

2. Quantum Theory of Solids

2A. Free Electron Model

2B. Periodic Potential and Band Structure

2C. Lattice Vibration

2C. Lattice Vibration (Bube Ch. 3)

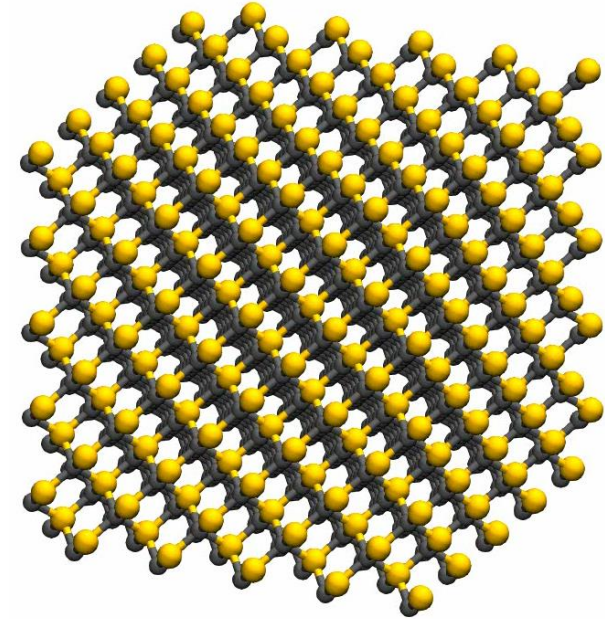
2C.1. 1D Monoatomic Lattice

2C.2. 1D Diatomic Lattice

2C.3. Band Structure and DOS of Phonon

2C.4. Heat Capacity

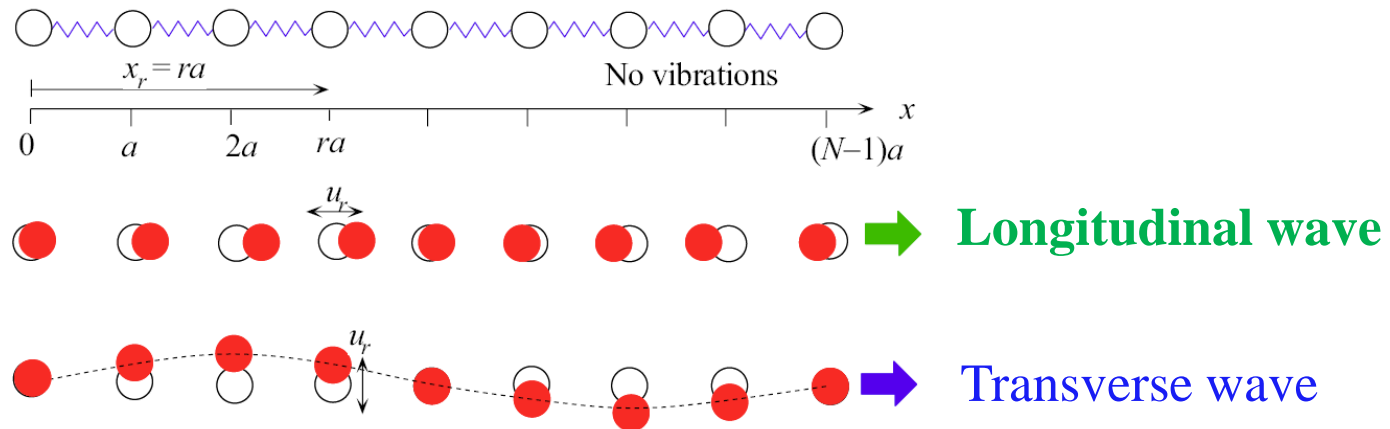
- Lattice vibration or wave describes the vibrational motion of atoms in a crystalline solid, in terms of a wave passing through the atoms of the crystal, as they are displaced by their thermal energy from their equilibrium positions.
- The thermal properties of solids and the electronic transport are strongly related to these lattice waves.
- The behavior of lattice waves and the derivation of the suitable wave equation can be based on the same classical mechanics approach we have used for waves in a string.
- Many of the major characteristics of the lattice waves can be derived from the consideration of a one dimensional crystal lattice, which can be thought as a kind of discontinuous string.



SiC at 600 K

2C.1. 1D Monoatomic Lattice

We first consider vibrations associated with a one-dimensional crystal in which all the atoms have the same mass (M) and the same atomic spacing of a . The spring constant, which reflects interatomic interaction, is also a constant K . The displacement of n^{th} atom from the equilibrium point is denoted as $u_n(t)$.



Let's consider the longitudinal vibration. The force on the n^{th} atom is affected by the stretch or compression of the two springs attached to it.

$$F = K(u_{n+1} - u_n) - K(u_n - u_{n-1}) = K(u_{n+1} + u_{n-1} - 2u_n) = M \frac{d^2 u_n}{dt^2}$$

This is the wave equation for the discrete atoms. When a is very small, the left-hand side becomes the second derivative of the displacement and the above equation becomes the wave equation for the continuum.

$$\frac{\partial^2 u(x, t)}{\partial t^2} = v^2 \frac{\partial^2 u(x, t)}{\partial x^2}$$

We look for a steady-state solution or **normal mode** in the form of $u_n(t) = A \exp i(kna - \omega t)$, where k is the wave number. Inserting this into above,

$$u_{n+1} = e^{ika}u_n, \quad u_{n-1} = e^{-ika}u_n, \quad \ddot{u}_n = -\omega^2u_n$$

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

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

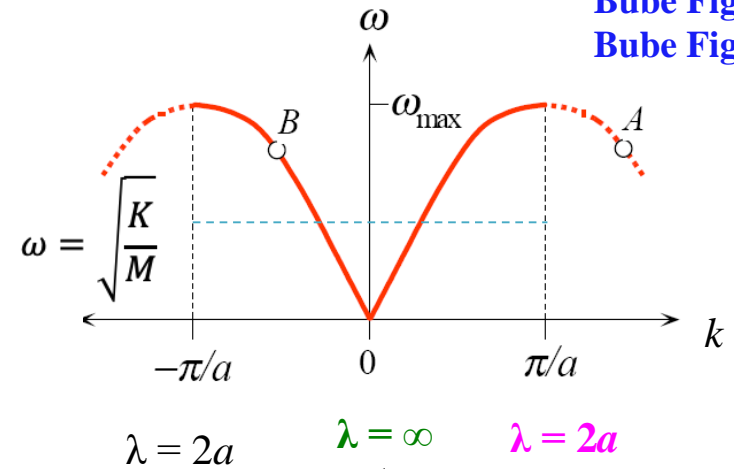
$$4K \sin^2 \frac{ka}{2} = M\omega^2$$

$$\omega = 2 \sqrt{\frac{K}{M}} \left| \sin \frac{ka}{2} \right| \quad : \text{dispersion relation for acoustic wave}$$

There is a **maximum frequency** $\omega_{\max} = 2 \sqrt{\frac{K}{M}}$.

This wave is called the **acoustic mode** and neighboring atoms in acoustic waves move in the same direction. **When sound waves travel in solid, they involve this type of lattice oscillation near $k = 0$ (long wavelength limit).**

Bube Fig. 3.2
Bube Fig. 3.3

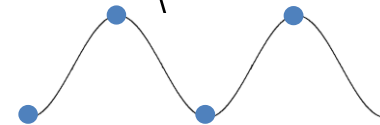


The largest wavelength for an infinite string.

All the atoms displaced by the same amount in the same direction.

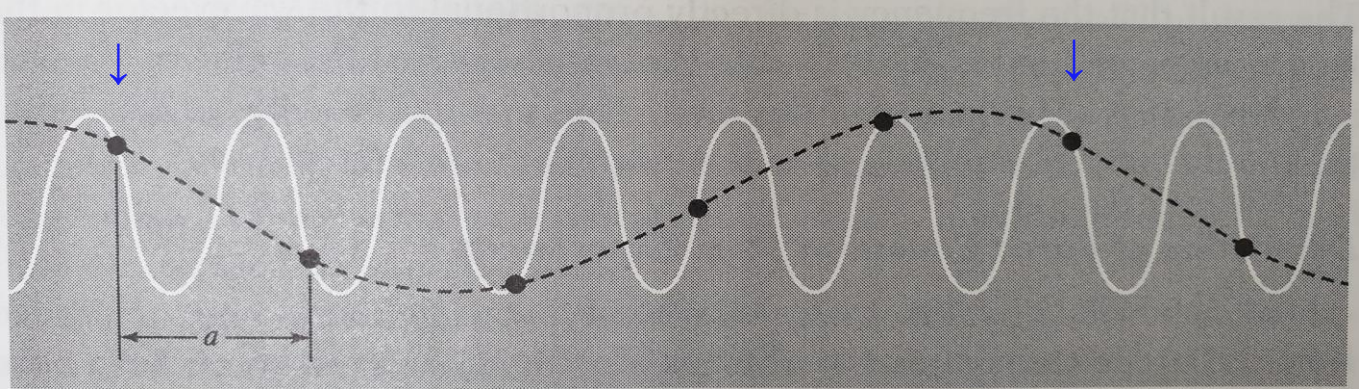


The shortest wavelength.



$$-\frac{\rho}{a} < k \leq \frac{\rho}{a}$$

Since the lattice spacing is a , the shortest possible wavelength is $2a$, and **any wavelength shorter than this is unphysical** in this system. This means that $|k|$ bigger than π/a practically corresponds to k within the 1st BZ (see below). This is also true for 2D and 3D systems.



$$\lambda = 5a/6 \text{ or } k = 12\pi/5a = 10\pi/5a + 2\pi/5a$$

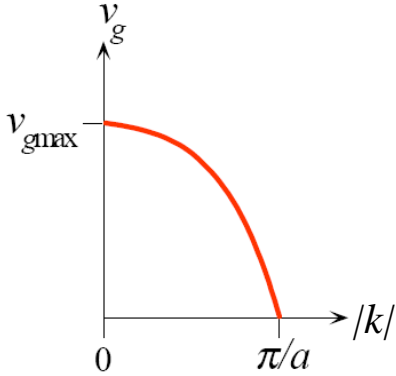
$$\lambda = 5a \text{ or } k = 2\pi/5a$$

Figure 5 The wave represented by the solid curve conveys no information not given by the dashed curve. Only wavelengths longer than $2a$ are needed to represent the motion.

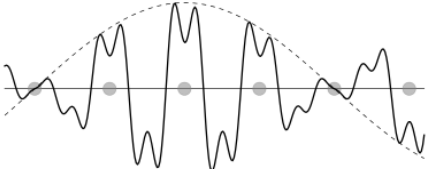
Kittel Chap. 4

The velocity at which traveling waves carry energy is the **group velocity**:

$$v_g = \frac{dW}{dk} = \left(\frac{K}{M}\right)^{1/2} a \cos\left(\frac{1}{2}ka\right) = \text{sound velocity}$$



The v_{gmax} is obtained at the long wavelength limit, which corresponds to the sound wave.



$$\psi(r) = e^{ik \cdot r} u(r)$$

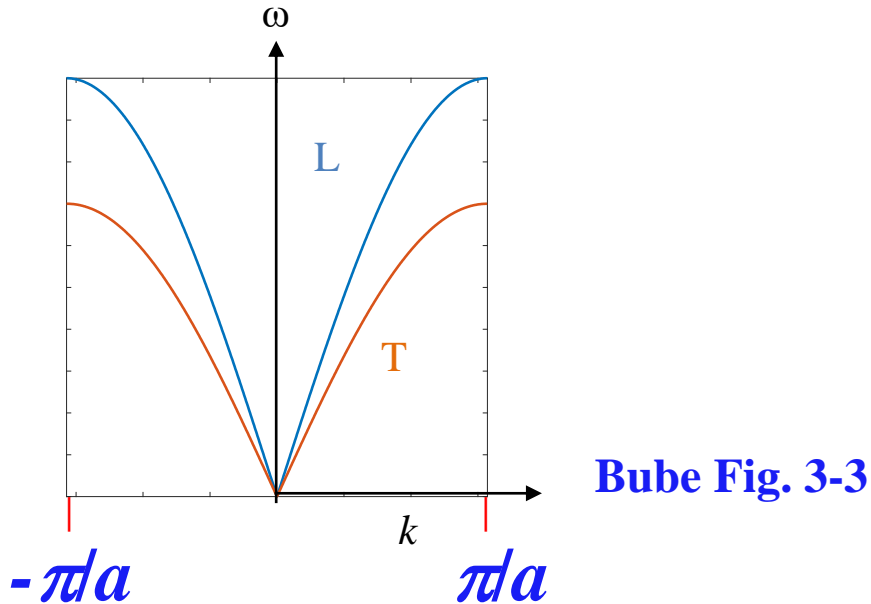
Bloch Wave

Speed of sound in normal air is 343 m/s. In water the speed of sound is 1433 m/s. Sound velocity in some common solids are indicated in the table below:

~300 m/s in air

Medium	Velocity(m/s) (ft/min)
Aluminum, shear - longitudinal wave	3040 - 6420
Beryllium	12890
Brass	3500 - 4700
Brick	3600 - 4200
Concrete	3200 - 3700
Copper	3560 - 3900
Cork	366 - 518
Diamond	12000
Glass	3950 - 5000
Glass, Pyrex	5640
Gold	3240
Granite	5950
Iron	3850 - 5130
Lead	1160 - 1320
Lucite	2680
Rubber, butyl	1830
Rubber	40 - 150
Silver	3650
Steel	4880 - 5050
Steel, stainless	5790
Titanium	6070
Wood (hard)	3960
Wood	3300 - 5000

The transverse mode can be described in similar approach. The only difference is that atoms displace vertically, so the restoring force is weaker than for longitudinal modes. In terms of spring constant, $K_L > K_T$ (L : **longitudinal** mode, T : **transverse** mode).



Coupled oscillator \rightarrow independent normal modes with certain oscillation frequency

Phonon

We have seen in the [simple harmonic oscillators](#) that the energy of an oscillator with the angular frequency of ω is quantized as $(n + 1/2)\hbar\omega$ ($n = 0, 1, 2, \dots$).

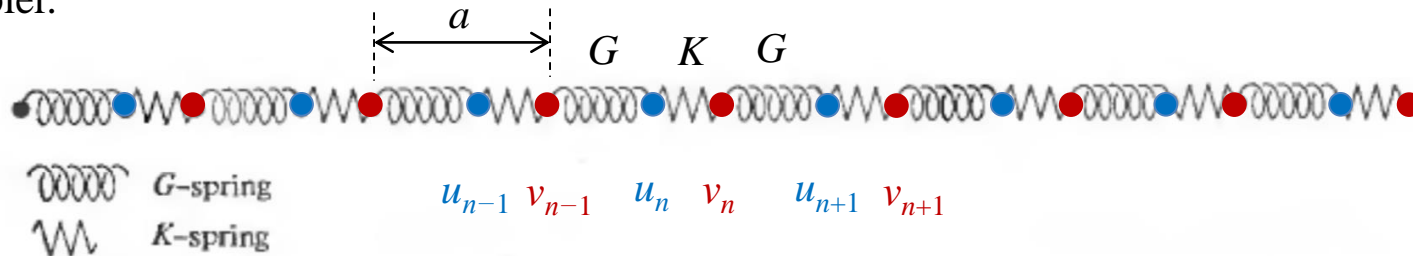
[The same is true for the vibration in solids](#): energy of each normal mode is quantized as $(n + 1/2)\hbar\omega$, meaning that the energy-exchange with lattice waves occurs in integer multiples of $\hbar\omega$.

The quantized vibration is called **phonon**, similar to photon. And, the energy of **phonon is $E_{\text{phonon}} = \hbar\omega = h\nu$** . The **phonon momentum is $\hbar k$** , similar to photon. However, the momentum of the phonon is sometimes called a **phonon crystal momentum** because the lattice wave itself does not have a real physical momentum.

Phonon behaves as if it had a momentum $\hbar k$ in its interactions (**with electrons or photons**) inside the crystal, and is involved in the **momentum conversation** law.

2C.2. 1D Diatomic Lattice

Next, we consider when the unit cell of the 1D lattice contains **two basis atoms**. The two atoms could be **of different kind or the same species** with different left and right spring constants. The two cases give qualitatively the same results so we will assume the latter case because it is slightly simpler.



$$\begin{aligned}
 M \frac{d^2 u_n}{dt^2} &= -K(u_n - v_n) - G(u_n - v_{n-1}) \\
 M \frac{d^2 v_n}{dt^2} &= -K(v_n - u_n) - G(v_n - u_{n+1})
 \end{aligned}
 \quad
 \begin{aligned}
 u_n &= A e^{i(kna - \omega t)} \\
 v_n &= B e^{i(kna - \omega t)}
 \end{aligned}
 \quad
 \begin{aligned}
 [M\omega^2 - (K + G)]A + (K + G e^{-ika})B &= 0 \\
 (K + G e^{ika})A + [M\omega^2 - (K + G)]B &= 0
 \end{aligned}$$

Normal mode

$$\begin{pmatrix}
 M\omega^2 - (K + G) & K + G e^{-ika} \\
 K + G e^{ika} & M\omega^2 - (K + G)
 \end{pmatrix}
 \begin{pmatrix}
 A \\
 B
 \end{pmatrix}
 =
 \begin{pmatrix}
 0 \\
 0
 \end{pmatrix}$$

(Eigenvalue problem of dynamical matrix)

For non-trivial solution, the determinant should be zero.

$$[M\omega^2 - (K + G)]^2 = |K + G e^{-ika}|^2 = K^2 + G^2 + 2KG \cos ka$$

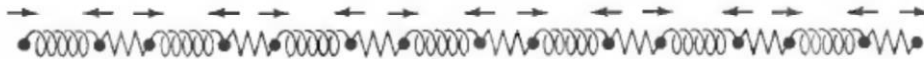
~Bube Fig. 3.5

~Bube Fig. 3.6

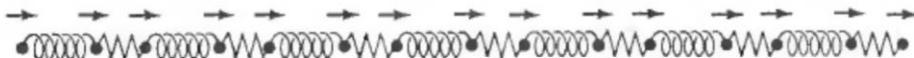
$$\omega^2 = \frac{K+G}{M} \pm \frac{1}{M} \sqrt{K^2 + G^2 + 2KG \cos ka}, \quad \frac{B}{A} = \frac{K + Ge^{ika}}{K + Ge^{-ika}}$$

i) $k \sim 0$ (long wavelength) $\cos ka \sim 1 - (ka)^2/2$

$$\omega = \sqrt{\frac{2(K+G)}{M}} - O(ka)^2, \quad \frac{B}{A} = -1$$



$$\omega = \sqrt{\frac{KG}{2M(K+G)}} |ka|, \quad \frac{B}{A} = 1$$

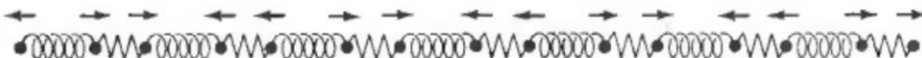


ii) $k = \pi/a$ ($K > G$)

$$\omega = \sqrt{\frac{2K}{M}}, \quad \frac{B}{A} = -1$$



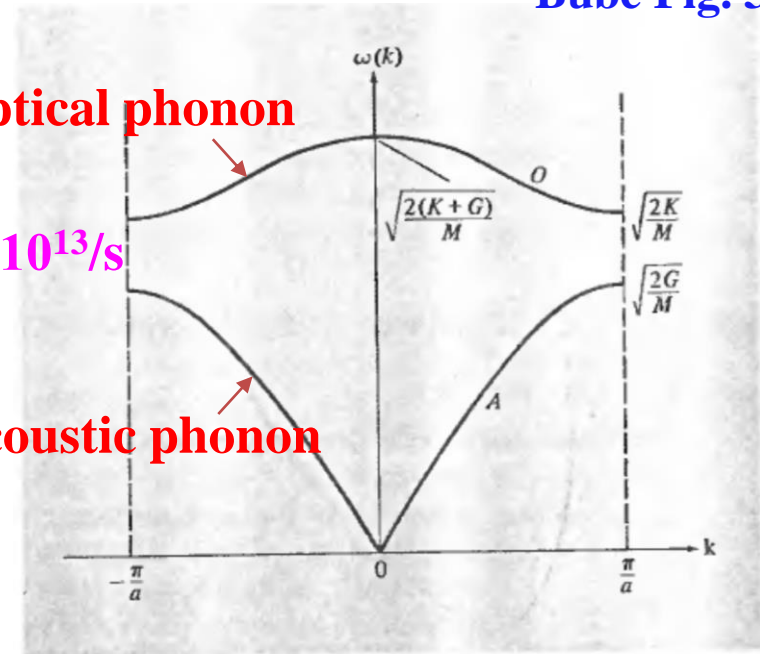
$$\omega = \sqrt{\frac{2G}{M}}, \quad \frac{B}{A} = 1$$



Optical phonon

$\nu \approx 10^{13}/s$

Acoustic phonon



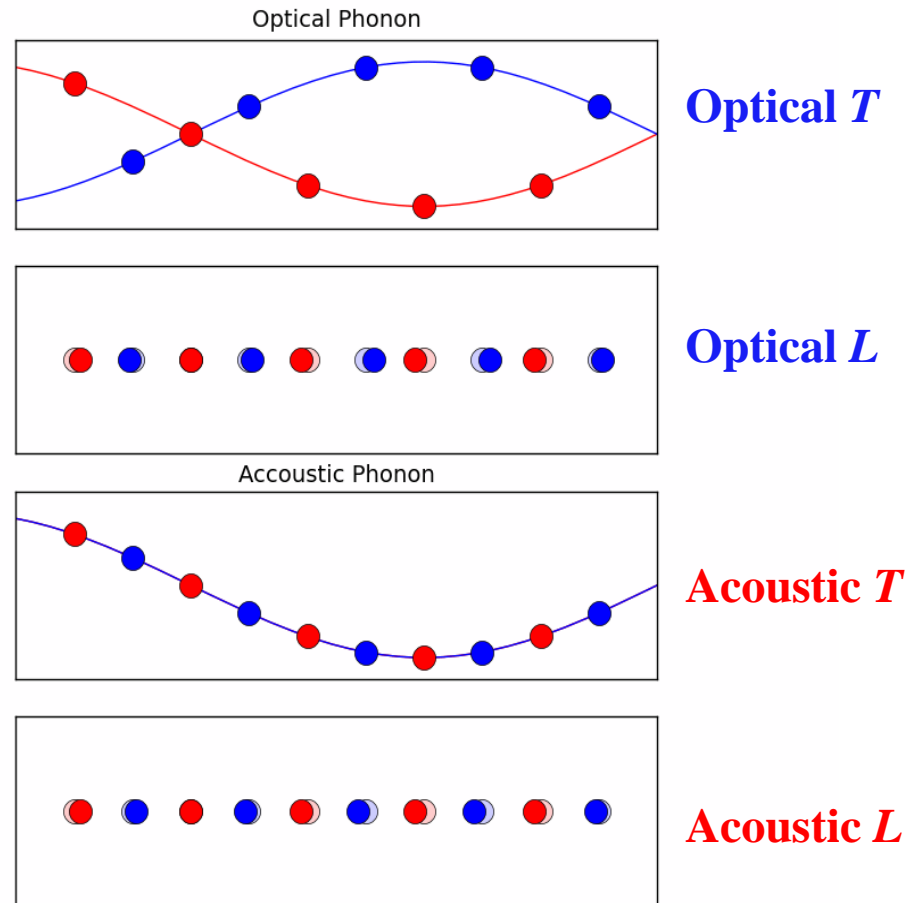
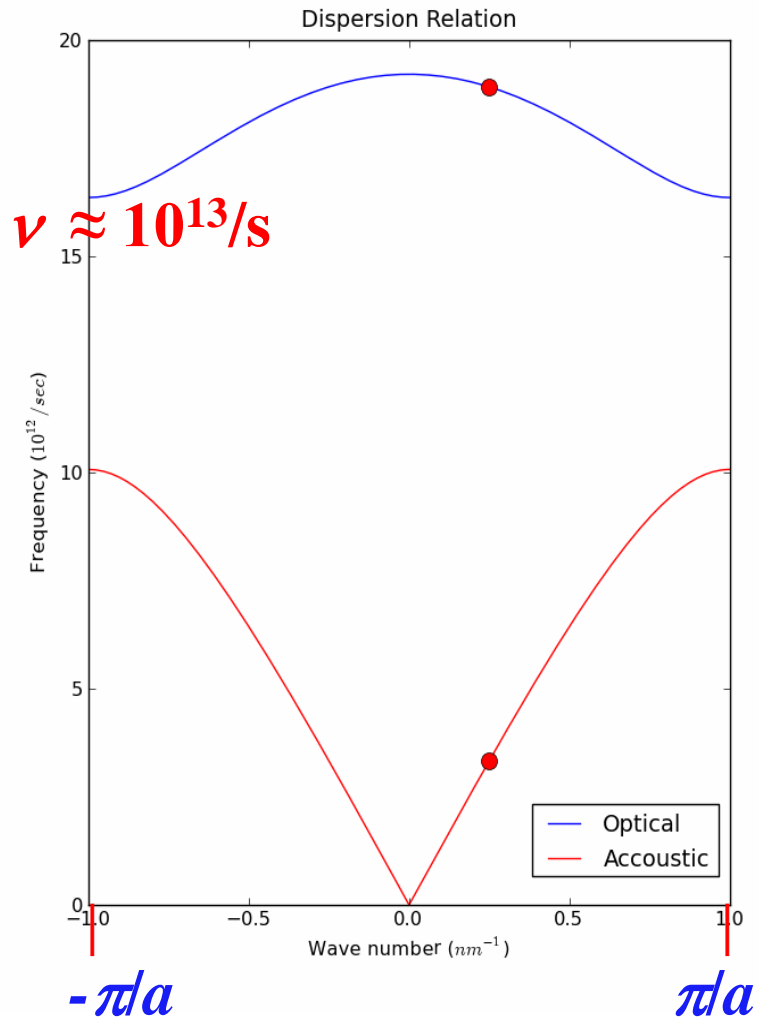
Optical phonons, especially in ionic solids, is critical in electron scattering. This is called optical phonon because it is activated by the electric field as the ions with different charges move in the opposite direction under the electric field.

Fractional Ionic Character:

NaCl = 94%

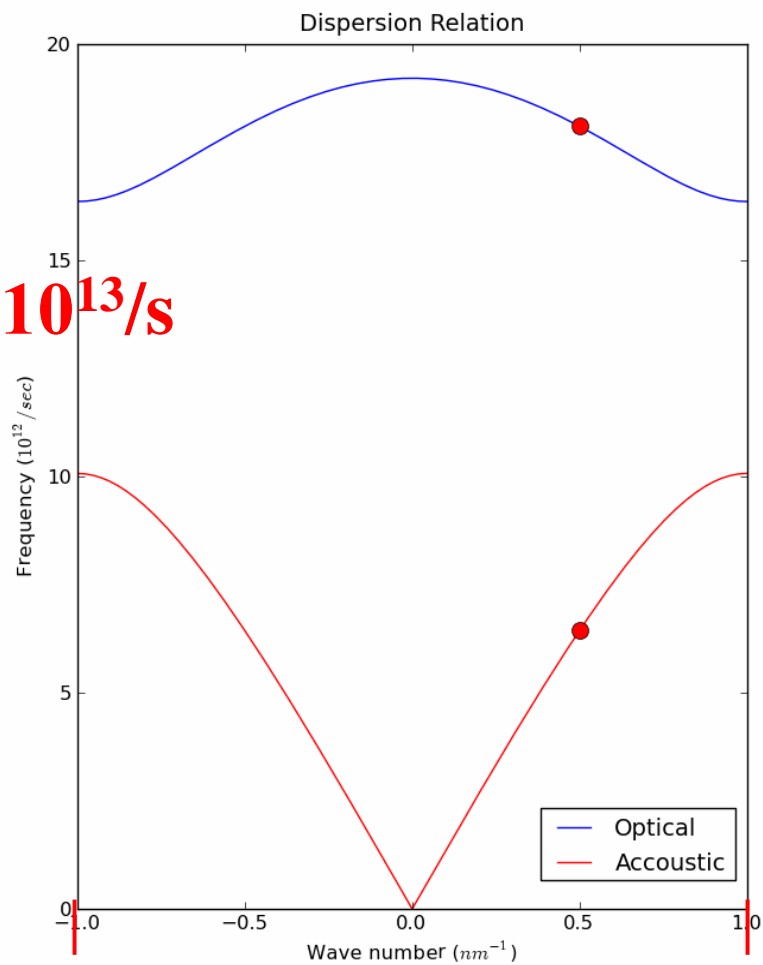
GaAs = 31%

at $k = \pi/4a$ ($\lambda = 8a$)



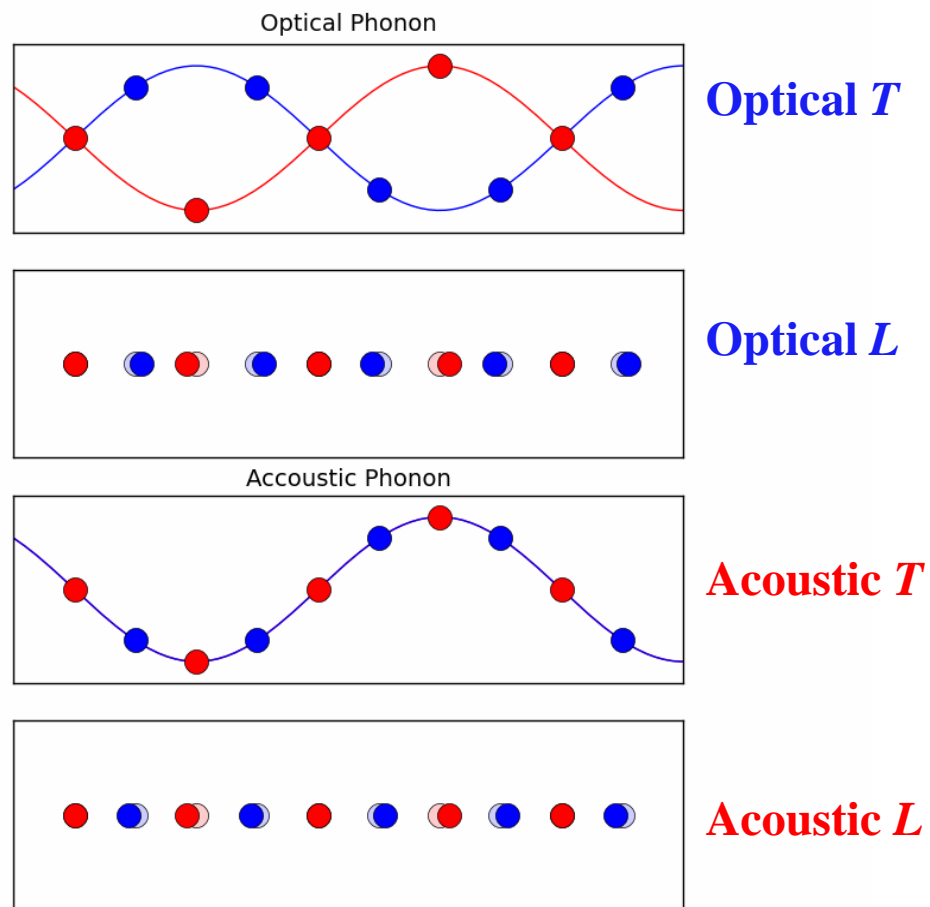
at $k = \pi/2a$ ($\lambda = 4a$)

$\nu \approx 10^{13}/s$



$-\pi/a$

π/a



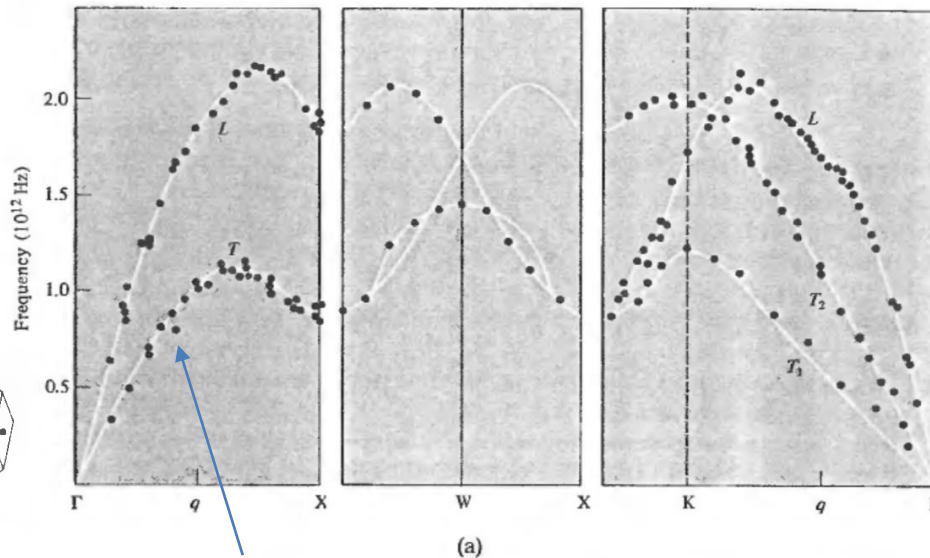
2C.3. Band Structure and DOS of Phonon

In **real 3D** materials with **p number of basis atoms**, for each normal mode identified by k in the 1st BZ, the $3p \times 3p$ dynamical matrix (like K and G) is constructed. This results in **$3p$ normal modes**, among which **three are acoustic branches**. Collecting the (ω, \mathbf{k}) gives the phonon band structure.

Dispersion curves or phonon band structure of fcc Pb. Since there is only one basis atom, only acoustic modes appear.

In 3D, there are two transverse modes for each propagating direction of \mathbf{k} , they are indexed as TA_1 and TA_2 .

THz



FCC

3 Acoustic Branches
 $3(p-1)$ Optical Branches

TA_1 and TA_2 are degenerate.

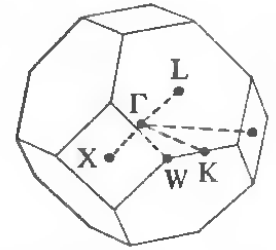
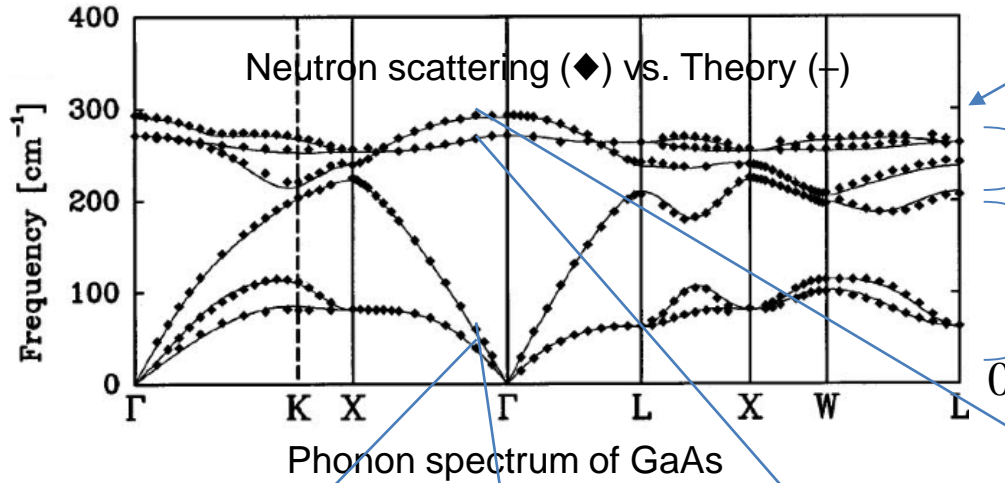
Figure 22.13

(a) Typical dispersion curves for the normal-mode frequencies in a monatomic Bravais lattice. The curves are for lead (face-centered cubic) and are plotted in a repeated-zone scheme along the edges of the shaded triangle shown in (b). Note that the two transverse branches are degenerate in the $[100]$ direction. (After Brockhouse et al., *Phys. Rev.* **128**, 1099 (1962).)

The phonon band structure can be measured to high precision using **neutron inelastic scattering**.

Phonon Band of GaAs (2 basis atoms)

Phonon Energy
 $\approx 9 \text{ THz}$ or
 $\approx 0.037 \text{ eV}$

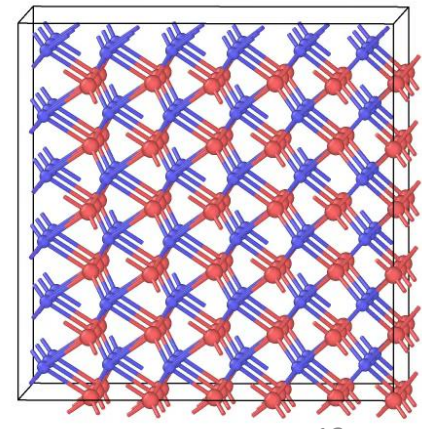
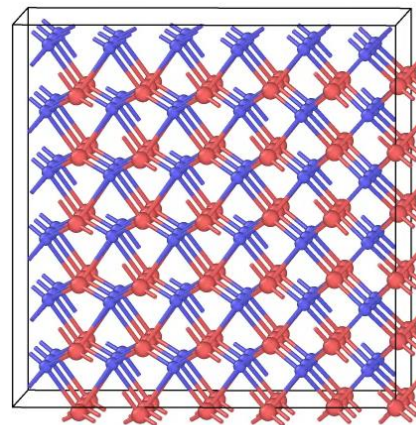
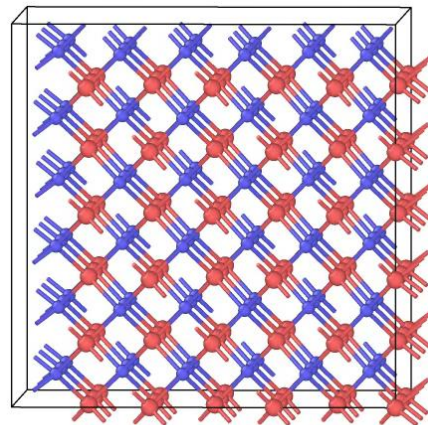
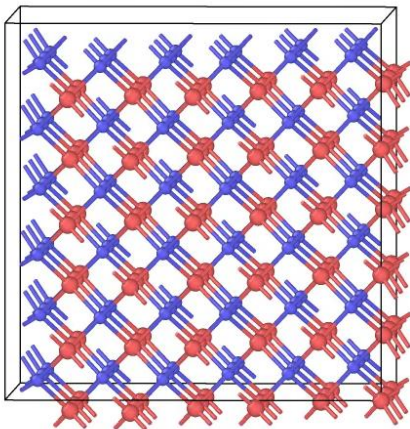


Optical
 Acoustic

Courtesy by Kyuhyun Lee

Note that these modes are all independent.

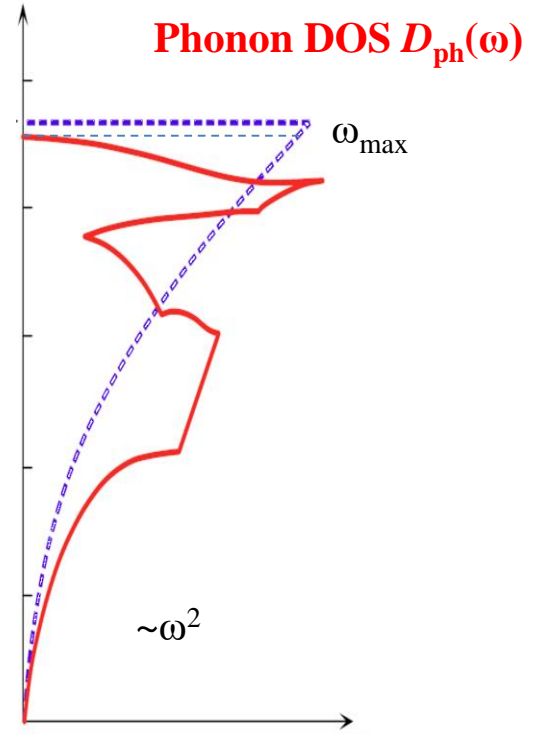
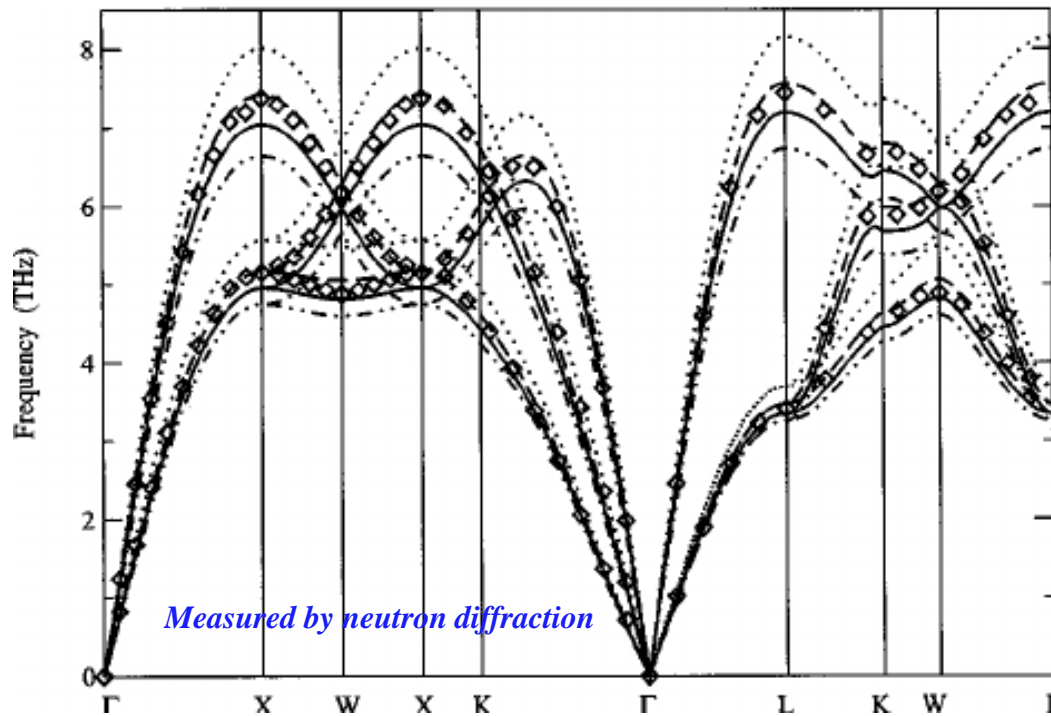
$x \rightarrow$



Transverse acoustic (TA) Longitudinal acoustic (LA) Transverse optical (TO) Longitudinal optical (LO)

Phonon Density of States (DOS)

Like in the electronic band structure, **k is discrete**, rather than continuous, for finite crystals, which can be neatly handled by the periodic boundary condition. The mathematical procedure is exactly the same, which shows that k is discrete with a small spacing, and the number of k points in each band is exactly the same as the number of unit cell in the crystal. Like electronic DOS, this results in the phonon DOS. The total number of normal modes is $3pN = 3 \times (\text{basis atom}) \times (\text{number of unit cell}) = 3 \times (\text{total number of atoms in solid})!$



2B.4
ppt 2B-33

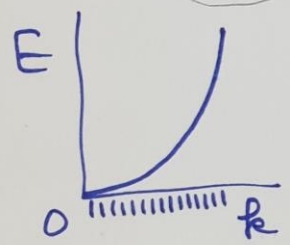
$$-\frac{\rho}{a} < k \leq \frac{\rho}{a} \rightarrow -\frac{\rho}{a} < \frac{2m\rho}{Na} \leq \frac{\rho}{a} \leftrightarrow -\frac{N}{2} < m \leq \frac{N}{2}$$

Electron Density of States (DOS) in Metal and Semiconductor

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m^* L^2} (n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m^*}$$

$$\lambda = \frac{2L}{n}$$

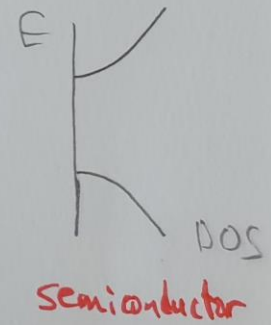
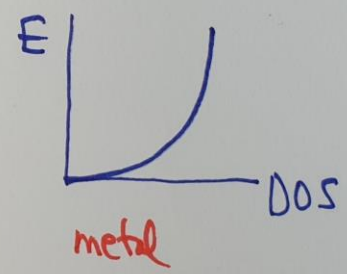
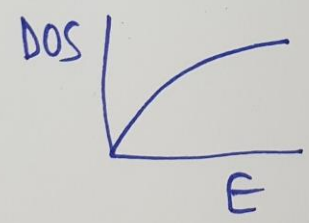
$$k = \frac{\pi n}{L}$$



quantized k space

$$N(E) = \frac{\pi}{6} \left(\frac{E}{E_1} \right)^{3/2}$$

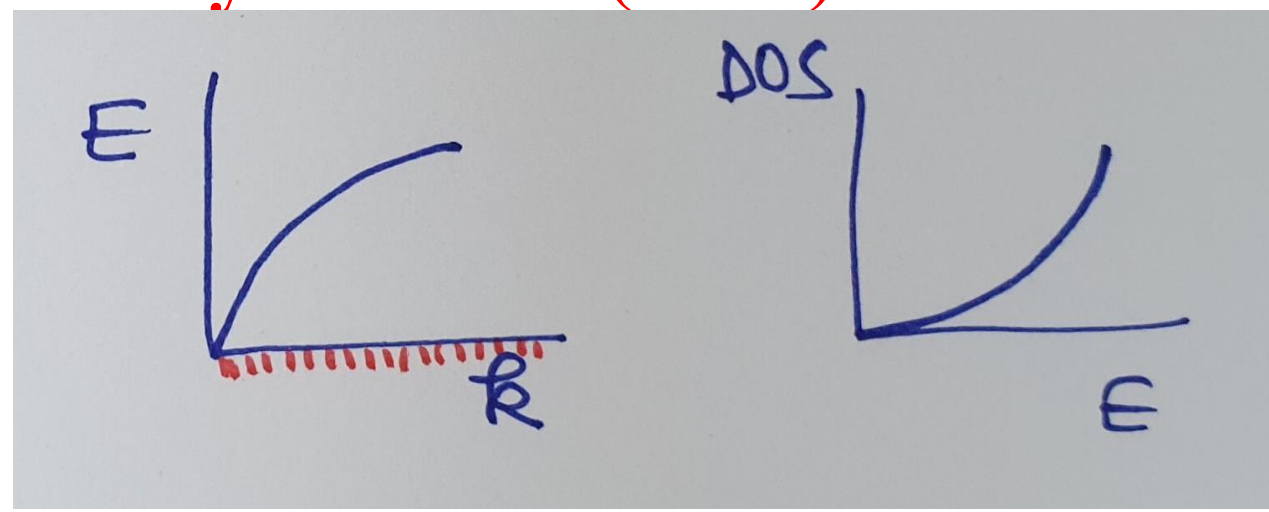
$$\text{DOS} \propto \sqrt{E} \quad D(E) = \frac{1}{4\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E}$$



PPT 2A-8
PPT 2A-9
PPT 2B-2

Phonon Density of States (DOS)

schematically



Mean thermal energy of normal modes

i) Semiclassical approach

At finite T , normal modes vibrate with certain amplitude and carry thermal energies. For a certain normal mode with the angular frequency of ω , the mean energy at T can be calculated using Boltzmann factor. The probability P_n for the oscillator in the n^{th} quantum state is proportional to the Boltzmann factor: $P_n \propto \exp(-E_n/kT)$ where $E_n = n\hbar\omega$. (Here the zero-point energy is neglected.) From normalization condition,

$$P_n = \frac{e^{-n\hbar\omega/kT}}{\sum_{m=0}^{\infty} e^{-m\hbar\omega/kT}} = \frac{e^{-n\hbar\omega/kT}}{1 - e^{-\hbar\omega/kT}} = (1 - e^{-\hbar\omega/kT})^{-1} e^{-n\hbar\omega/kT}$$

The mean energy \bar{E} of the normal mode is then

$$\begin{aligned} \bar{E} &= \sum_{n=0}^{\infty} E_n P_n = \sum_{n=0}^{\infty} n\hbar\omega (1 - e^{-\hbar\omega/kT})^{-1} e^{-n\hbar\omega/kT} \\ &= (1 - e^{-\hbar\omega/kT})^{-1} \hbar\omega \sum_{n=0}^{\infty} n e^{-n\hbar\omega/kT} = (1 - e^{-\hbar\omega/kT})^{-1} \hbar\omega \sum_{n=0}^{\infty} n (e^{-\hbar\omega/kT})^n \\ &= \hbar\omega \frac{e^{-\hbar\omega/kT}}{(1 - e^{-\hbar\omega/kT})} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \end{aligned}$$

$$\sum_{n=0}^{\infty} n x^n = \sum_{n=1}^{\infty} n x^n = \frac{x}{(1-x)^2}$$

ii) Quantum approach

Another way is to consider a normal mode as the bosonic system and each energy quanta as one phonon particle. That is to say, a certain normal mode is a state that can be occupied by phonons. According to the Bose-Einstein statistics, the number of bosons occupying a state with the energy of E is

$$f(E) = \frac{1}{e^{(E-m)/kT} - 1}$$

The chemical potential is zero for phonons or photons because the total number of particles are not conserved and so cannot be a constraint for $f(E)$. (Note that for electrons, μ or E_F was determined by the total number of electrons.) Therefore, the occupation number for the normal mode with the energy of $\hbar\omega$ is

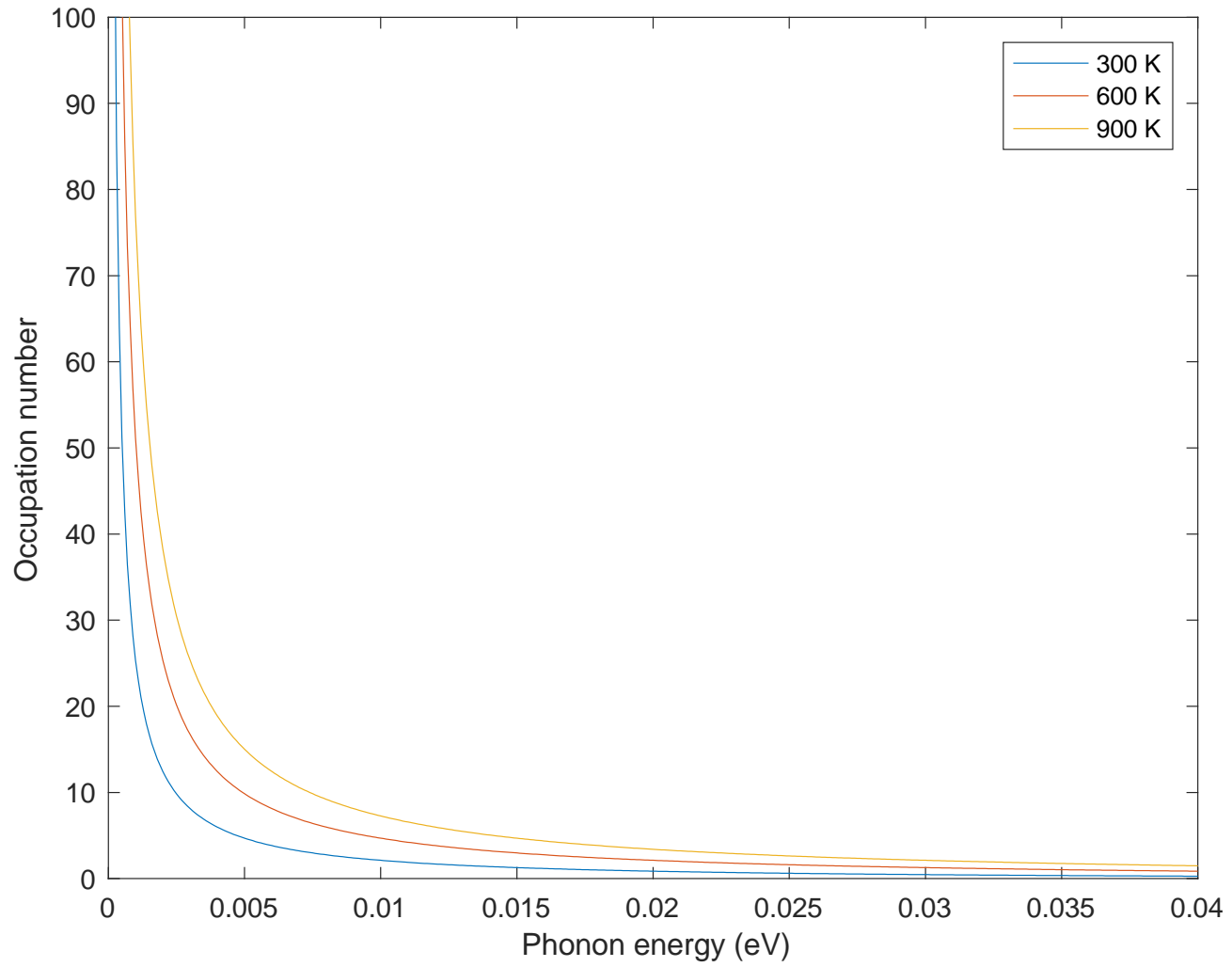
$$f(E) = \frac{1}{e^{\hbar\omega/kT} - 1}$$

The mean energy of the normal mode is then

$$\bar{E} = Ef(E) = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$$

which is the same as the previous result.

For acoustic modes near the zone center, the average energy is kT which is equal to the classical equipartition theorem.

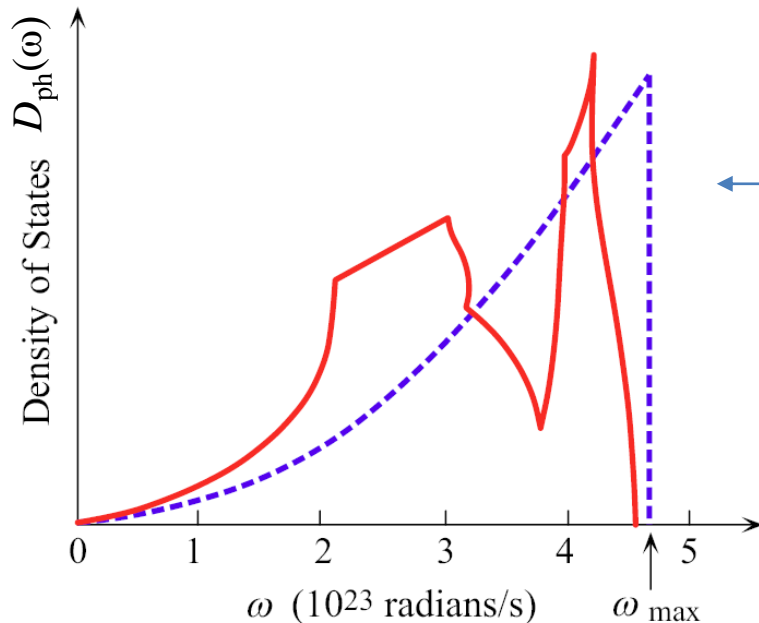


Total energy of lattice vibration (phonons)

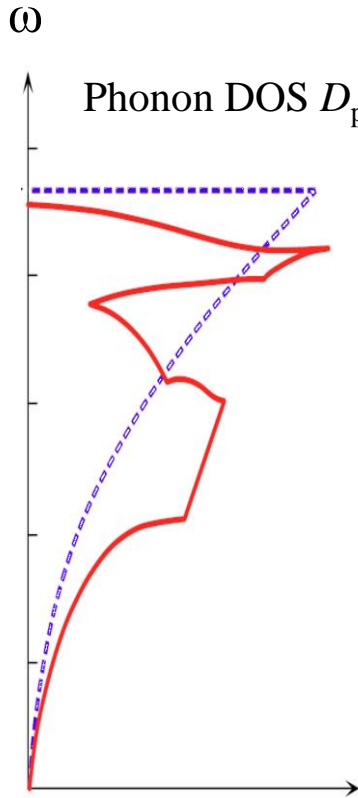
The total energy of phonons is given as follows:

$$U_L = \int_0^{\omega_{\max}} \bar{E}(\omega) D_{\text{ph}}(\omega) d\omega = \int_0^{\omega_{\max}} \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} D_{\text{ph}}(\omega) d\omega$$

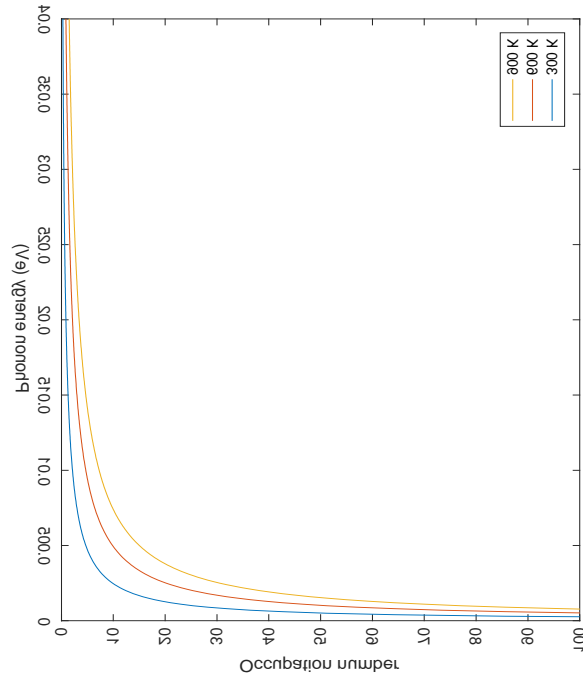
In **Debye approximation**, phonon DOS is simplified by assuming a linear dispersion ($\omega = v|\mathbf{k}|$). This results in $D_{\text{ph}}(\omega) \propto \omega^2$. (v is the effective sound velocity.) ω_{\max} for the Debye model is determined by the fact that the total number of modes up to ω_{\max} should be $3 \times$ (total number of atoms in solid). It is called the Debye frequency. The **Debye temperature** (T_D) is given by $T_D = \hbar\omega_{\max}/k_B$. For detailed expression of the model, please refer to Kittel or Kasap.



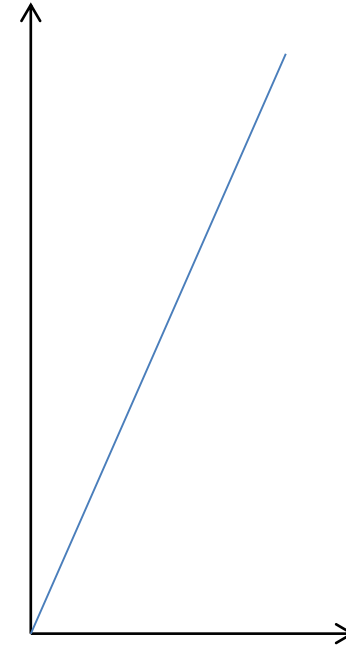
Density of states for phonons in copper. The solid curve is deduced from experiments on neutron scattering. The broken curve is the three-dimensional Debye approximation, scaled such that the areas under the two curves are the same. This requires that $\omega_{\max} \sim 4.5 \times 10^{13} \text{ rad s}^{-1}$, or a Debye characteristic temperature $T_D = 344 \text{ K}$.



$$f(E) = \frac{1}{e^{\hbar\omega/kT} - 1}$$



$$E = \hbar\omega$$



Phonon DOS

×

Occupation number

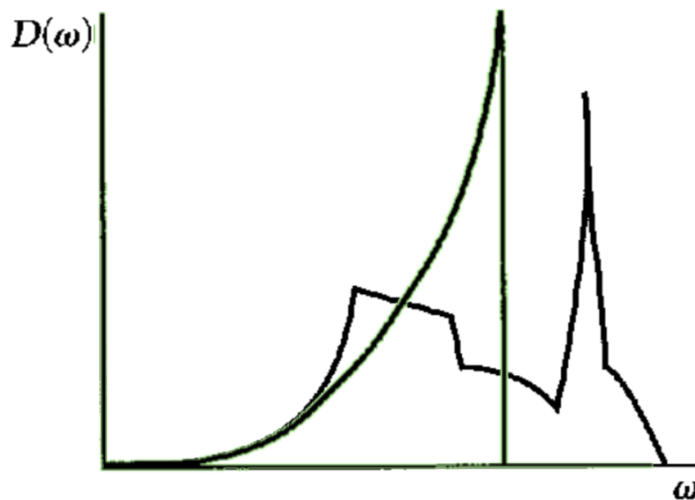
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Phonon energy

The v in the Debye model is the effective sound velocity. It is given by the average of three acoustic modes as follows:

$$\frac{1}{v^3} = \frac{1}{3} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right)$$

where v_L and v_T are sound velocities of longitudinal and transverse modes that are experimentally measured.



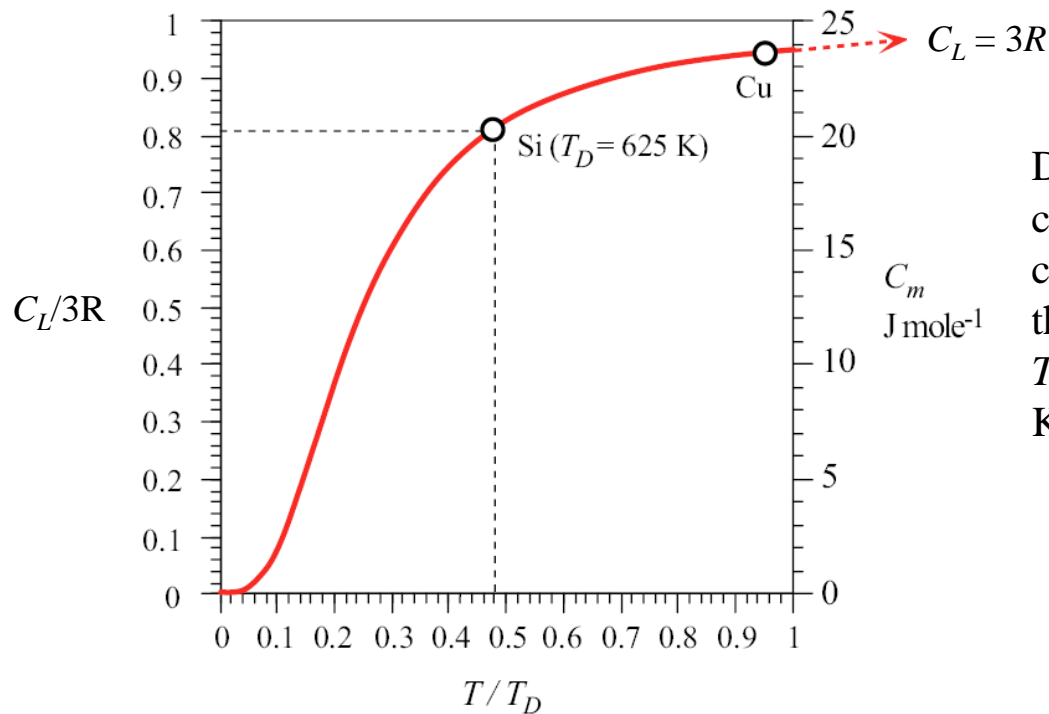
More correct Debye approximation
From Kittel

$$\omega_{\max} \approx v(6\pi^2 N_A/V)^{1/3} \quad (N_A: \text{total number of atoms})$$

and v is related to the hardness (Young's modulus). Therefore, T_D reflects the hardness.

By putting the analytic expression of $D_{\text{ph}}(\omega)$ from the Debye model into the total energy formula and differentiating with respect to temperature gives the following formula for the Debye molar heat capacity.

$$C_L(T) \approx 9R \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2} \quad \rightarrow \quad \begin{cases} C_L \gg 3R = 24.9 & (\text{at high } T > T_D) \\ C_L \propto \left(\frac{T}{T_D} \right)^3 & (\text{at low } T) \end{cases}$$



Debye constant-volume molar heat capacity curve. The dependence of the molar heat capacity C_m on temperature with respect to the Debye temperature: C_L vs. T/T_D . For Si, $T_D = 625 \text{ K}$ so that at room temperature (300 K), $T/T_D = 0.48$ and C_L is only $0.81(3R)$.

Table 4.5 Debye temperatures T_D , heat capacities, and thermal conductivities of selected elements

	Crystal							
	Ag	Be	Cu	Diamond	Ge	Hg	Si	W
T_D (K)*	215	1000	315	1860	360	100	625	310
C_m (J K ⁻¹ mol ⁻¹) [†]	25.6	16.46	24.5	6.48	23.38	27.68	19.74	24.45
c_s (J K ⁻¹ g ⁻¹) [†]	0.237	1.825	0.385	0.540	0.322	0.138	0.703	0.133
κ (W m ⁻¹ K ⁻¹) [†]	429	183	385	1000	60	8.65	148	173

C_m : molar heat capacity

c_s : specific heat capacity