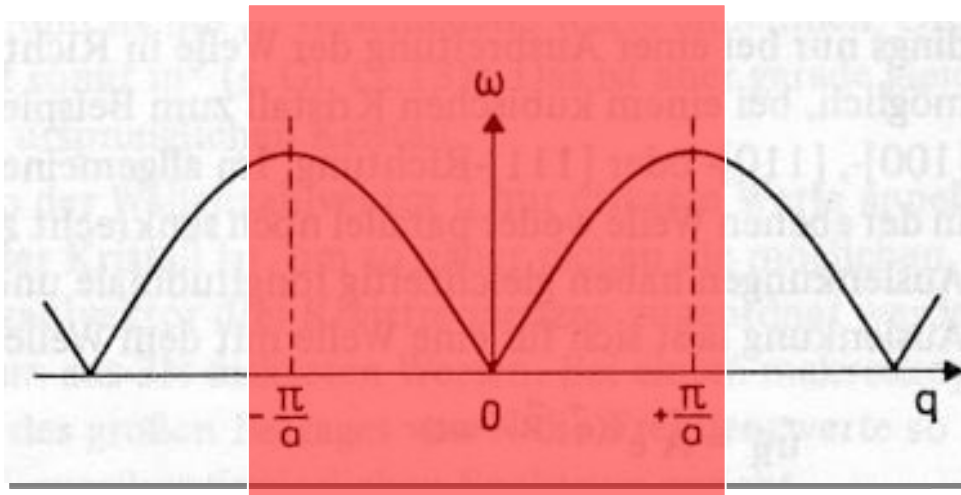
$$\omega^2 = \frac{2}{M} \sum_{n=1}^{\infty} f_n (1 - \cos(qna))$$

**Dispersion Relation**





## Crystal with **one atom** in the basis – graphical representation of solution



$$\omega^2 = \frac{2f_1}{M} (1 - \cos qa) = \frac{4f_1}{M} \sin^2 \frac{qa}{2}$$

$$\omega = \sqrt{\frac{4f_1}{M}} \left| \sin \frac{qa}{2} \right|$$

The representation can be reduced to the **first Brillouin zone!**

➤ Limitation of wavenumber range:  $-\frac{\pi}{a} < q \leq \frac{\pi}{a}$

➤ Transition  $q \rightarrow \left( q + \frac{2\pi m}{a} \right)$  provides identical lattice vibration mode!



## Limit cases

### 1. Short wavelength limit

$$(q = \pm\pi / a) \longrightarrow v_s = \frac{d\omega}{dq} = \sqrt{\frac{f_1 a^2}{M}} \cos \frac{qa}{2}$$

Group velocity = 0 at the edge of the Brillouin zone; standing wave and therefore the transmission velocity for the energy is zero).

### 2. Long wavelength limit ( $\lambda \gg a$ , $qa \ll 1$ )

$$qa \ll 1 \rightarrow \omega = \sqrt{\frac{f_1 a^2}{M}} q \quad \text{linear dispersion}$$

$$v_s = \frac{d\omega}{dq} = \sqrt{\frac{f_1 a^2}{M}}$$

Velocity of longitudinal sound waves  
(velocity is independent of frequency)

## Crystal with **two atoms** in the basis

(considering only interaction between nearest neighbors)

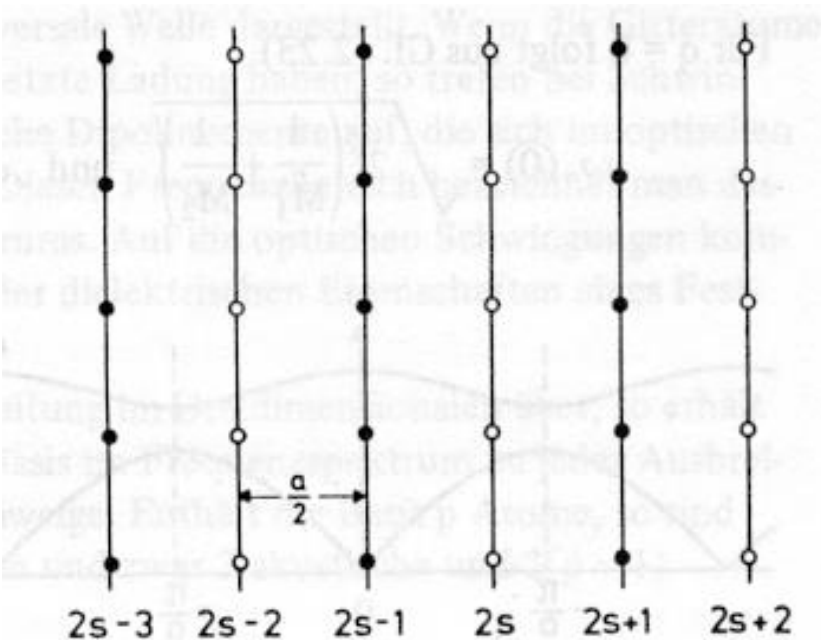
$$M_1 \frac{d^2 u_{2s+1}}{dt^2} = f(u_{2s} + u_{2s+2} - 2u_{2s+1})$$

$$M_2 \frac{d^2 u_{2s}}{dt^2} = f(u_{2s-1} + u_{2s+1} - 2u_{2s})$$

Solution of the form

$$u_{2s+1} = A \exp i \left( q \frac{(2s+1)a}{2} - \omega t \right)$$

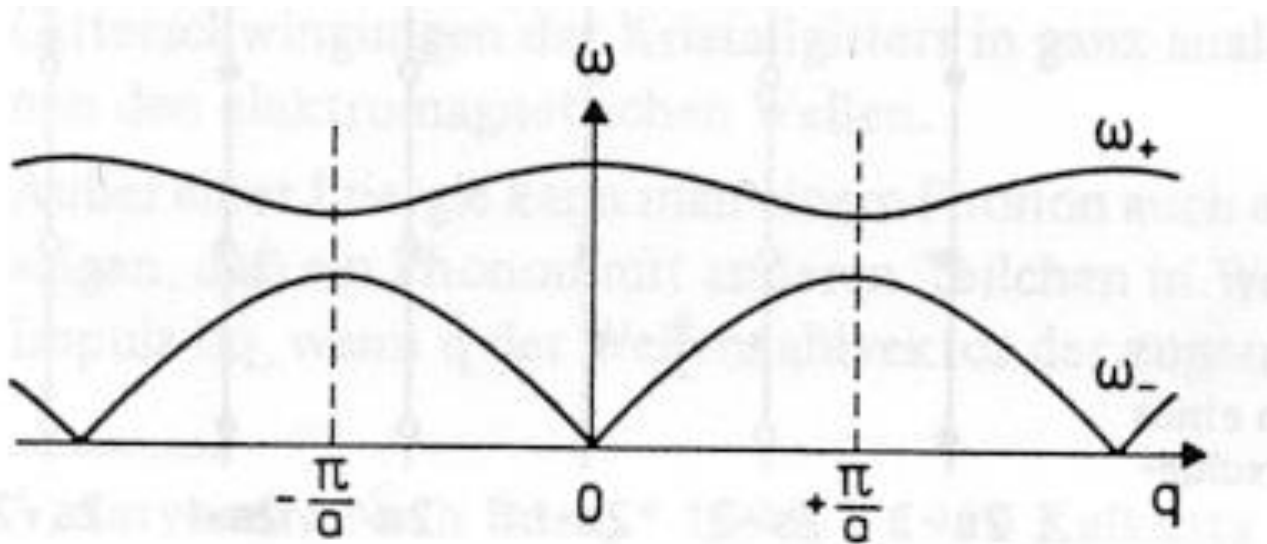
$$u_{2s} = B \exp i(qsa - \omega t)$$



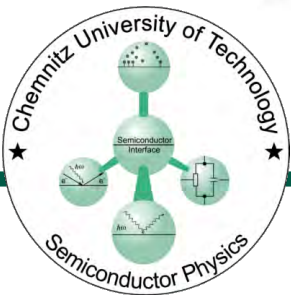


## Crystal with **two atoms** in the basis - considering only interaction between nearest neighbors

Dispersion relation: 
$$\omega^2 = f \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \pm f \sqrt{\left( \frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4}{M_1 M_2} \sin^2 \frac{qa}{2}}$$



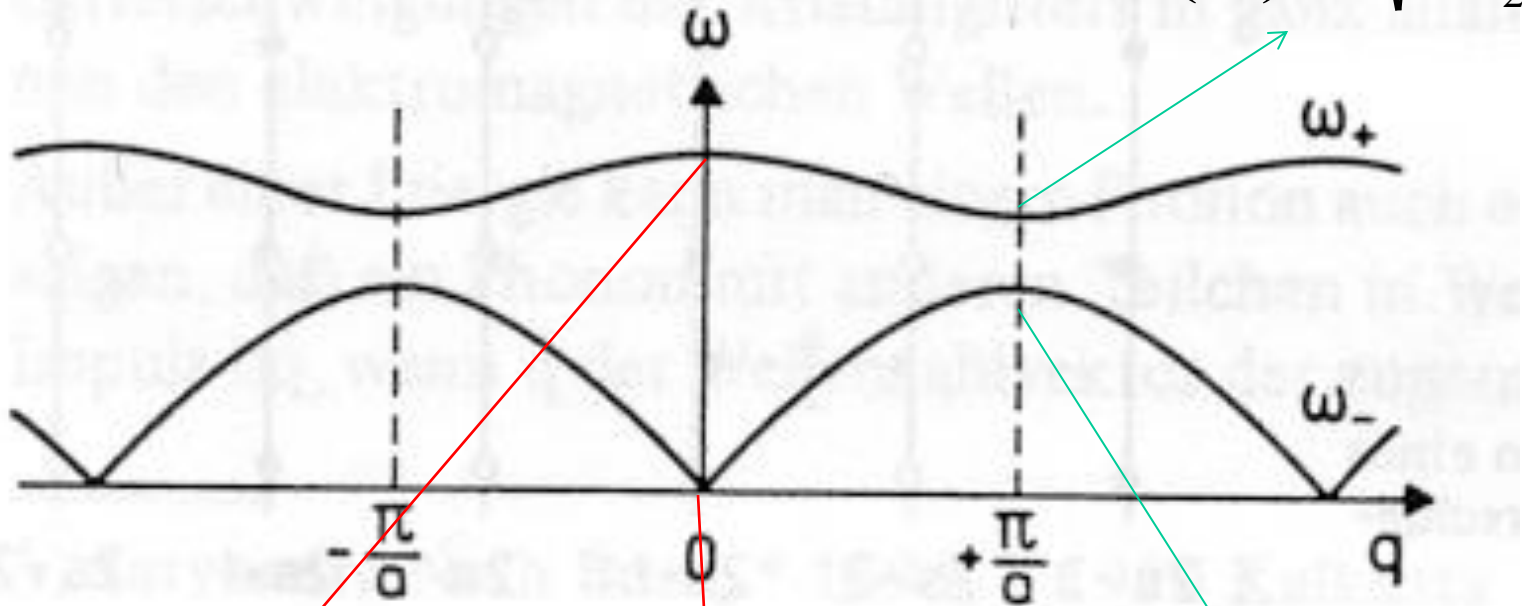
$$M_1 > M_2$$



# Limit cases

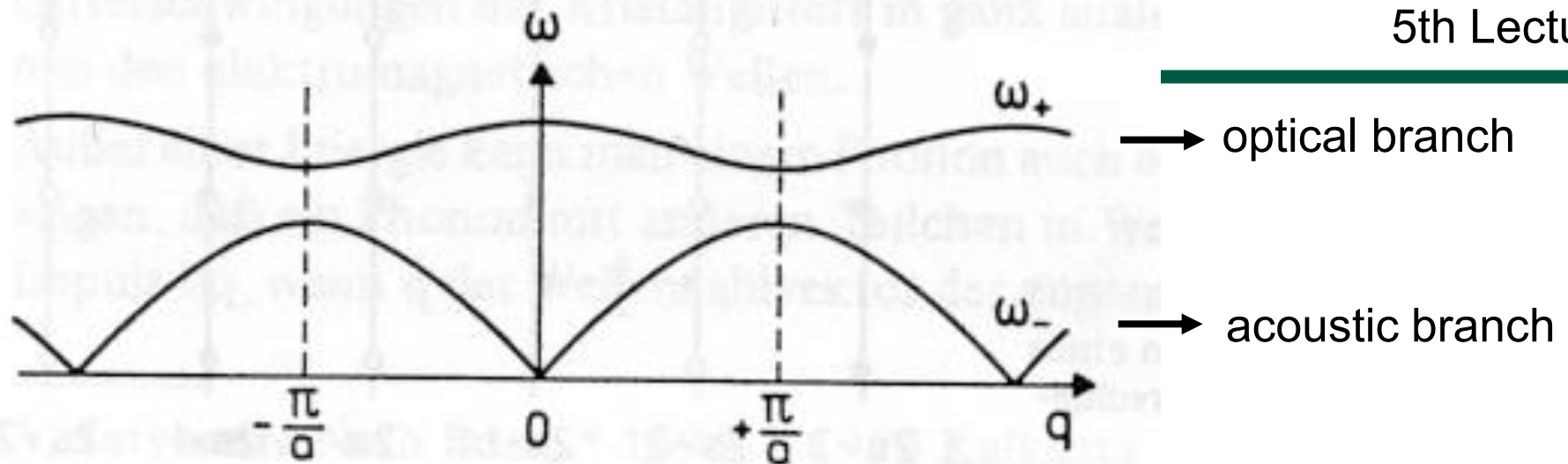
$$M_1 > M_2$$

$$\omega_+\left(\frac{\pi}{a}\right) = \sqrt{\frac{2f}{M_2}}$$



$$\omega_+(0) = \sqrt{2f\left(\frac{1}{M_1} + \frac{1}{M_2}\right)}; \omega_-(0) = 0$$

$$\omega_-\left(\frac{\pi}{a}\right) = \sqrt{\frac{2f}{M_1}}$$



acoustic branch: begins at  $q=0$  and  $\omega=0$ .

with increasing  $q$  the frequency increases in a linear fashion called acoustic; it corresponds to elastic waves or sound.

optical branch - has a nonzero frequency at zero  $q$

The frequency of the vibrations are in the infrared region which is the reason for referring to this branch as optical.

- The **gap** (forbidden band) between the optical and acoustic branch is the region where frequencies are not allowed to propagate. The width of this forbidden band depends on the difference of the masses of the two atoms.

**Acoustic:** The two atoms in the cell have the same amplitude and move in phase

$$\omega_{-}(0) = 0 \quad \rightarrow \quad A_1 = A_2$$

**Optic:** The center of mass of the two-atom-basis remains fixed & the two atoms move in out of phase.

$$\omega_{+}(0) = \sqrt{2f \left( \frac{1}{M_1} + \frac{1}{M_2} \right)} \quad \rightarrow \quad M_1 A_1 + M_2 A_2 = 0$$



In a **3-D crystal**, the atoms vibrate in three dimensions with 3 vibrational branches, 1 longitudinal and 2 transverse.

For a 3-D Lattice with  $N$  atom per lattice point, there is  **$3(m-1)$  optical branches**, of which  **$2(m-1)$**  are transverse optical phonons and the remaining phonons are longitudinal optical phonons.

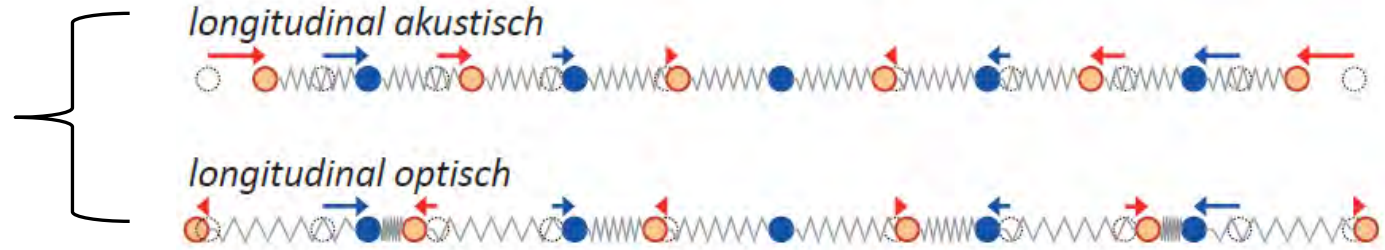
- In a **transverse wave**, the atomic displacement direction is **perpendicular to the direction of the propagated wave**.
- In a **longitudinal wave**, the atomic displacement is **parallel to the direction of the propagated wave**.

**Polarisation**  $\left\{ \begin{array}{l} \textit{longitudinal} \text{ (A parallel to } q) \\ \textit{transverse} \text{ (A perpendicular to } q) \end{array} \right.$

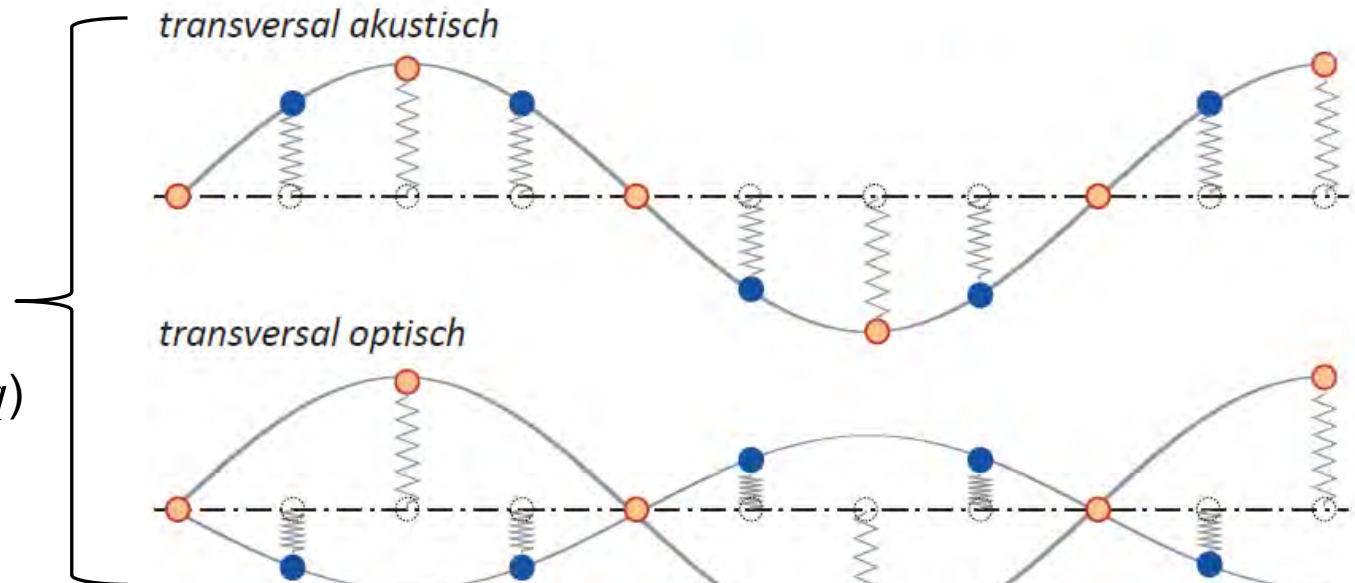
The remaining two transverse waves will overlap if the two vibrational directions are symmetric.

# Polarization

*longitudinal*  
(A parallel to  $q$ )



*transverse*  
(A perpendicular to  $q$ )





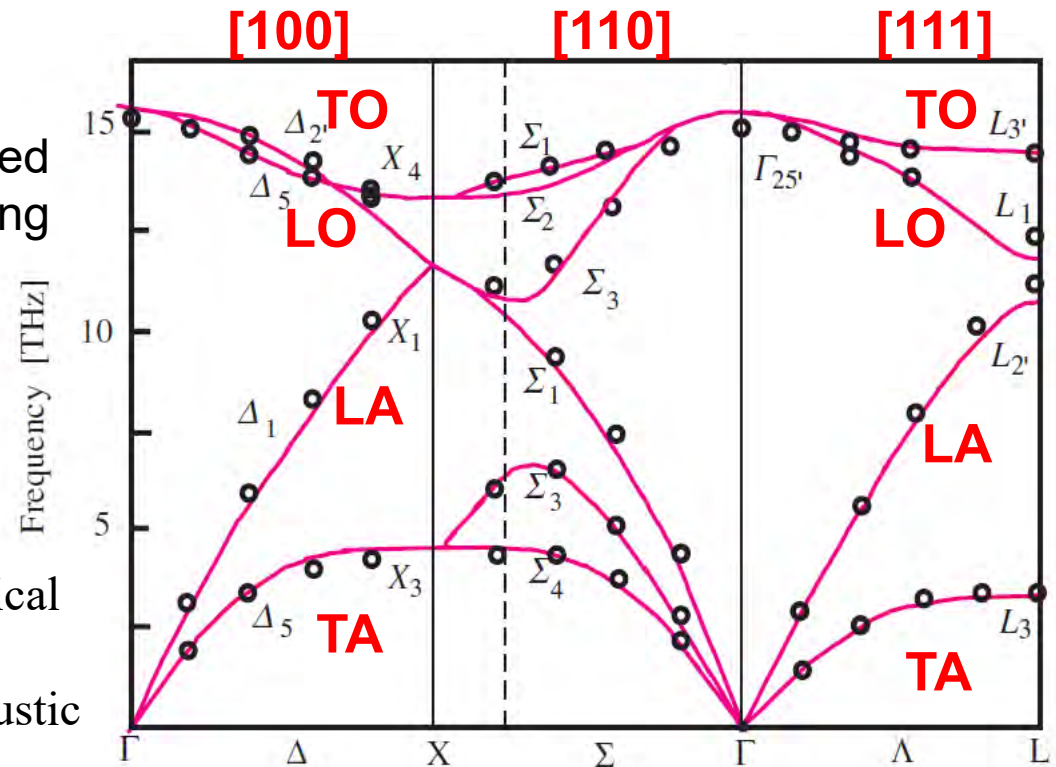
## 3D Crystal with $p$ atoms in the basis: phonon branches and polarization

3p phonon branches:

- 3 acoustic (2 - transversal and 1 - longitudinal)
- 3 (p-1) optical with: 2(p-1) - transversal and (p-1) = longitudinal.

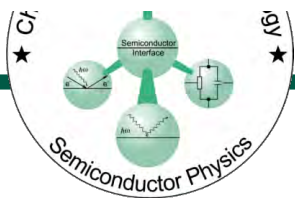
**Example:**

measured (symbols) and calculated phonon dispersion in **Silicon** along high-symmetry axes.



LO/ TO = Longitudinal / Transversal Optical

LA/ TA = Longitudinal/ Transversal Acoustic

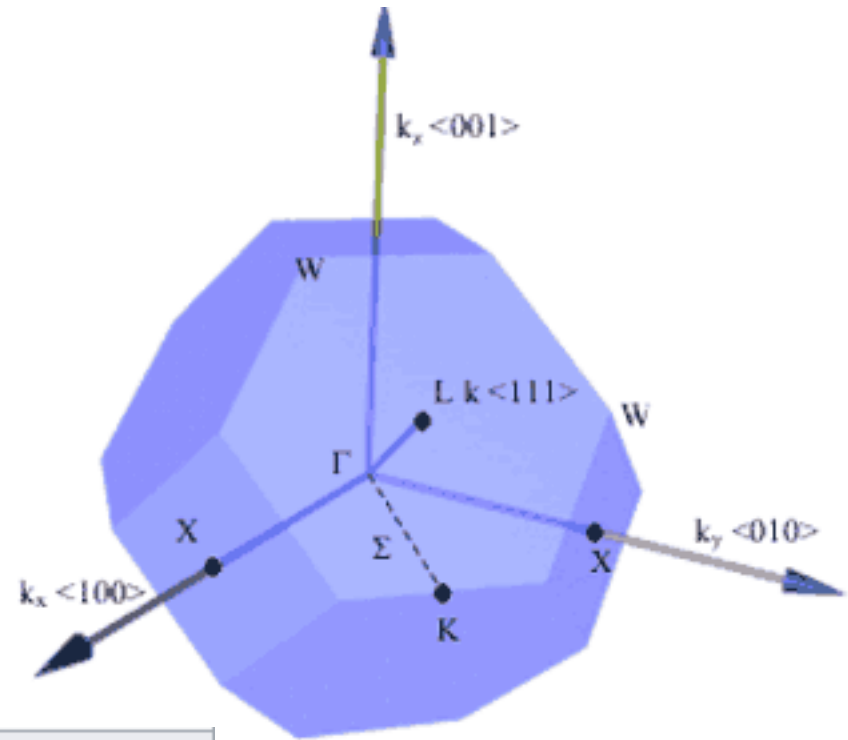


## Brillouin zone of Silicon (fcc)

$\Gamma$  – center of the Brillouin zone

Greek letters – high symmetry points and lines inside Brillouin zone

Roman letters - points on the surfaces of the Brillouin zone

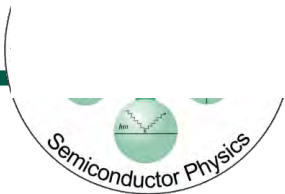


### Face-centered cubic

K	Middle of an edge joining two hexagonal faces
L	Center of a hexagonal face
U	Middle of an edge joining a hexagonal and a square face
W	Corner point
X	Center of a square face

## Phonon density of states (DOS):

- Describes the number of states per interval of energy at each energy level available to be occupied.
- It is mathematically represented by a density distribution.
- It's generally an average over the space and time domains of the various states occupied by the system.
- A high DOS at a specific energy level means that there are many states available for occupation.
- A DOS of zero means that no states can be occupied at that energy level.
- The DOS is usually represented by one of the symbols  $g$ ,  $\rho$ ,  $D$ ,  $n$ , or  $N$ .



The phonon density of states in a solid can be calculated from the periodicity of the lattice.

1D atom chain with periodic boundary conditions:  $u_n = u_{n+N}$

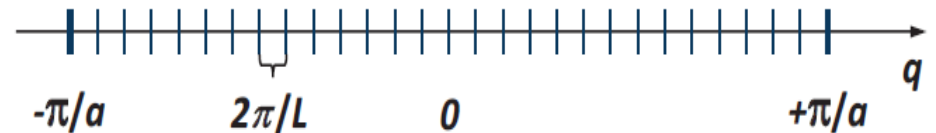
$$Z(q) = \frac{\text{number of states}}{\text{corresponding } q\text{-space volume}}$$

- the number of standing waves with wave vector  $q$  to  $q+dq$

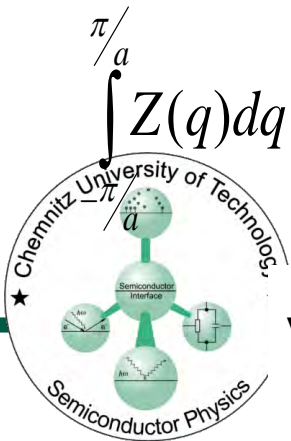
$$Z(q)dq = \frac{L}{2\pi} dq$$

- the total number of phonon states in the 1. Brillouin zone is  $N$

$$\int_{-\pi/a}^{\pi/a} Z(q) dq = \frac{L}{2\pi} \frac{2\pi}{a} = \frac{L}{a} = N$$



Volume corresponding to the wavevector of a given lattice vibration:  $\frac{2\pi}{L}$



### 3D crystal with periodic boundary conditions

Density of states in the phonon spectrum:

$$V_{\underline{q}} = \frac{1}{N} \left( \underline{a}^* \cdot \underline{b}^* \times \underline{c}^* \right) \quad \text{Volume, which one } q\text{-value occupies in the 3D reciprocal space}$$

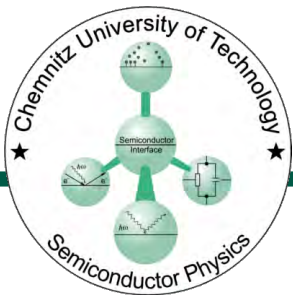
$$V_{\underline{q}} = \frac{1}{N} \frac{8\pi^3}{\underline{a} \cdot \underline{b} \times \underline{c}} = \frac{1}{N} \frac{8\pi^3}{V_Z} = \frac{8\pi^3}{V}$$

Volume of the unit cell

Total volume of the crystal

Wave vector density in reciprocal space:

$$\rho_{\underline{q}} = \frac{V}{8\pi^3} = Z(q) \text{ in 3D}$$



# Phonon density of states in 3D crystals, 3D crystal with periodic boundary conditions

$$\frac{L_x L_y L_z}{(2\pi)^3} dq_x dq_y dq_z = \frac{V}{8\pi^3} dq_x dq_y dq_z$$

Isotropic crystal –  $\omega$  depends only on magnitude of  $q$  (not direction)

$$dq_x dq_y dq_z = 4\pi q^2 dq$$

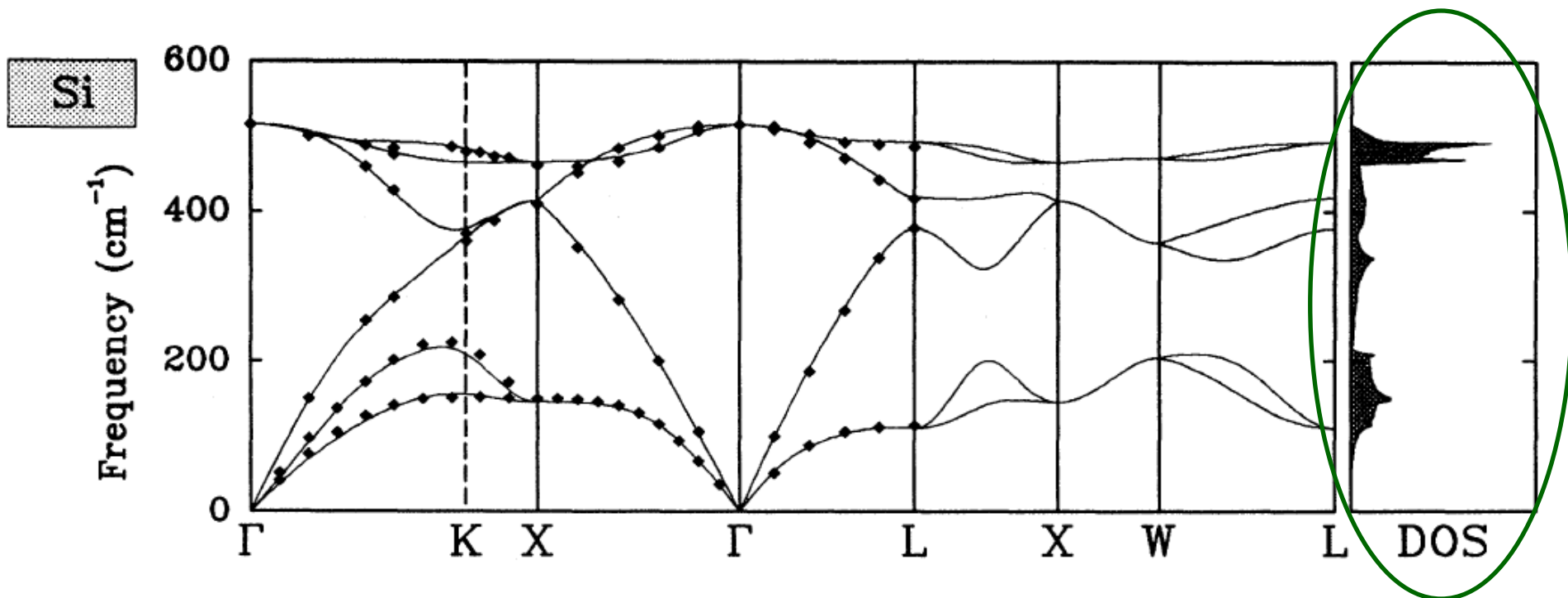
$$Z(q) dq = \frac{V}{8\pi^3} 4\pi q^2 dq = \frac{V}{2\pi^2} q^2 dq$$

$$Z(q) dq = Z(\omega) d\omega \longrightarrow Z(\omega) = Z(q) \frac{dq}{d\omega}$$

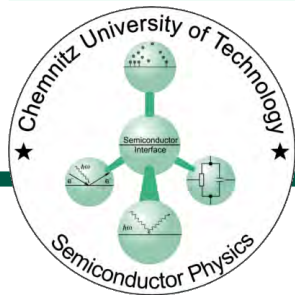
$$Z(\omega) = \frac{V}{2\pi^2} q(\omega)^2 \left( \frac{d\omega}{dq} \right)^{-1}$$



# Phonon density of states in 3D crystals



In general the DOS is proportional to the inverse of the slope of the dispersion relation. The flatter the band the greater is the density of states.



$$Z(\omega) = \frac{V}{2\pi^2} q(\omega)^2 \left( \frac{d\omega}{dq} \right)^{-1}$$

Dispersion curves for phonons can be determined

theoretically

&

experimentally



Using previous  
mathematical formalism

- Inelastic scattering of neutrons
- IR spectroscopy
- Raman spectroscopy



Next Lecture

# Phonon Spectroscopies: Raman & IR

