Fundamentals of Solid State Physics

Thermal Properties

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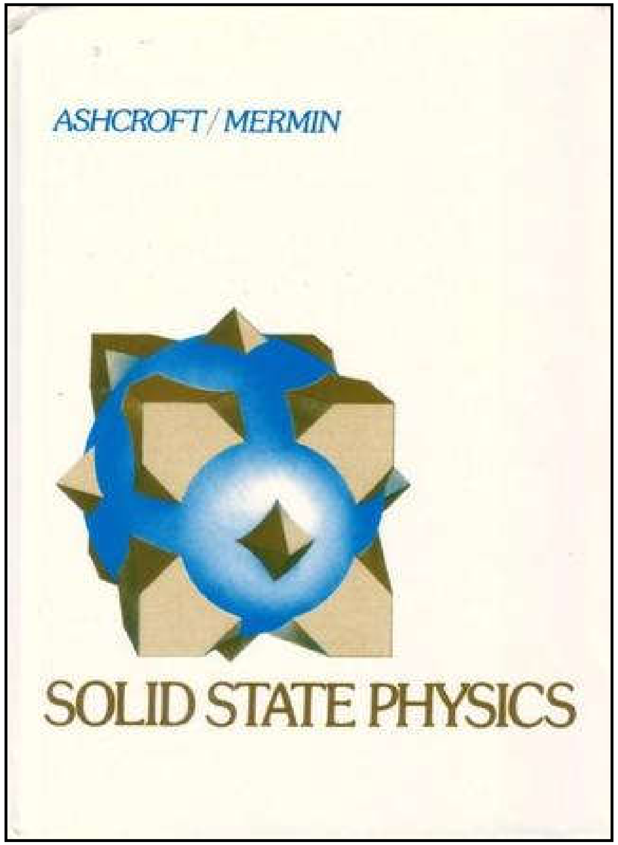
Further Reading

- **Ashcroft & Mermin, Chapter 21, 22, 23**

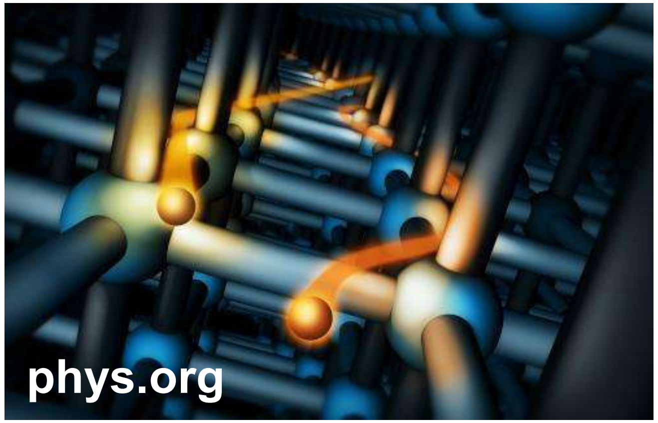


Born-Oppenheimer Approximation

- **Adiabatic Approximation 绝热近似**
- **Static Approximation 定核近似**
  - The behaviors of electrons and nuclei can be calculated separately.

$$\boxed{\Psi_{\text{total}} = \Psi_{\text{electron}} * \Psi_{\text{nuclear}}}$$

  - Electrons move much faster than nuclei
  - When we consider the electronic behaviors, we assume the atomic lattice is static.



Failures of the Static Lattice Model

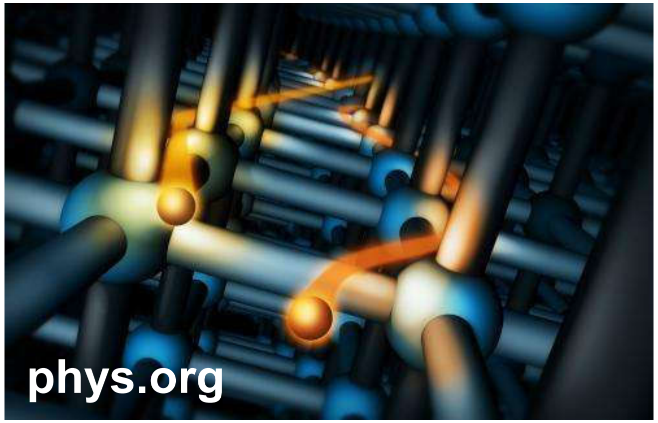
It *cannot* explain

- **Scattering of electrons**
- **Thermal properties**
  - Thermal Capacity
  - Thermal Conductivity
  - Thermal Expansion
- **Mechanical properties**
- ...

$$\sigma = ne\mu = ne^2 \frac{\tau}{m}$$

τ **- relaxation time (s)**

We have to analyze lattice vibration



Born-Oppenheimer Approximation

- Adiabatic Approximation 绝热近似

- The behaviors of electrons and nuclei can be calculated separately.

$$\boxed{\Psi_{total} = \Psi_{electron} * \Psi_{nuclear}}$$

- When we consider the electronic behaviors, we assume the atomic lattice is static.

- When we consider the lattice behaviors, we assume electrons are static.

Fundamentals of Solid State Physics

Lattice Vibration
- Classical Model

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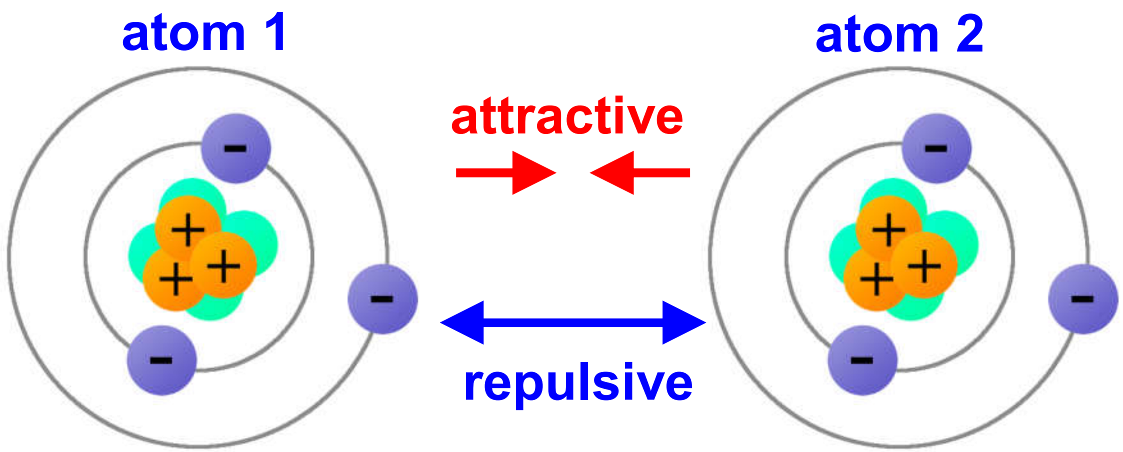
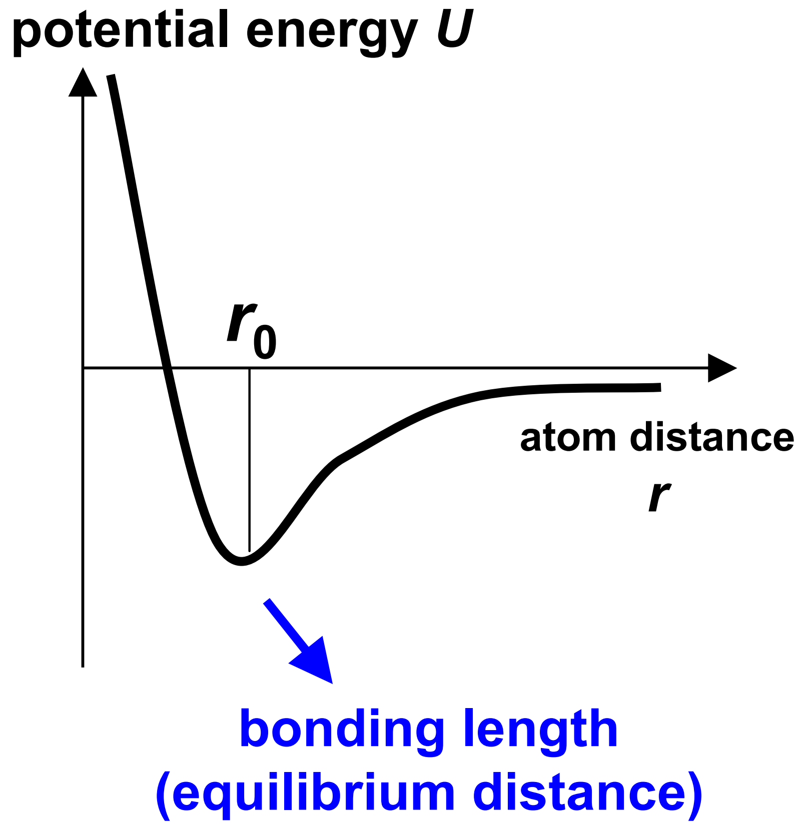
Atomic Interactions





- **Interatomic Potential *U***

$$\boxed{U(r) = U_{\text{repulsion}}(r) - U_{\text{attaction}}(r)}$$

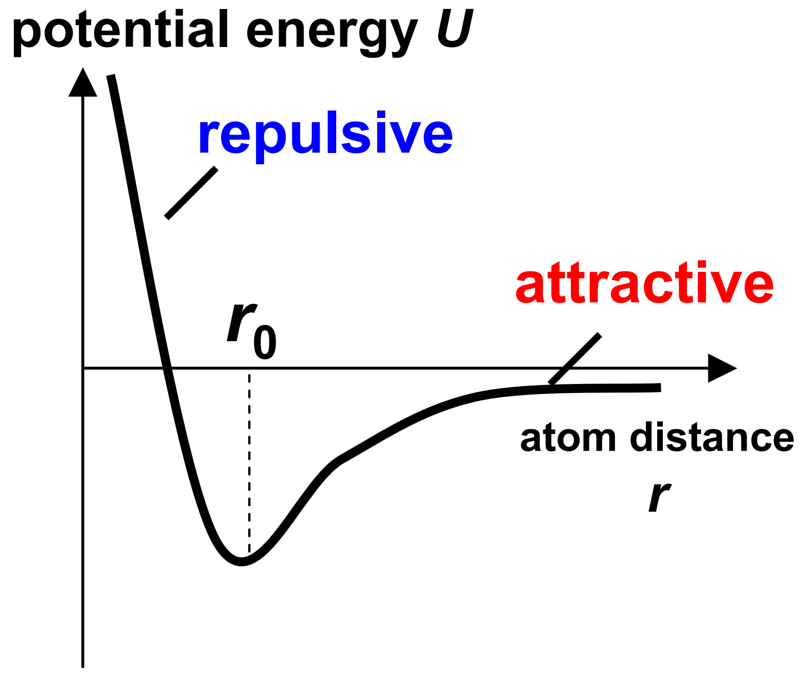
U **- potential energy (J, eV)**
r **- atomic distance (nm, Å)**

Interatomic Potential: Examples

- **Lennard-Jones (L-J)**

$$\boxed{U(r)=\frac{A}{r^{12}}-\frac{B}{r^{6}}}$$

repulsive attractive



- **Ionic Crystals**

$$\boxed{U(r)=A\exp\left(\frac{r}{\rho}\right)-\frac{B}{r}}$$

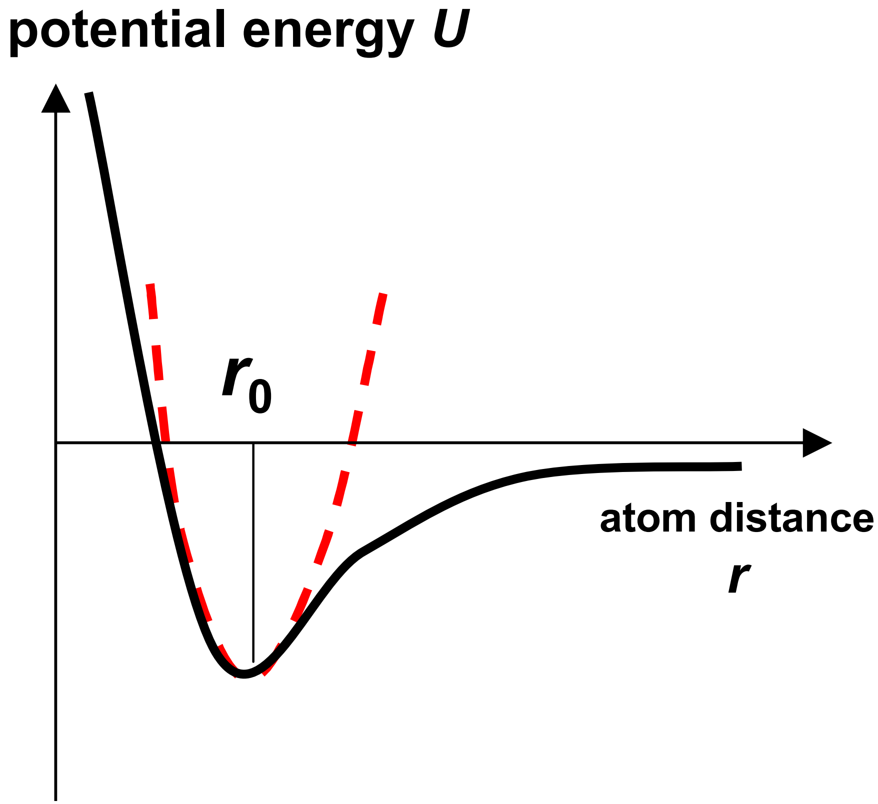
repulsive attractive

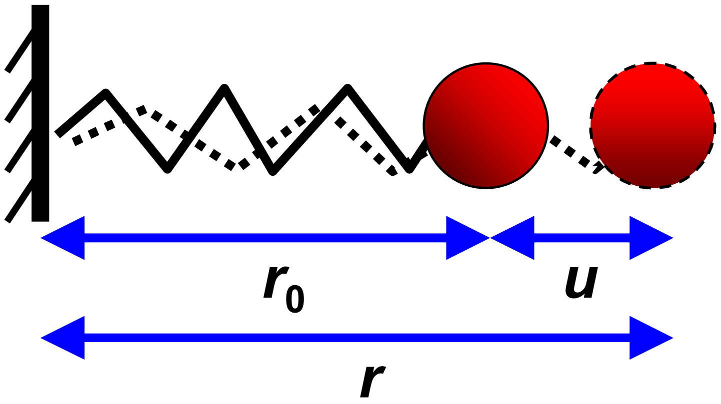
- **Morse Potential**

$$\boxed{U(r)=D\left(e^{-2a(r-r_0)}-2e^{-a(r-r_0)}\right)}$$

repulsive attractive

Atomic Interactions





Harmonic Approximation (parabolic curve)

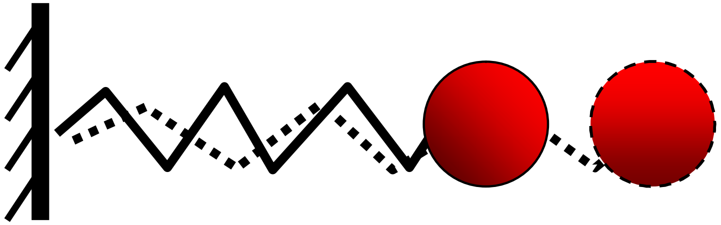
$$U(r) = U_0 + \frac{1}{2}K(r - r_0)^2$$
$$= U_0 + \frac{1}{2}K \cdot u^2$$

$$F = -\frac{\partial U}{\partial r} = -K \cdot u$$

Hooke's Law

K **- spring constant (N/m)**
u **- atomic displacement (m)**

Harmonic Oscillator 谐振子



$$F = -\frac{\partial V}{\partial r} = -K \cdot u$$

Hooke's Law

$$F = m\frac{\partial v}{\partial t} = m\frac{\partial^2 u}{\partial t^2}$$

Newton's Second Law

$$\rightarrow \quad m\frac{\partial^2 u}{\partial t^2} + Ku = 0$$

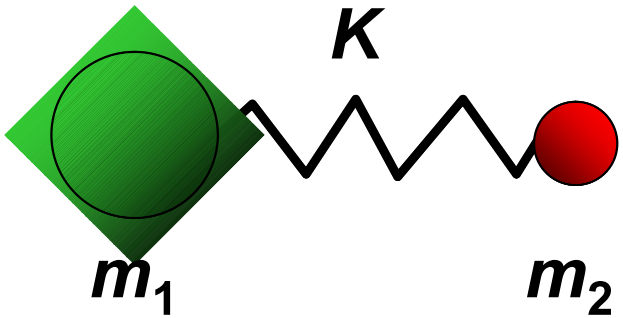
$$\rightarrow \quad u = Ae^{-i\omega t}$$

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

ω - angular frequency (Hz)

Diatomic Molecule 双原子分子

Homework 8.1

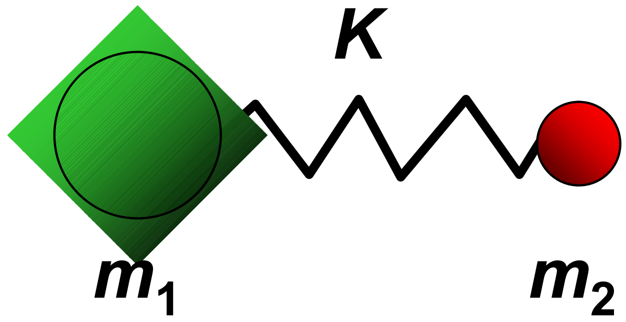


$$\omega = \sqrt{\frac{K}{m^*}} = \sqrt{\frac{m_1 + m_2}{m_1 m_2} K}$$

ω - angular frequency (Hz)
m^* - reduced mass (kg)

Diatomic Molecule 双原子分子

Homework 8.1



$$\omega = \sqrt{\frac{K}{m^*}} = \sqrt{\frac{m_1 + m_2}{m_1 m_2} K}$$

ω - angular frequency (Hz)
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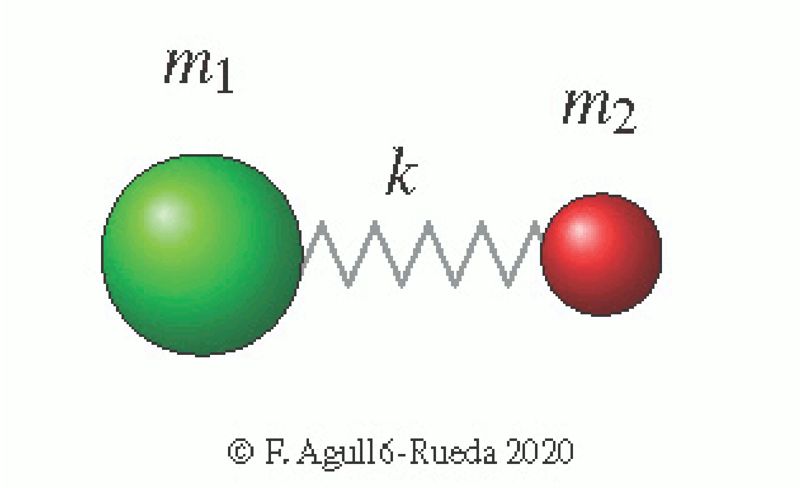
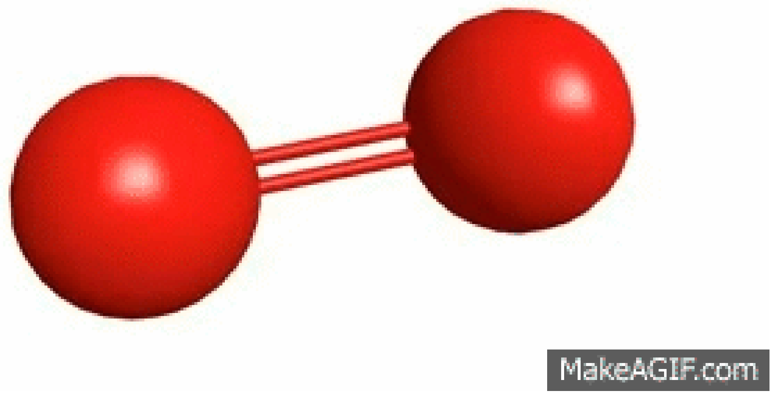
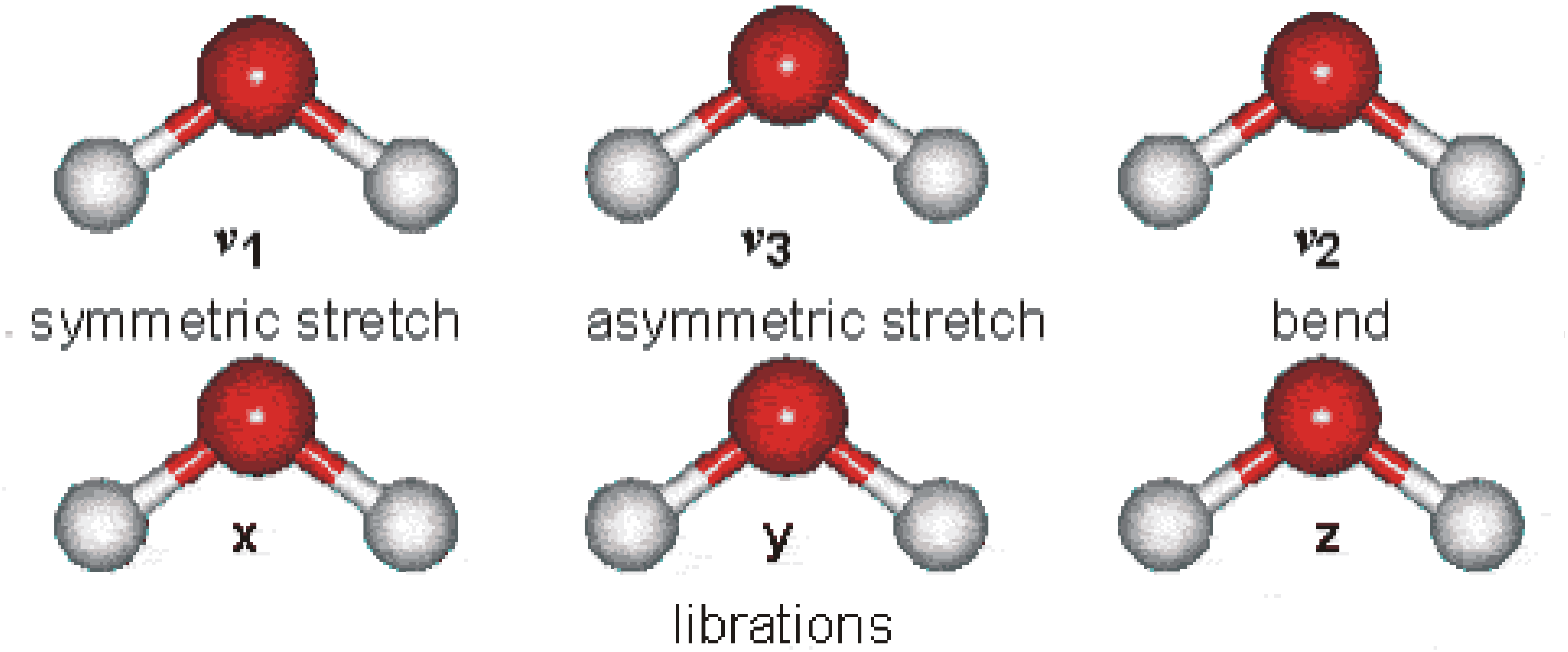
CO molecule



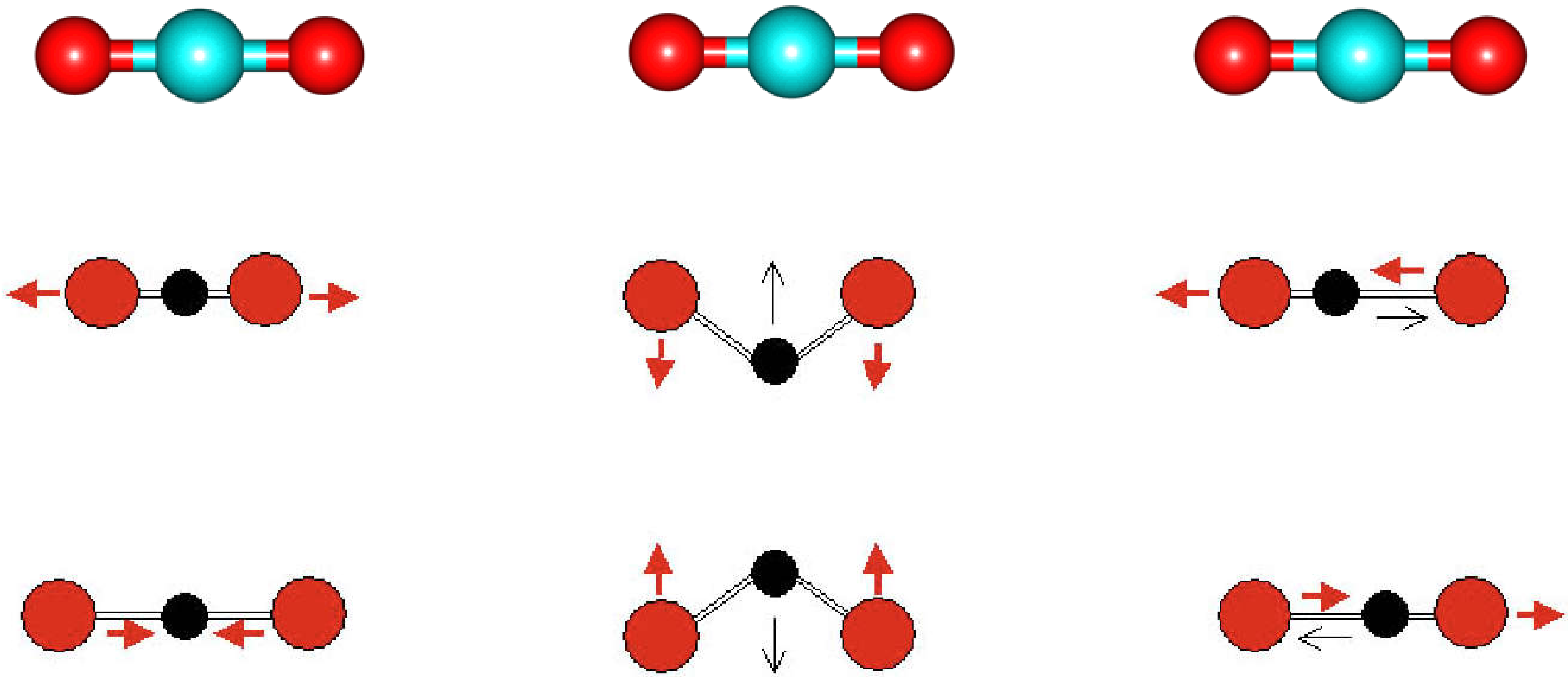
O_2 molecule



H_2O Vibration



CO_2 Vibration



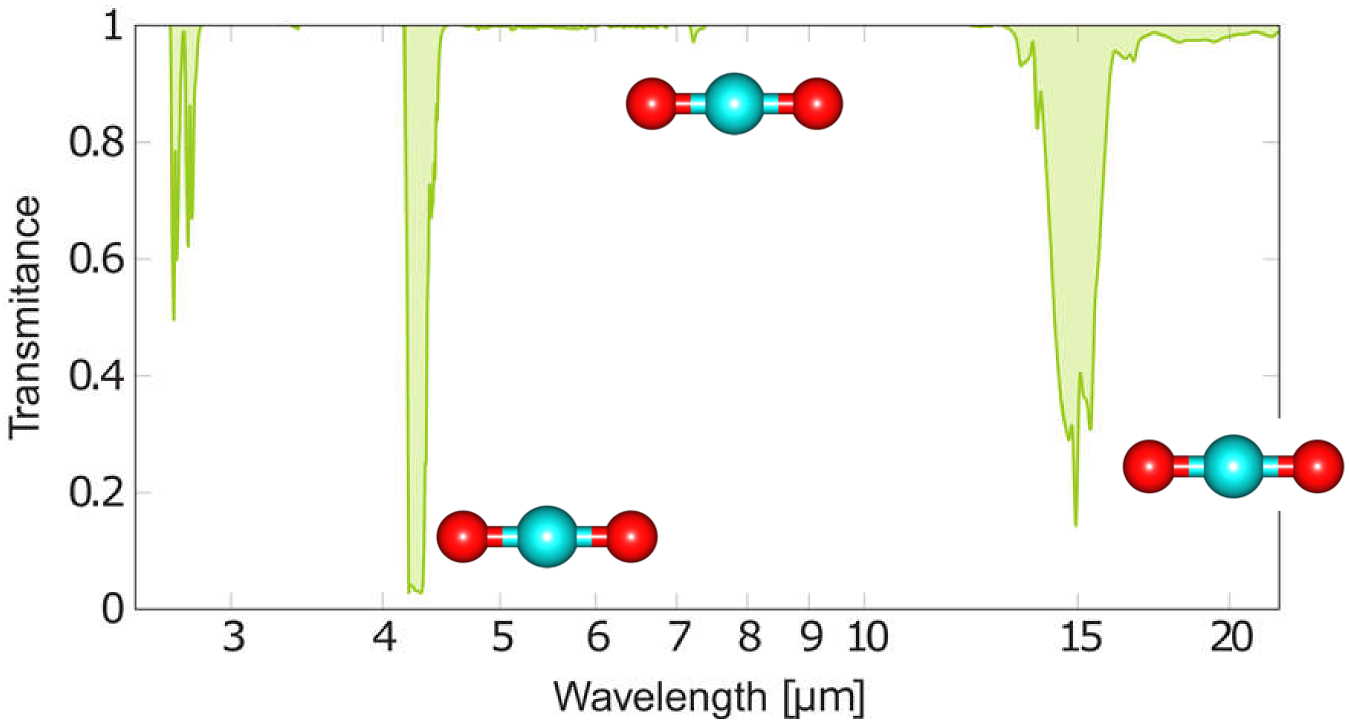
Symmetric Stretch
1366 cm^{-1} or 7.32 μm

Bending
667 cm^{-1} or 15 μm

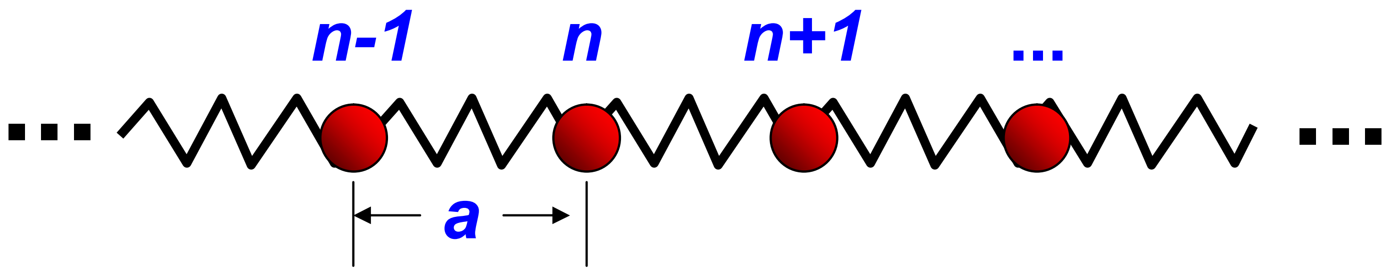
Asymmetric Stretch
2349 cm^{-1} or 4.23 μm

Molecule Vibration

- Vibration modes of molecules can be measured by **infrared absorption spectrum**
- Infrared absorption of CO_2 causes **greenhouse effect**



1D *Monatomic* Chain 单原子链



$$F = m\frac{\partial^2 u}{\partial t^2} \rightarrow m\frac{\partial^2 u_n}{\partial t^2} + K(u_n - u_{n-1}) + K(u_n - u_{n+1}) = 0$$

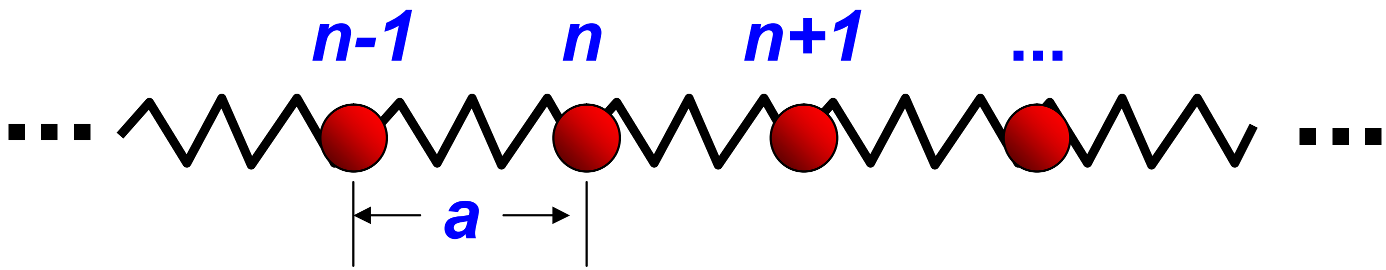
$$\rightarrow u_n = Ae^{i(kx-\omega t)}$$

Wave Function

Acoustic Wave (声波)
Elastic Wave (弹性波)
Mechanical Wave (机械波)
Lattice Wave (格波)
...

k **- wave vector (m^{-1})**
ω **- angular frequency (Hz)**

1D *Monatomic* Chain 单原子链



$$F = m\frac{\partial^2 u}{\partial t^2}$$

$$m\frac{\partial^2 u_n}{\partial t^2} + K(u_n - u_{n-1}) + K(u_n - u_{n+1}) = 0$$

$$u_n = Ae^{i(kx-\omega t)}$$

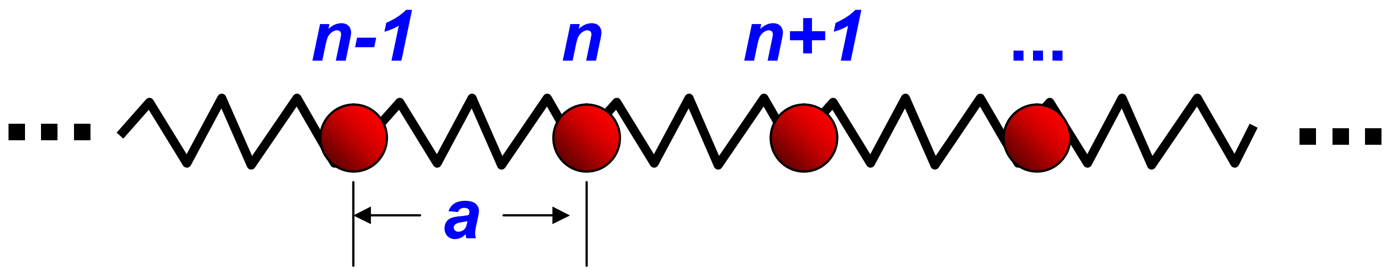
Wave Function

$$u_{n\pm1} = Ae^{i(kx-\omega t)}e^{\pm ika}$$

k **- wave vector (m^{-1})**

ω **- angular frequency (Hz)**

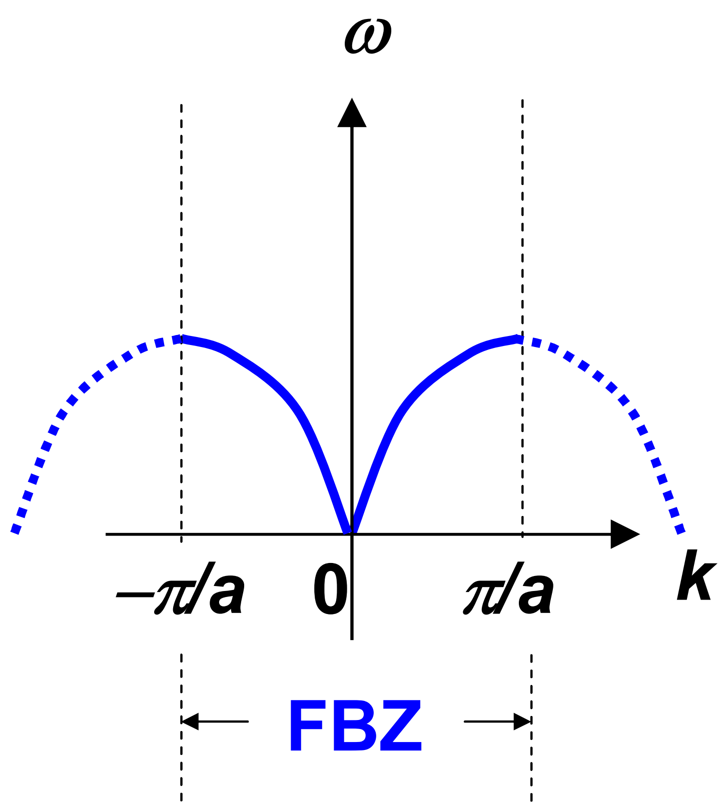
1D *Monatomic* Chain



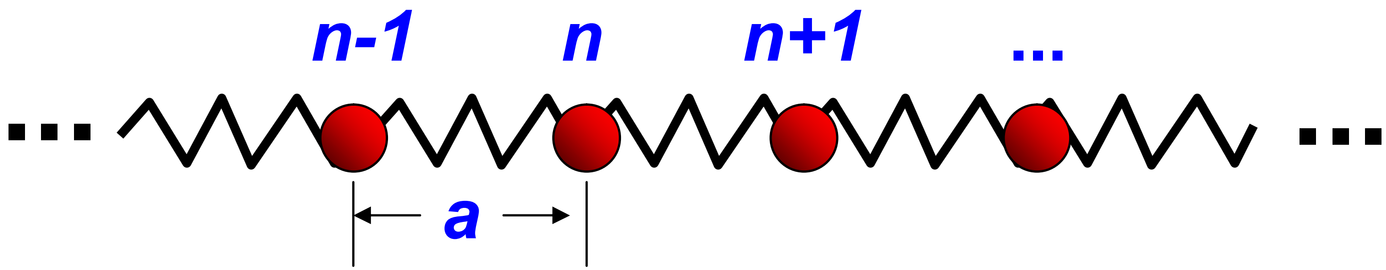
$$\omega^2 = \frac{K}{m}\left(2 - e^{-ika} - e^{+ika}\right)$$
$$= \frac{4K}{m}\sin^2\left(\frac{ak}{2}\right)$$

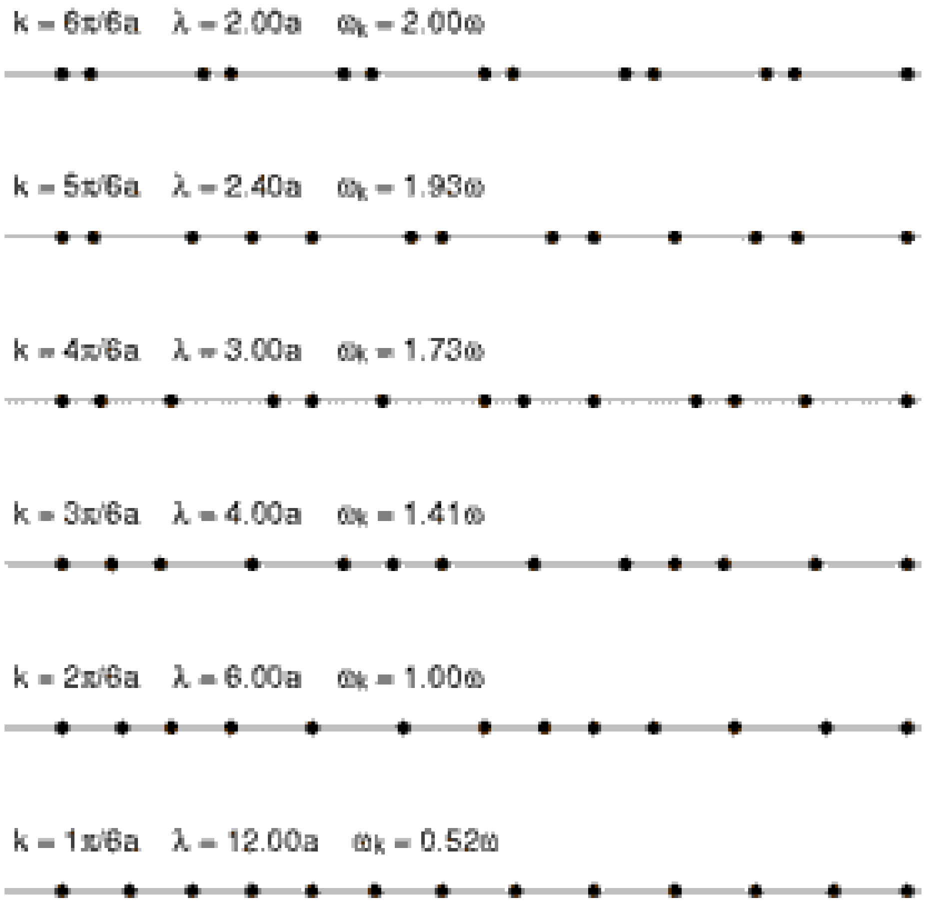
$$\omega = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{ak}{2}\right)\right|$$

ω-*k* diagram (dispersion curve)

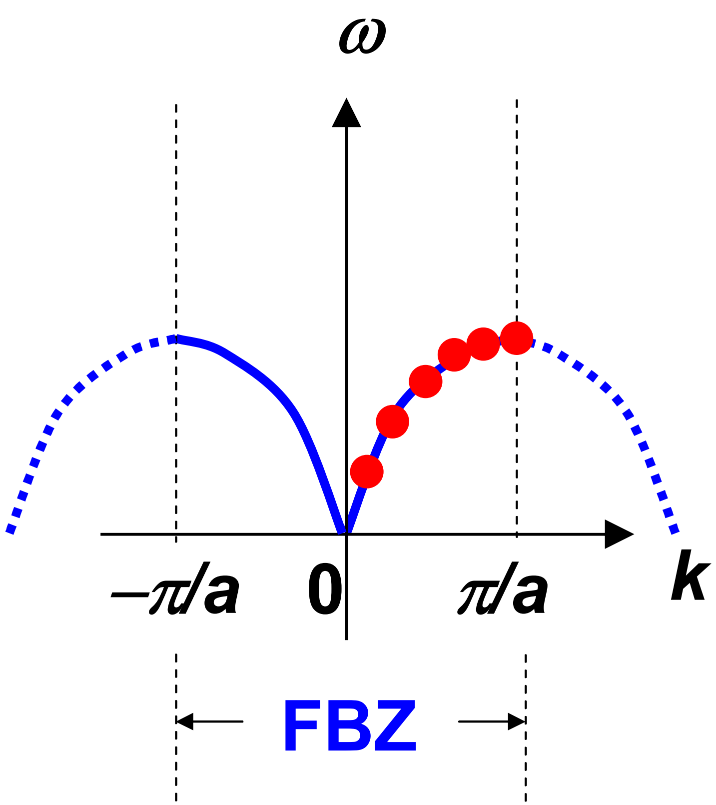


1D *Monatomic* Chain





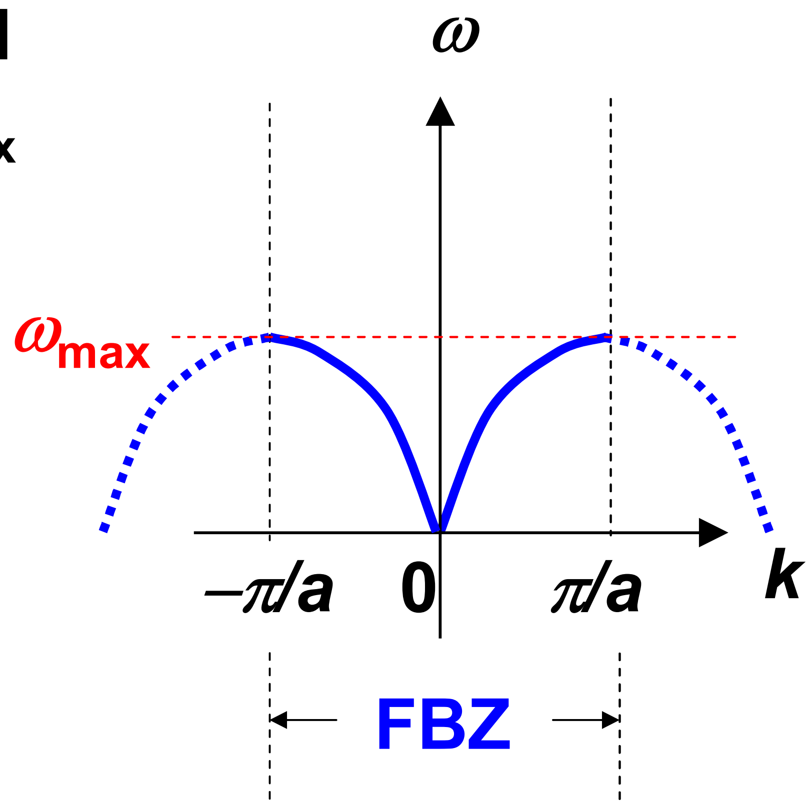
ω-*k* diagram (dispersion curve)



1D *Monatomic* Chain

- **Crystals cannot transmit sound above the cutoff frequency ω_{max}**

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



- **Phase velocity** $v_p = \omega / k$

- **Group velocity** $v_g = \partial\omega / \partial k$

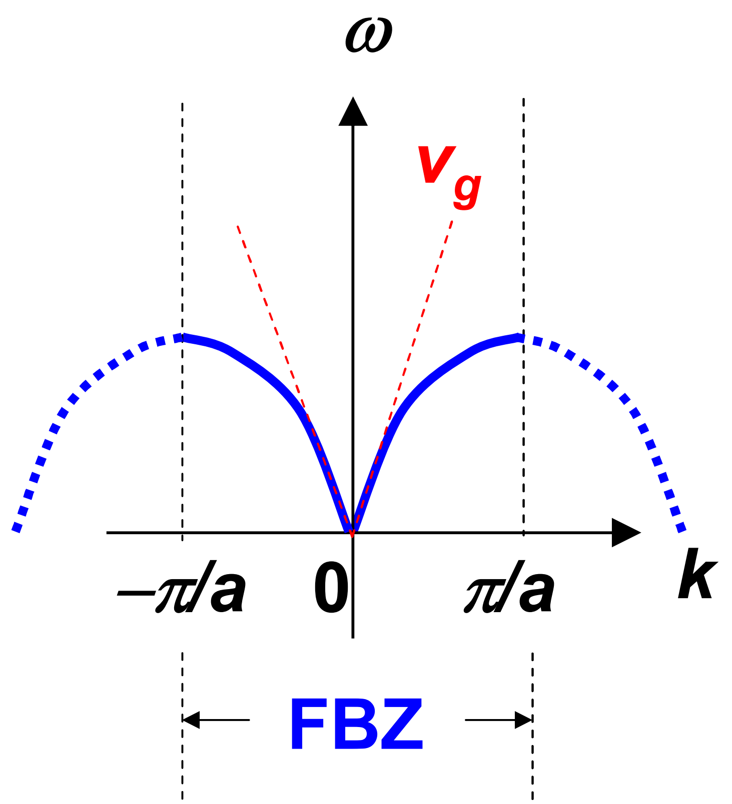
- **Standing wave (v_g = 0) at** $k = \pm\dfrac{\pi}{a}$

Speed of Sound 声速

- At long wavelength limit *ka* ~ 0, **speed of sound** is a constant **independent of frequency**

$$\omega = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{ak}{2}\right)\right| \approx \sqrt{\frac{K}{m}}ak$$

$$v_g = \partial\omega/\partial k$$
$$= a\sqrt{\frac{K}{m}}$$

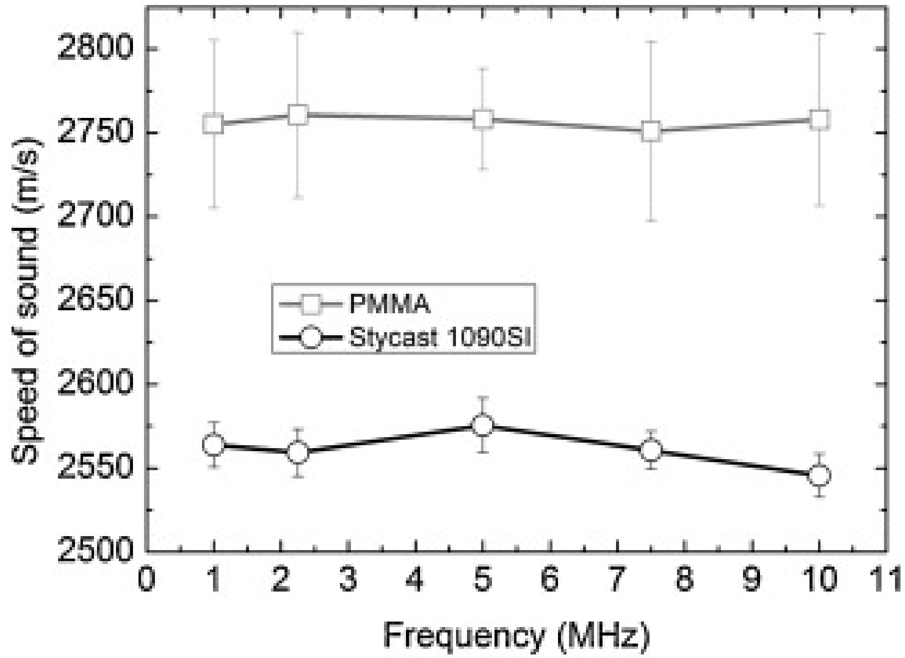


Speed of Sound 声速

- At long wavelength limit *ka* ~ 0, speed of sound is a constant independent of frequency

$$v_g = \partial\omega / \partial k$$
$$= a\sqrt{\frac{K}{m}}$$

sound speed in solids



W. Xia, *et al.*, *Photoacoustics* **1,** 9 (2013)

Speed of Sound 声速

- At long wavelength limit *ka* ~ 0, **speed of sound** is a constant **independent of frequency**

$$
\begin{aligned}
v_g &= \partial\omega / \partial k \\
&= a\sqrt{\frac{K}{m}}
\end{aligned}
$$

Material	Speed of Sound (m/s)
Rubber	60
Lead	1210
Gold	3240
Copper	4600
Aluminum	6320

http://www.classltd.com

- Higher v_g requires
  - stronger bonds (K)
  - smaller atoms (m)

Q: Which material has the highest sound speed?

Young's Modulus *E* 弹性模量

- ***E*** **(unit: Pa): stress σ divided by strain ε**
  - **stress σ: force per unit area**
  - **strain ε: ratio of elongation**

$$F = K \cdot u$$

$$E = \frac{\sigma}{\varepsilon} = \frac{F/a^2}{u/a} = K/a$$

$$= v_g^2 \frac{m}{a^3}$$

$$= v_g^2 \rho$$

or

$$v_g = \sqrt{\frac{E}{\rho}}$$

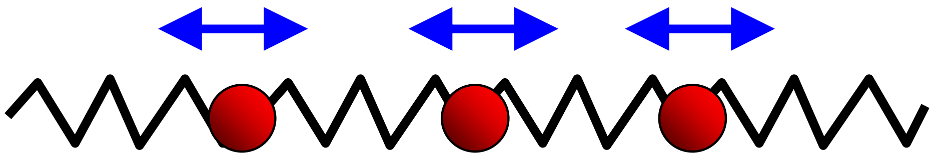
macroscopic properties

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

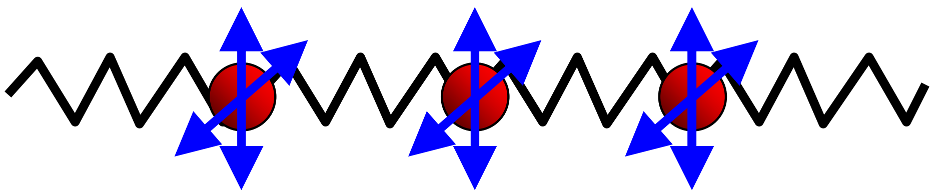
microscopic properties

ρ **- material density (kg/m^3)**

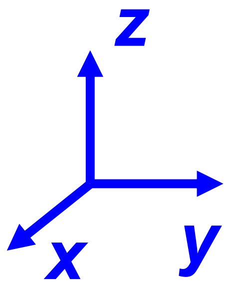
1D *Monatomic* Chain

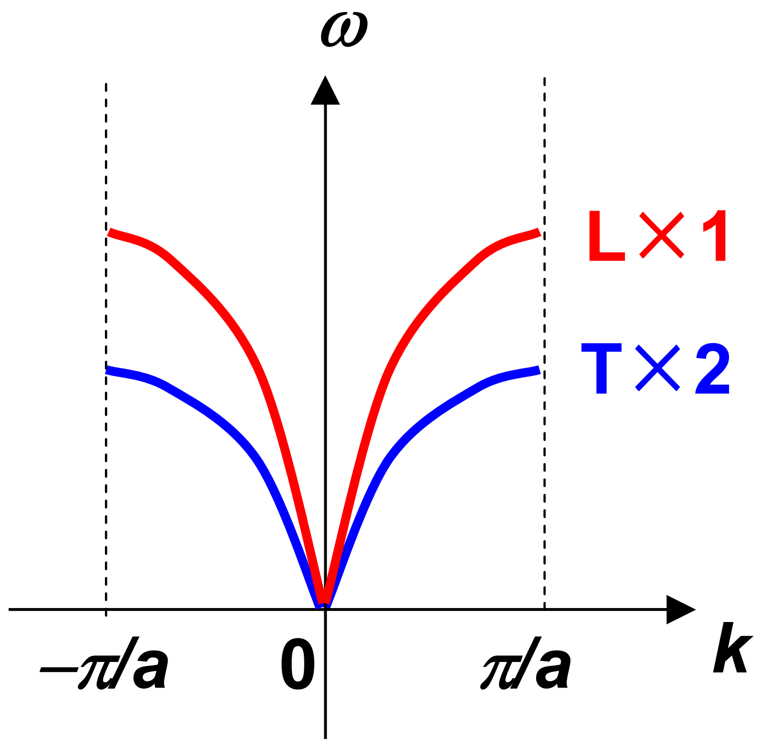


Longitudinal (L) 纵波×1



Transverse (T) 横波×2



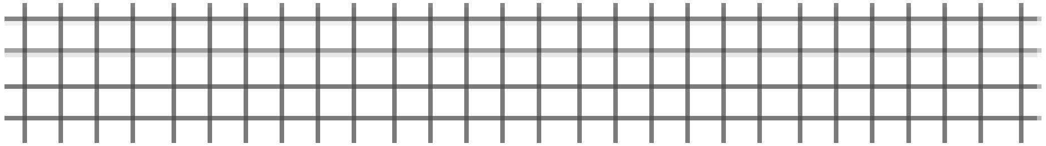


$$\omega = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{ak}{2}\right)\right|$$

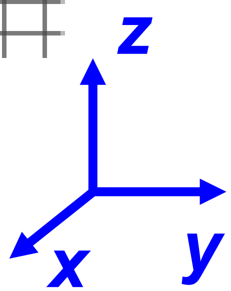
$$K_L > K_T$$

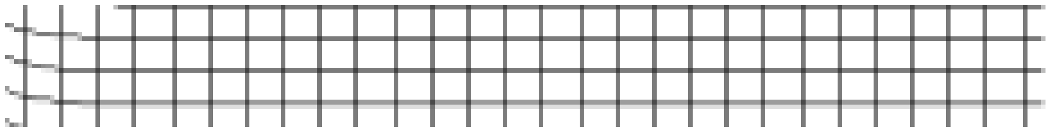
$$v_{gL} > v_{gT}$$

1D *Monatomic* Chain

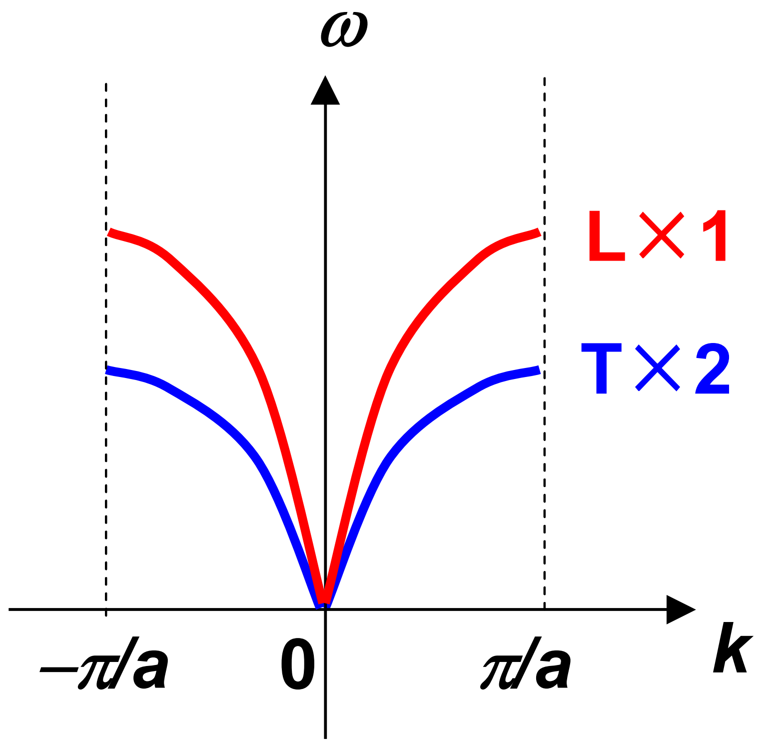


Longitudinal (L) 纵波×1





Transverse (T) 横波×2



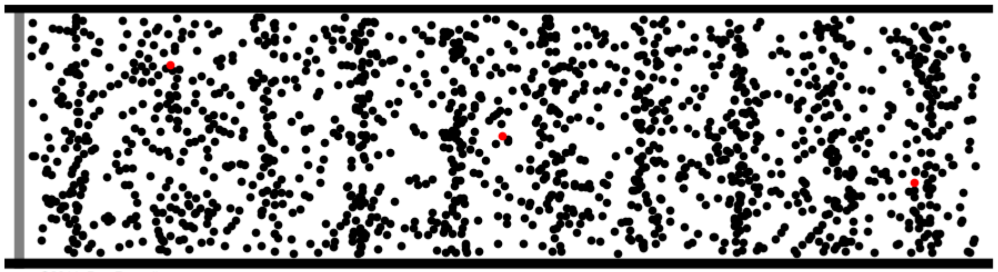
$$\omega = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{ak}{2}\right)\right|$$

$$K_L > K_T$$

$$v_{gL} > v_{gT}$$

Seismic Waves 地震波

$$\boxed{v_{gL} > v_{gT}}$$



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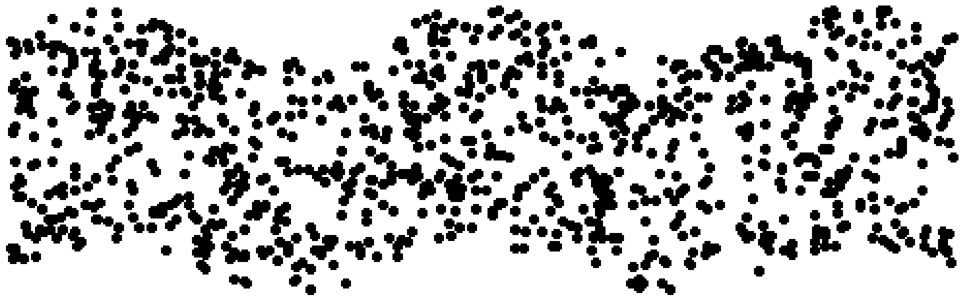
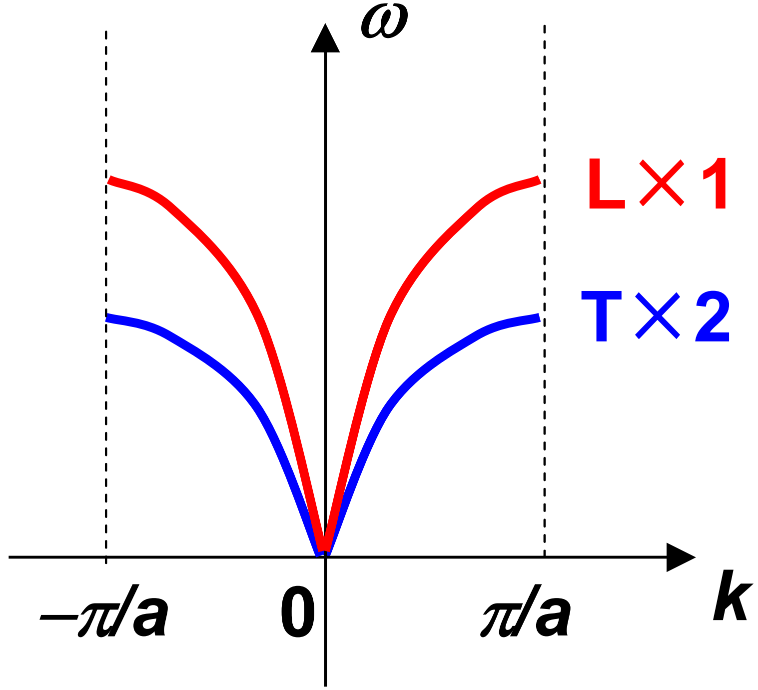
L wave arrives first, less damage

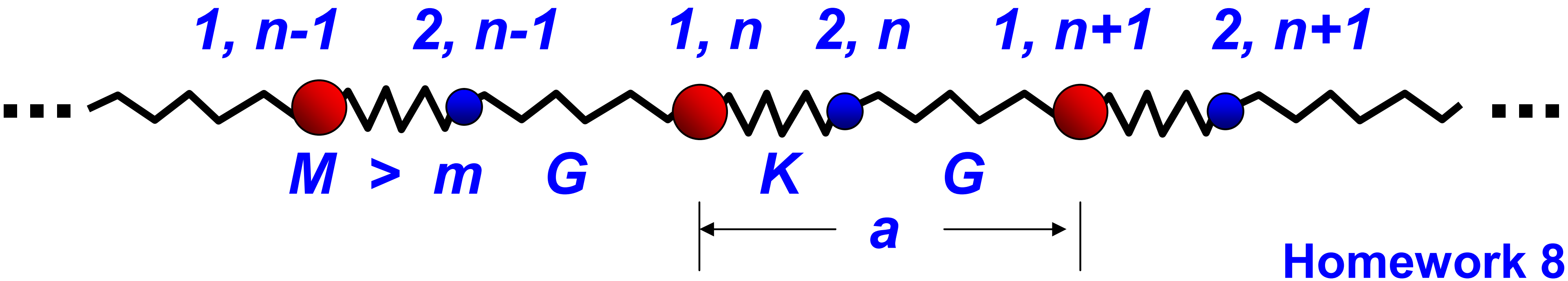


T wave arrives later, more damage!



[video - earthquake]

1D *Diatomic* Chain 双原子链



Homework 8.3

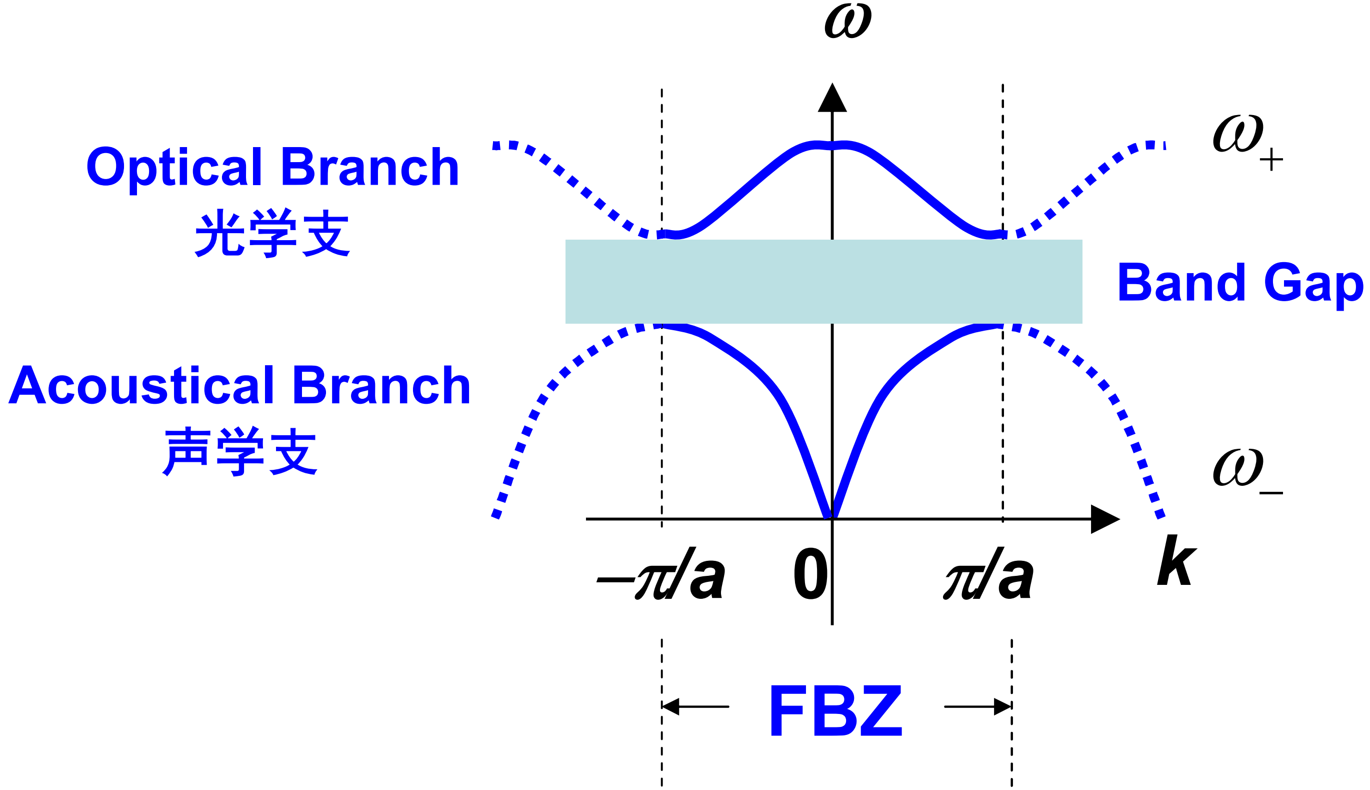
$$\begin{cases} M\dfrac{\partial^2 u_{1,n}}{\partial t^2} + K(u_{1,n} - u_{2,n}) + G(u_{1,n} - u_{2,n-1}) = 0 \\ m\dfrac{\partial^2 u_{2,n}}{\partial t^2} + K(u_{2,n} - u_{1,n}) + G(u_{2,n} - u_{1,n+1}) = 0 \end{cases}$$

$$\begin{cases} u_{1,n} = A_1 e^{i(kx-\omega t)} \\ u_{2,n} = A_2 e^{i(kx-\omega t)} \end{cases}$$

$$\rightarrow \quad \omega^2 = \frac{(K+G)(M+m) \pm \sqrt{(K+G)^2(M+m)^2 - 16MmKG\sin^2\left(\frac{ak}{2}\right)}}{2Mm}$$

1D *Diatomic* Chain 双原子链

$$\omega^2 = \frac{(K+G)(M+m) \pm \sqrt{(K+G)^2(M+m)^2 - 16MmKG\sin^2\left(\frac{ak}{2}\right)}}{2Mm}$$



1D *Diatomic* Chain 双原子链

When $K = G$ (example: NaCl, GaAs, ...),
Simplified solution:

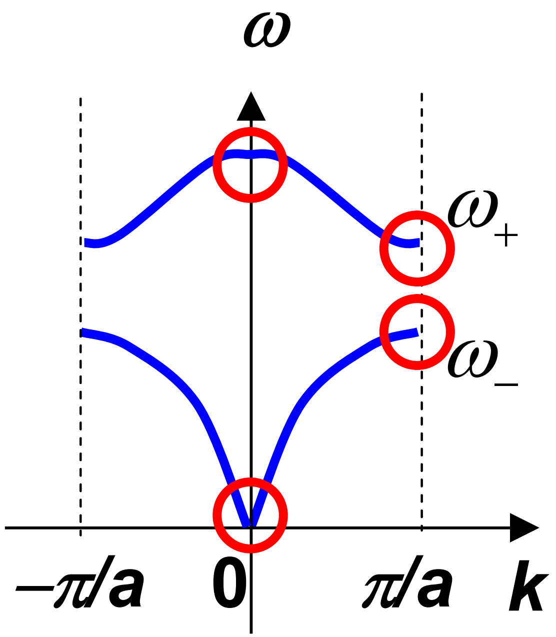
$$\omega^2 = K\frac{M+m}{Mm}\left[1 \pm \sqrt{1-\frac{4Mm}{(M+m)^2}\sin^2\left(\frac{ak}{2}\right)}\right]$$

$$\omega_+(k=0) = \sqrt{2K\frac{M+m}{Mm}}$$

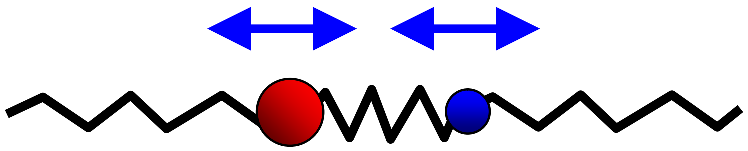
$$\omega_+(k=\pm\frac{\pi}{a}) = \sqrt{\frac{2K}{M}}$$

$$\omega_-(k\approx 0) = \sqrt{\frac{K}{2(M+m)}}ak$$

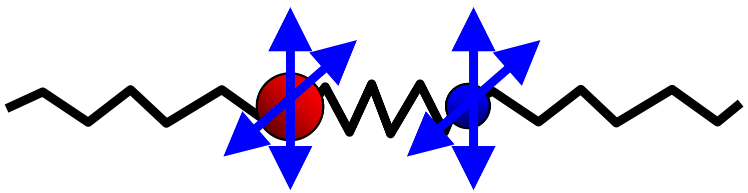
$$\omega_-(k=\pm\frac{\pi}{a}) = \sqrt{\frac{2K}{m}}$$



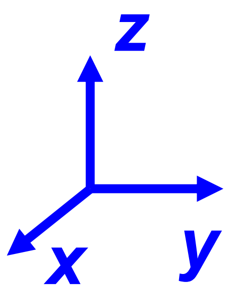
1D *Diatomic* Chain 双原子链

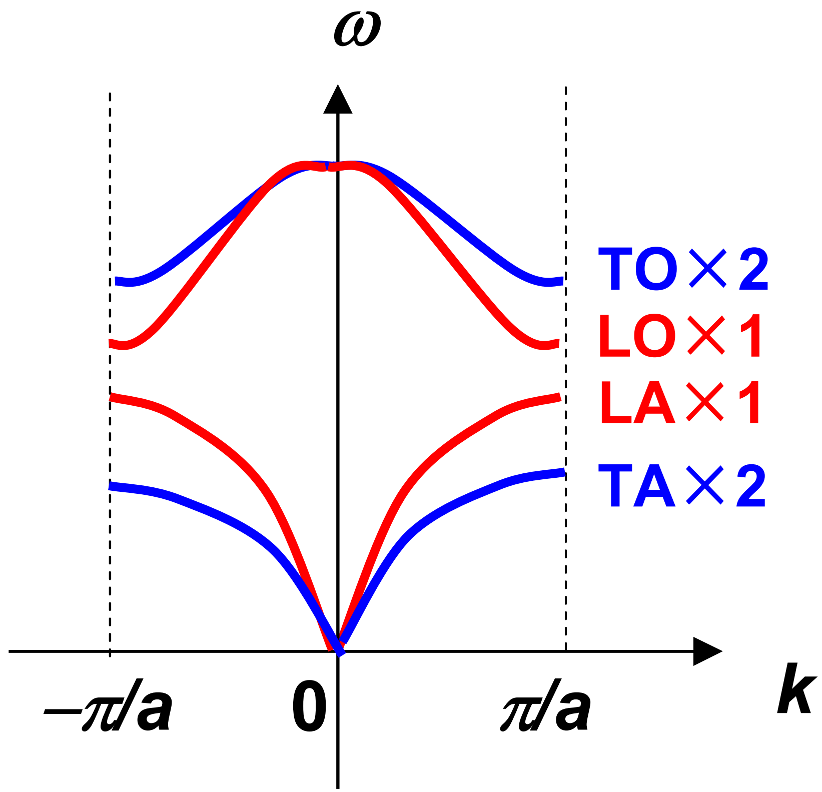


Longitudinal (L) 纵波×1



Transverse (T) 横波×2

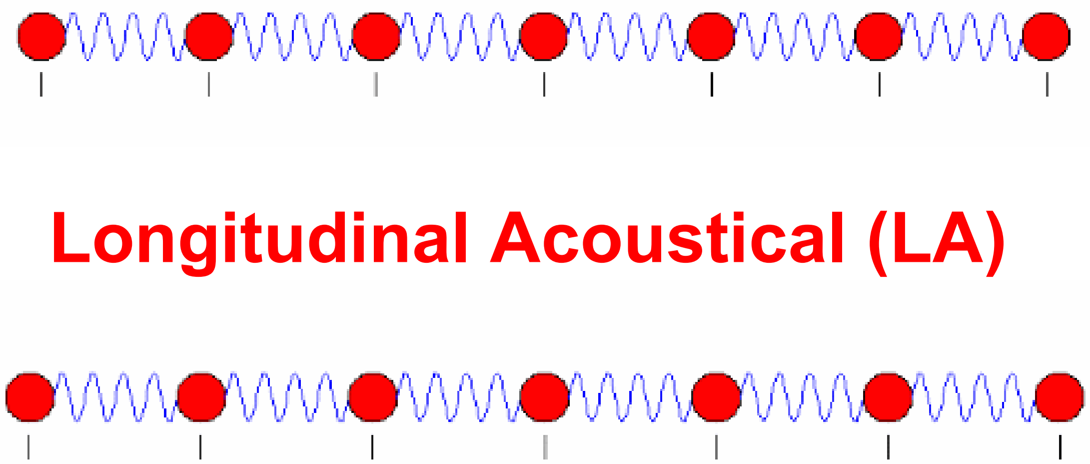


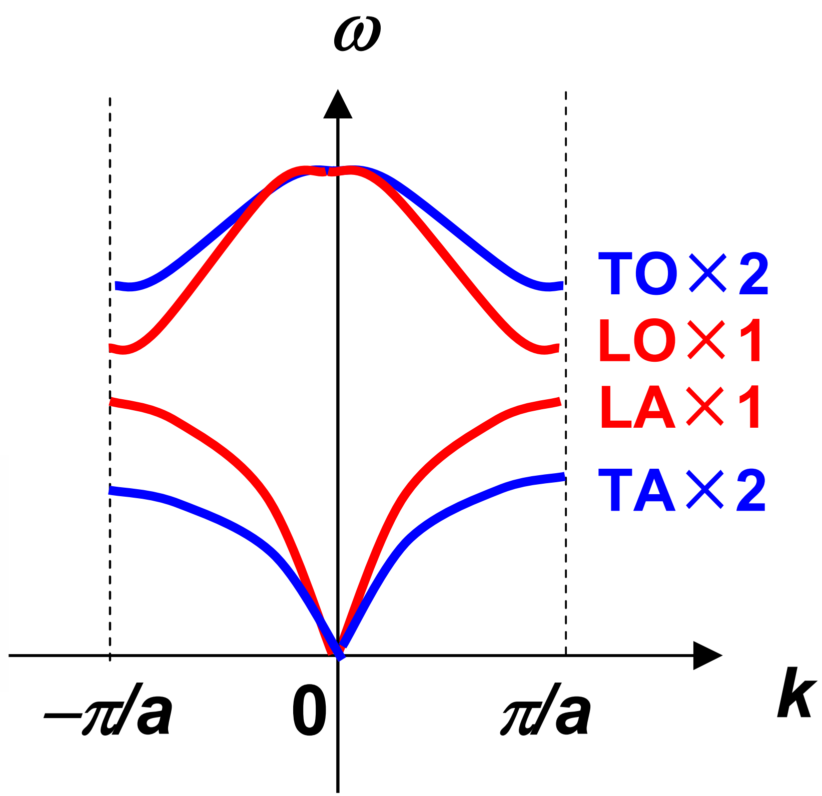


1D *Diatomic* Chain 双原子链

Longitudinal Optical (LO)

Longitudinal Acoustical (LA)





Acoustic modes are related to

the low frequency vibration across the entire crystal;

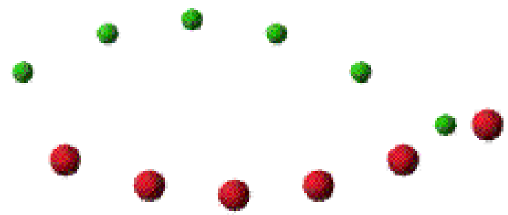
Optical modes are related to

the high frequency vibration inside the primitive cell.

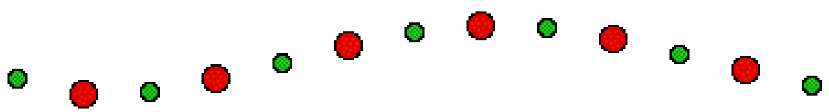
http://exafs.ucsc.edu/simulations/

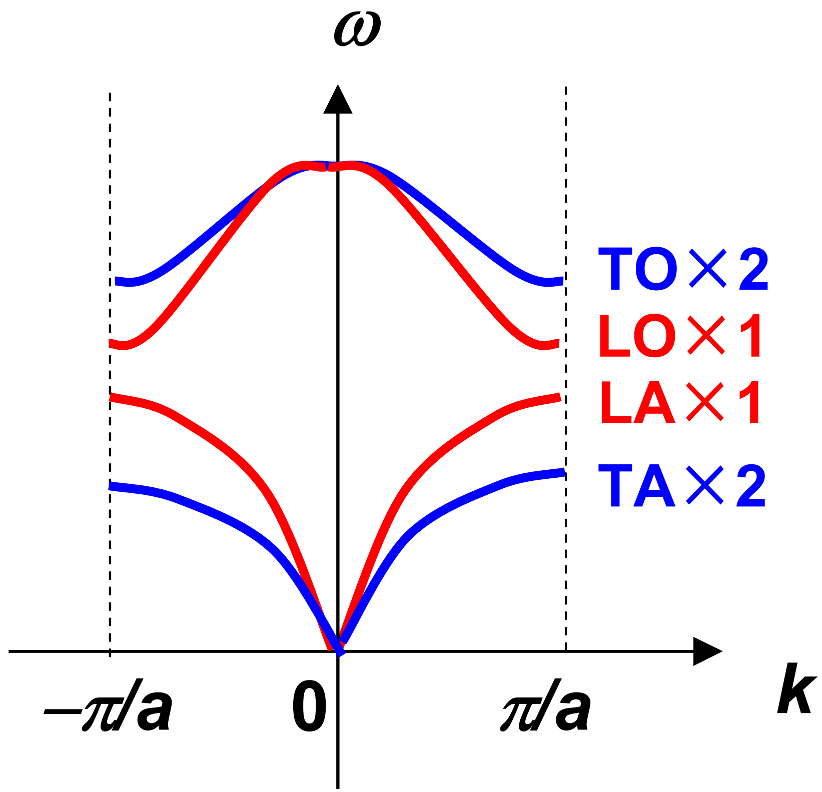
1D *Diatomic* Chain 双原子链

Transverse Optical (TO)



Transverse Acoustical (TA)





Acoustic modes are related to
the low frequency vibration across the entire crystal;
Optical modes are related to
the high frequency vibration inside the primitive cell.

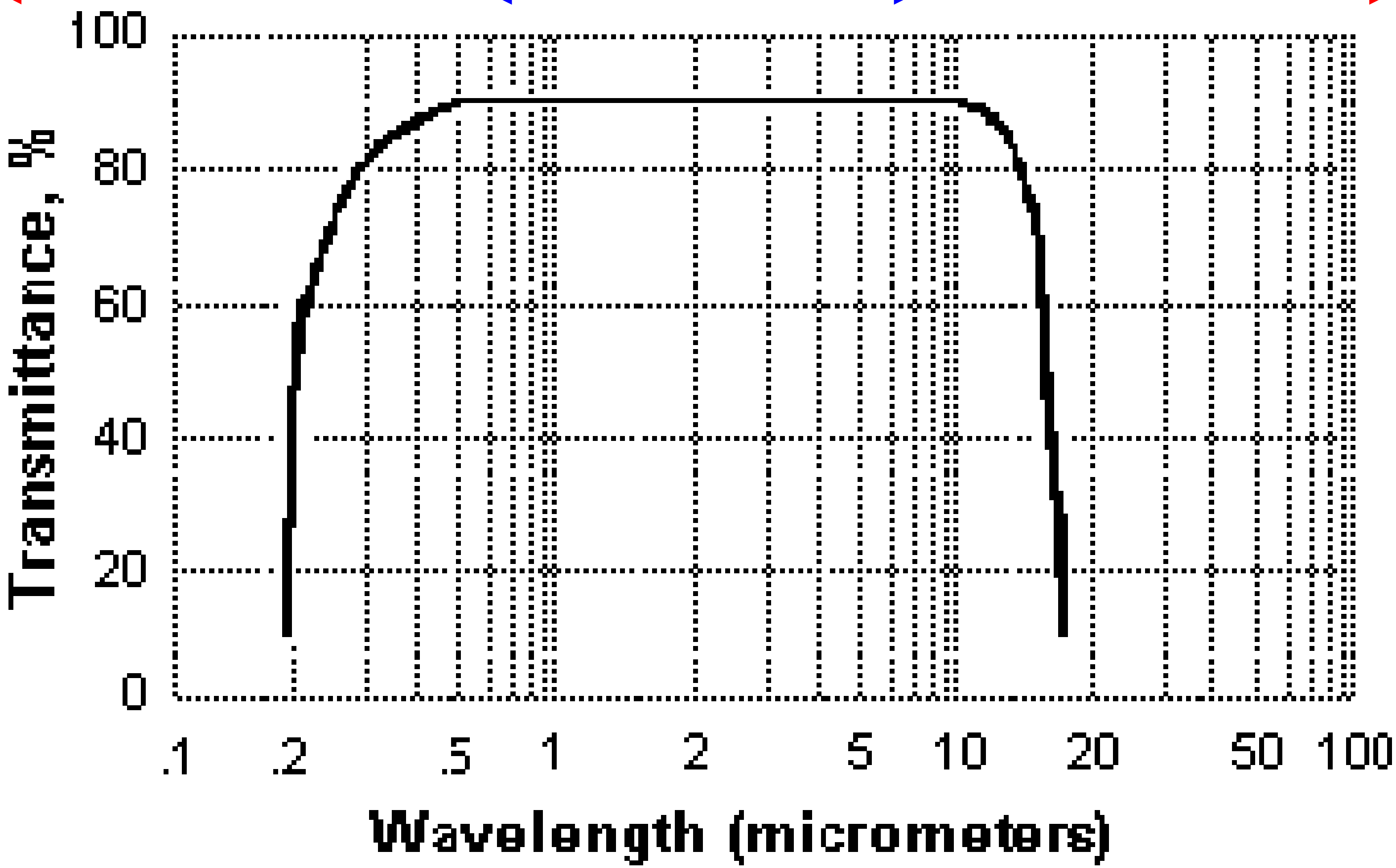
http://www.chembio.uoguelph.ca/educmat/chm729/Phonons/optmovie.htm

Optical Properties of NaCl

absorption above band gap (E_g ~ 8.5 eV)

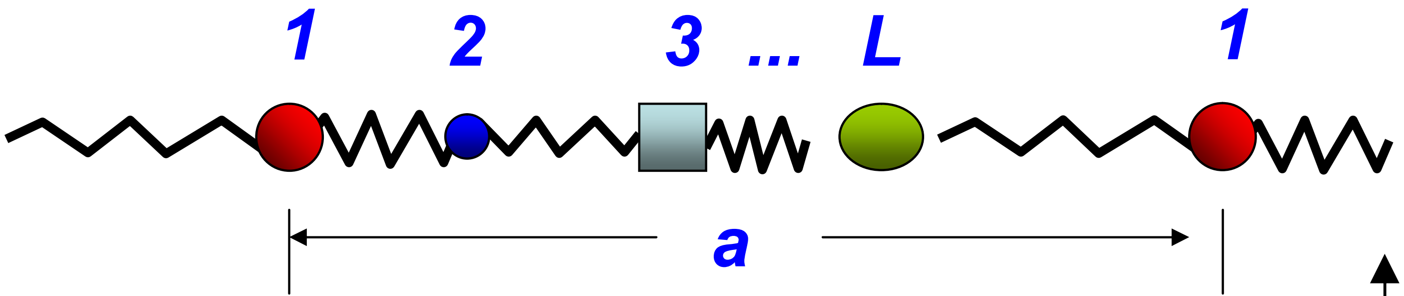
transparent

absorption by crystal vibration ($2\pi\omega_{max}/c$ ~ 10 um)

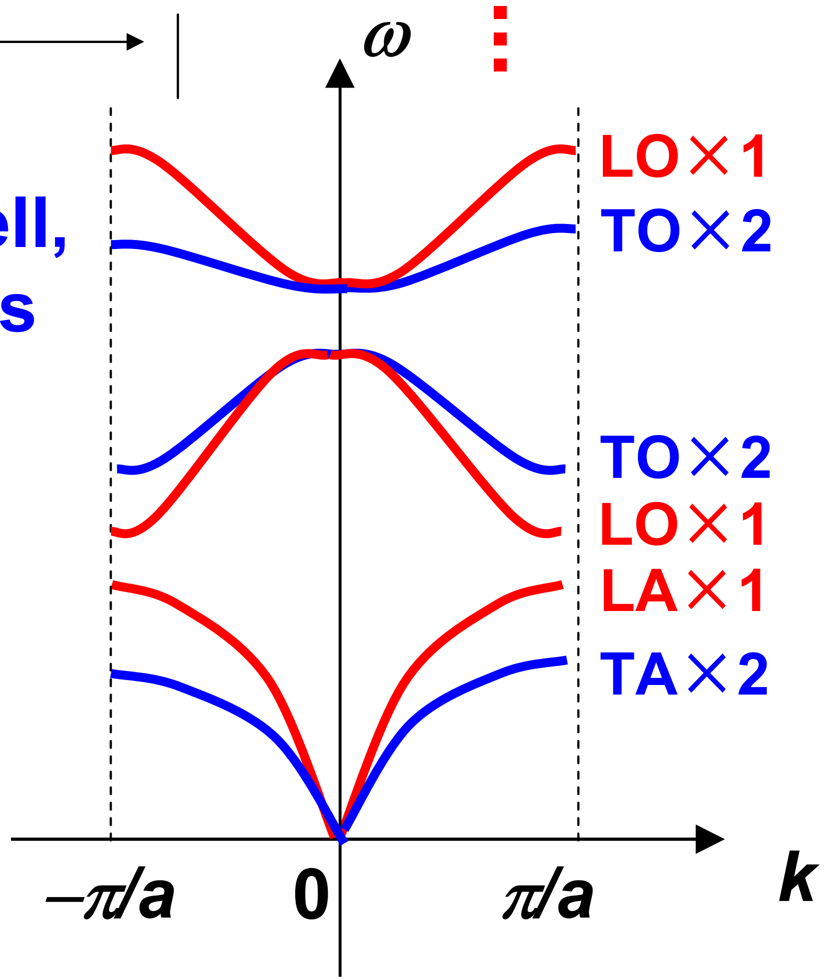


http://www.crystaltechno.com/NaCl_en.htm

1D *Multi-atomic* Chain 多原子链



If there are *L* atoms in a primitive cell, there will be more optical branches



There will be:

1 LA, 2 TA

$(L-1)$ LO, $2(L-1)$ TO

Fundamentals of Solid State Physics

Lattice Vibration
- Quantum Model

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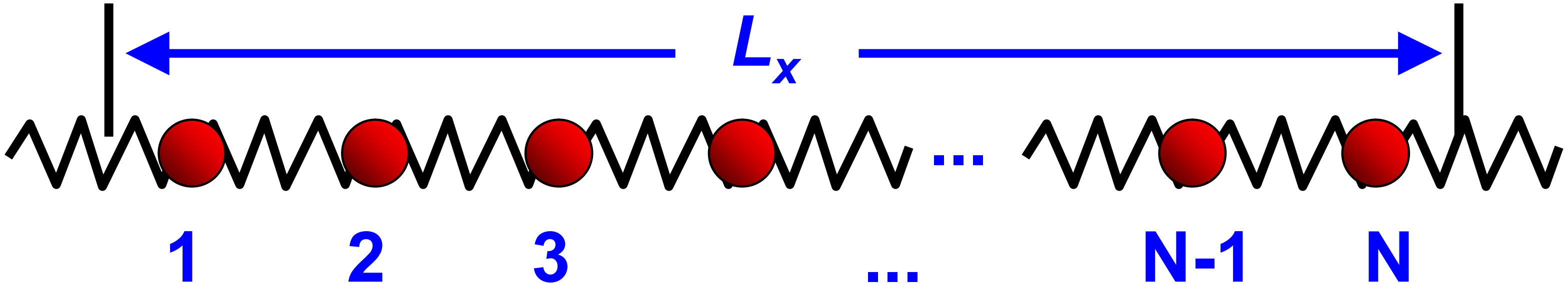
Quantization of the Bands 量子化



L_x = N*a, N is large ~ 10^{23}

Born-von Karman *periodic* boundary condition

$$\boxed{u(x) = u(x + L_x)} \rightarrow \boxed{\exp(ik_x L_x) = 1}$$

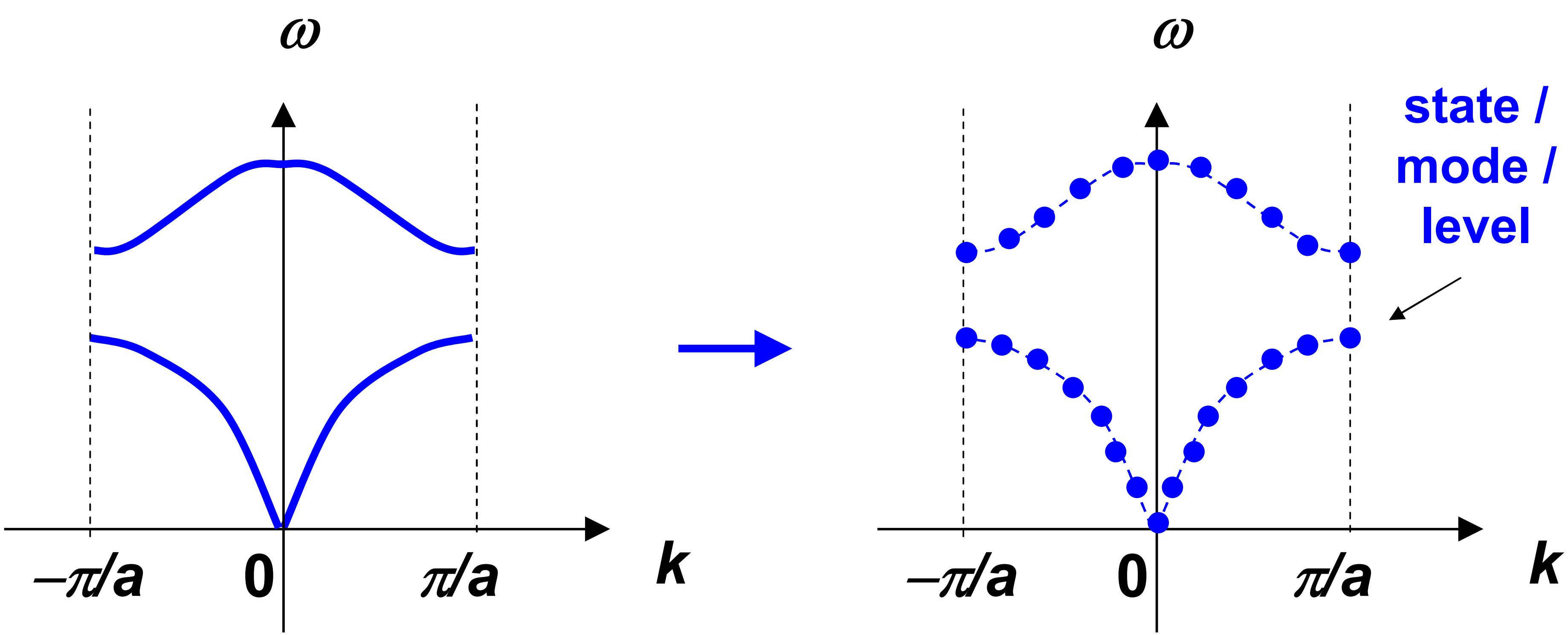
$$\rightarrow \boxed{k_x = \frac{2\pi n_x}{L_x}} \qquad n_x = 0, \pm 1, \pm 2, \ldots$$

***k* is a *quantized* value**

Quantization of the Bands 量子化

$$\boxed{k_x = \frac{2\pi n_x}{L_x}} \qquad n_x = 0, \pm 1, \pm 2, \ldots$$

quasi-continuous

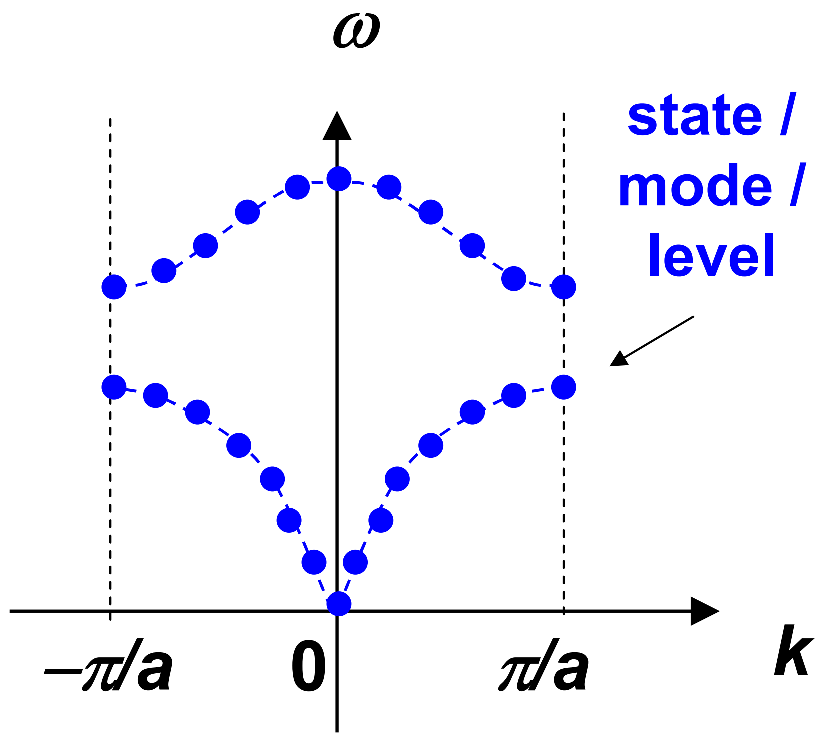


ω-k diagram (dispersion curve)

quantized state / level

Phonon Band Diagram

- A vibration state (phonon) is a collective movement of all the atoms in the lattice, not vibrations from a single atom
- There are *N* states in each band (*N*: number of primitive cells in the crystal)
- If there are *L* atoms in each primitive cell, there will be **3*L* bands, and 3*NL* states**
  - 1 LA + 2 TA
  - (L-1) LO + 2(L-1) TO



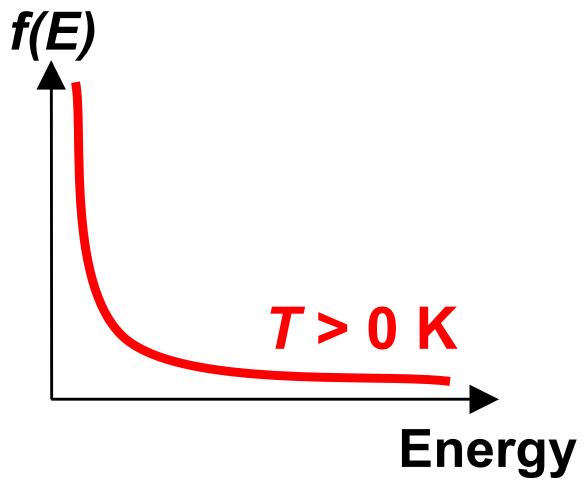
quantized state / level

Phonon 声子

- **Phonon is a boson**
  - **Each state can fill many phonons at the same time**
  - **Bose-Einstein Distribution**

number of phonons

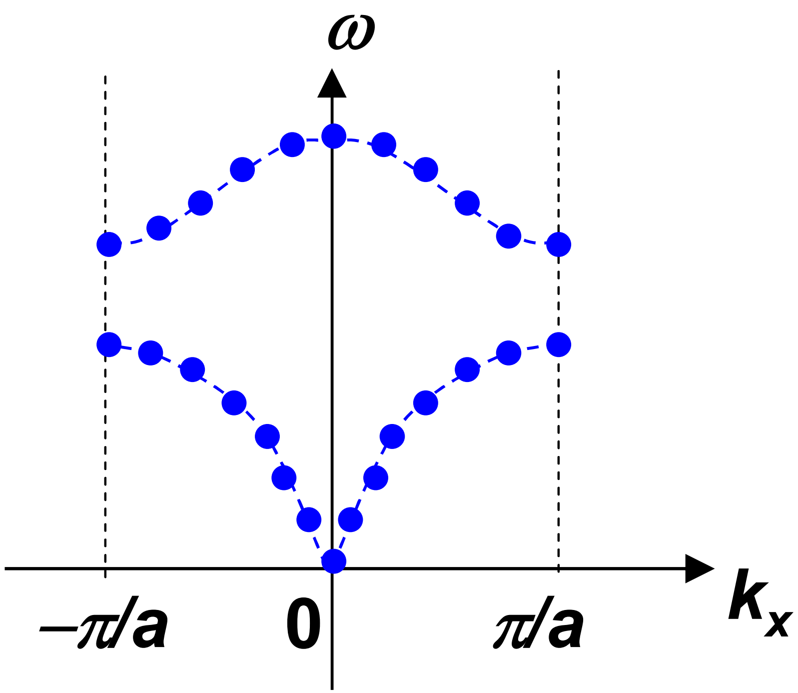
$$f(E=\hbar\omega)=\frac{1}{e^{\hbar\omega/k_BT}-1}$$



- **Phonon 声子 vs. Photon 光子**
  - **Both of them are bosons, but**
  - **Phonon is a collective atom vibration, quasi-particle (准粒子)**
  - **Photon is a fundamental particle (基本粒子)**

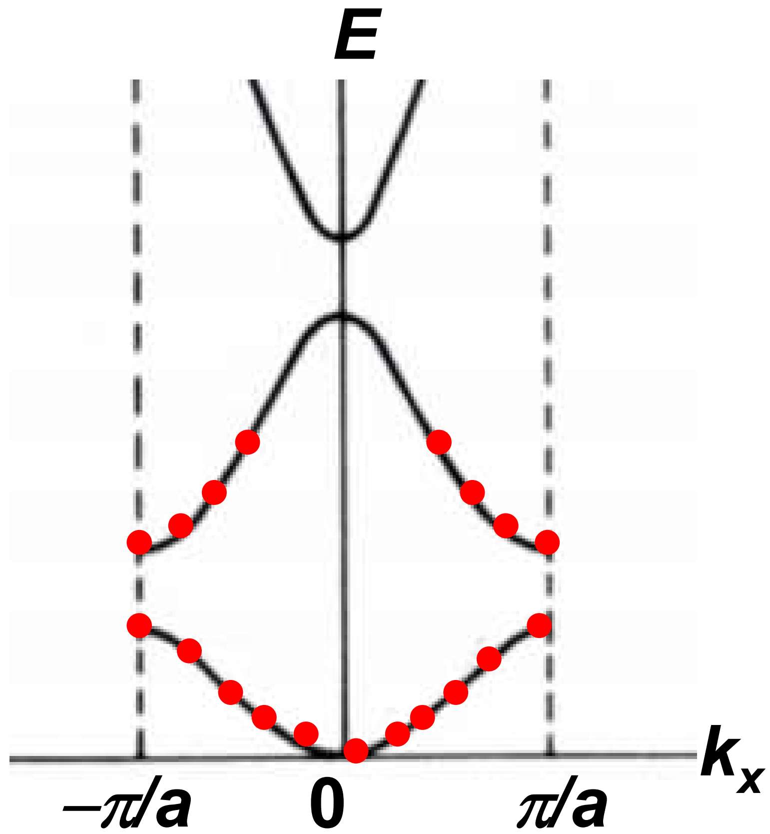
Phonon Band vs. Electron Band

- **Phonon Band**
  - max frequency ω_{max}
  - phonon number is not constant, depend on T



● phonon

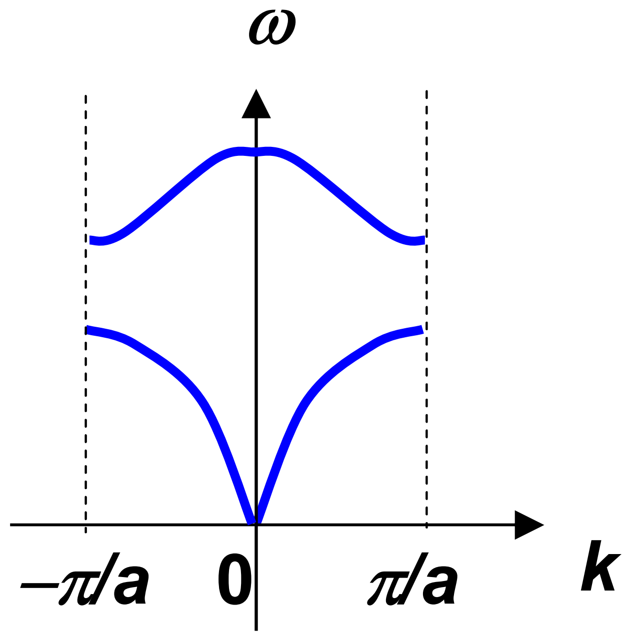
- **Electron Band**
  - no highest energy
  - electron number is fixed



● electron

Measure Phonon Band Diagram

- Optical Scattering
  - Brillouin Scattering 布里渊散射
  - Raman Scattering 拉曼散射
- Neutron Scattering 中子散射

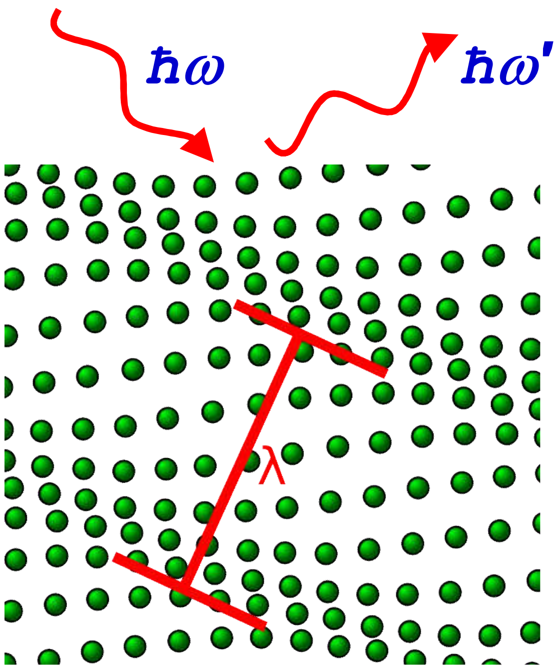


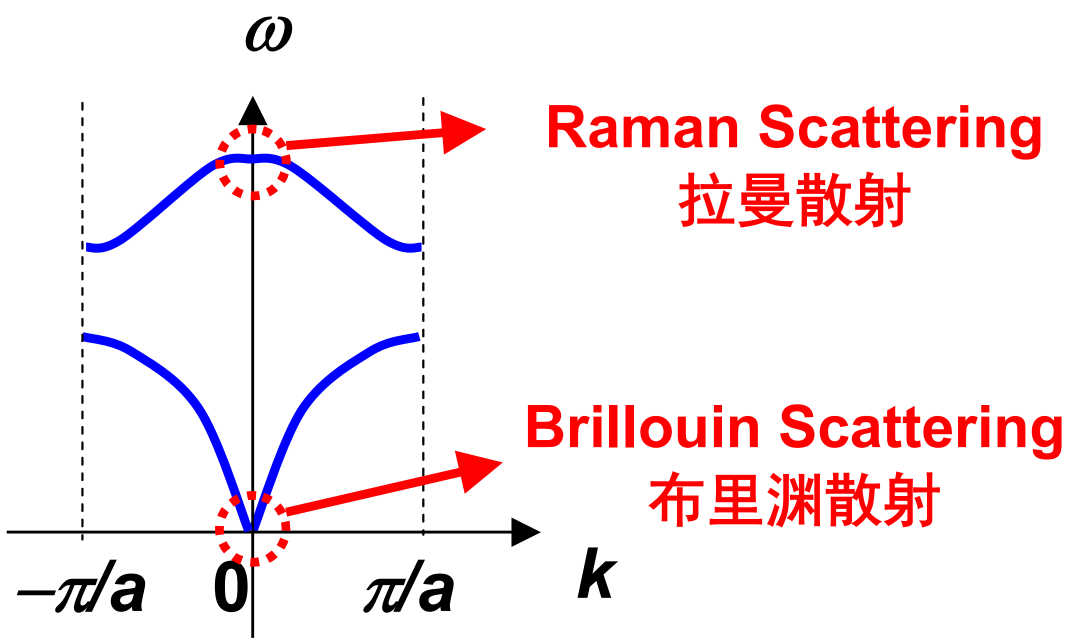
Measure Phonon Band Diagram

- **Optical Scattering**
  - Photons have much smaller momentum than phonons
  - can only measure *k* ~ 0

$$p = \frac{h}{\lambda} \ll \frac{h}{a}$$

$$\Delta p = \hbar k$$ $$\Delta E = \hbar \omega$$



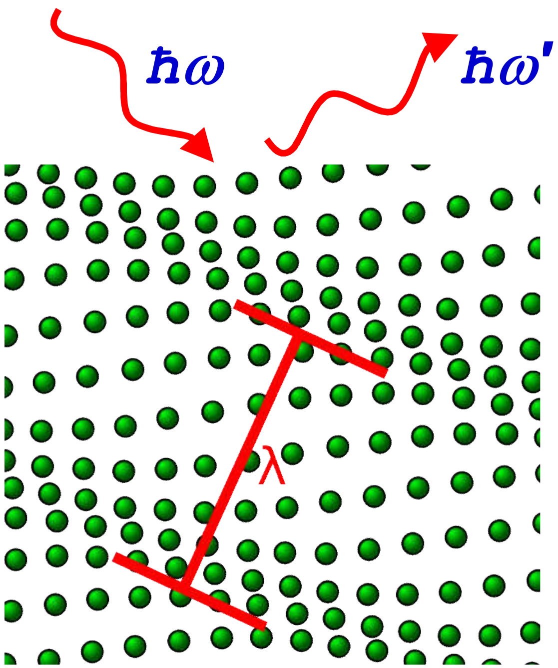


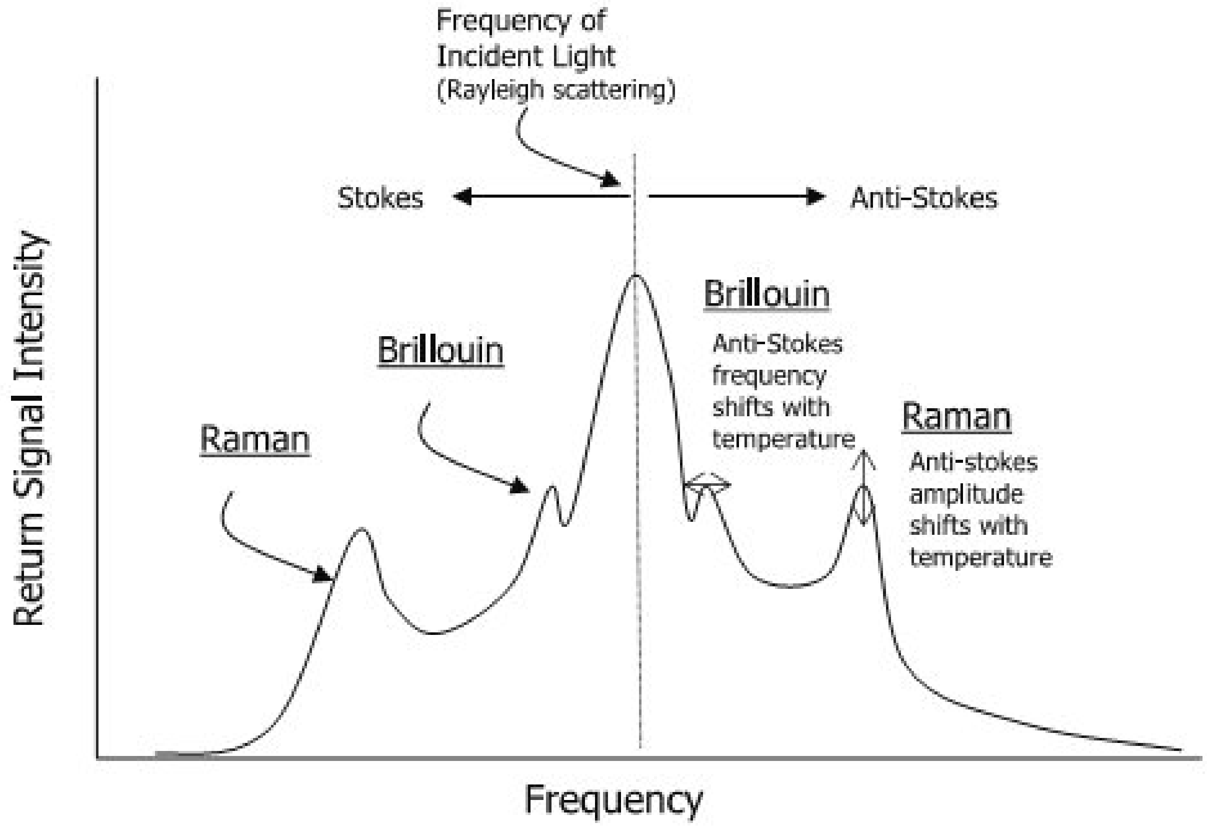
Measure Phonon Band Diagram

- **Optical Scattering**
  - **Photons have much smaller momentum than phonons**
  - **can only measure *k* ~ 0**

$$\Delta p = \hbar k$$

$$\Delta E = \hbar \omega$$



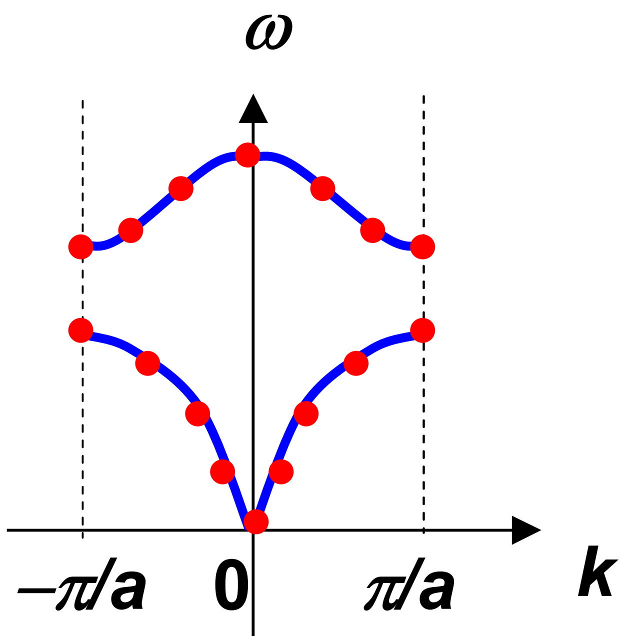


Neutron Scattering 中子散射

- Neutron has a similar mass with atoms
- Momentum and energy can cover the entire bands

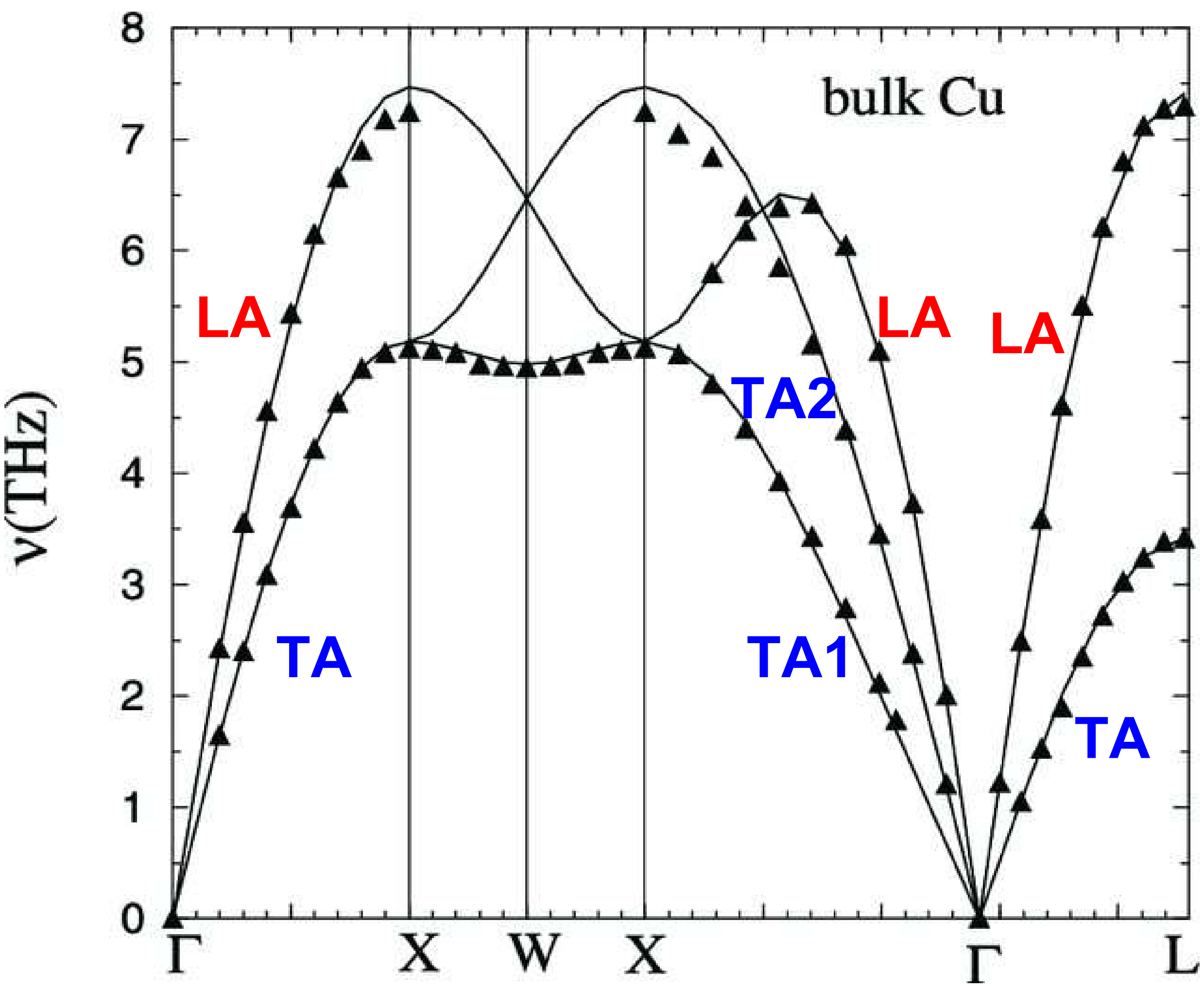
$$\boxed{\Delta p = \hbar k}$$ $$\boxed{\Delta E = \hbar \omega}$$

- **Need a nuclear reactor!**



散裂中子源，东莞

Phonon Band Diagram - Copper



▲ measured by neutron scattering

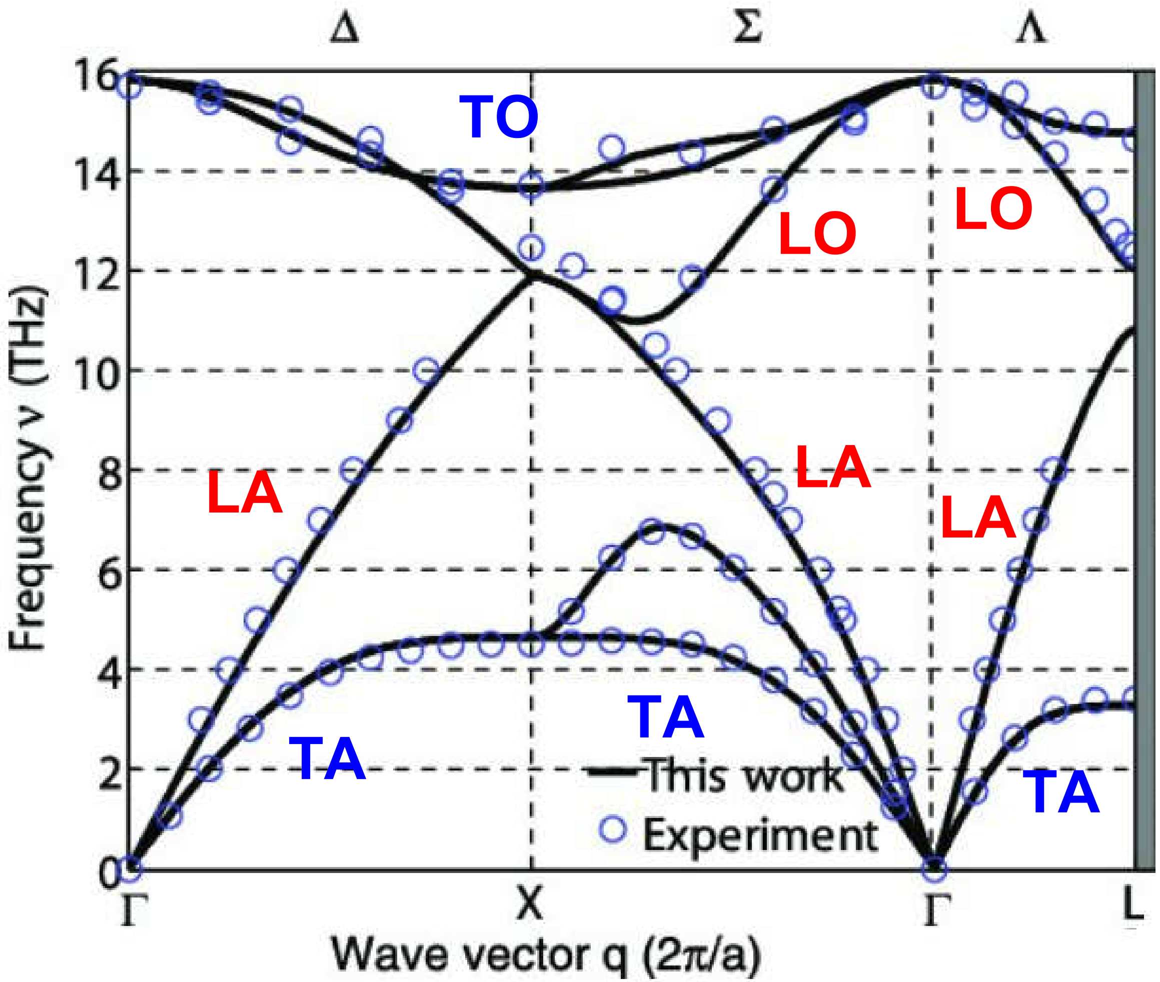
— calculation

Cu has FCC structure, with *one* atom in a primitive cell.

There are only acoustic branches, no optical branches

C. Barreteau, *et al.*, *J. Phys. Condens. Matter* **15,** S3171 (2003)

Phonon Band Diagram - Silicon



Si has FCC structure, but with *two* atoms in a primitive cell.

There are both acoustic and optical branches.

○ measured by neutron scattering

— calculation

A. Valentin, *et al.*, *J. Phys. Condens. Matter* **20,** 145213 (2008)

Density of States (DOS) 态密度

$$g(\omega)=\frac{dn}{d\omega}$$

DOS - number of frequency states/levels per unit frequency, per unit volume

For 1D chain LA mode

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

$$n=\frac{N}{L_x}=\frac{2k}{2\pi/L_x}\cdot\frac{1}{L_x}=\frac{k}{\pi}$$

$$\rightarrow \quad g(\omega)=\frac{dn}{d\omega}=\frac{dn}{dk}\Big/\frac{d\omega}{dk}=\ldots$$

Homework 8.2

Density of States (DOS) 态密度

$$g(\omega) = \frac{dn}{d\omega}$$

DOS - number of frequency states/levels per unit frequency, per unit volume

For 3D solid

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

$$n = \frac{3N}{V} = \frac{\frac{\frac{4\pi}{3}k^3}{\frac{(2\pi)^3}{V}}}{}\frac{3}{V} = \frac{1}{2\pi^2}k^3$$

at low ω limit →

$$\omega \approx v_g k = v_g\left(2\pi^2 n\right)^{1/3}$$

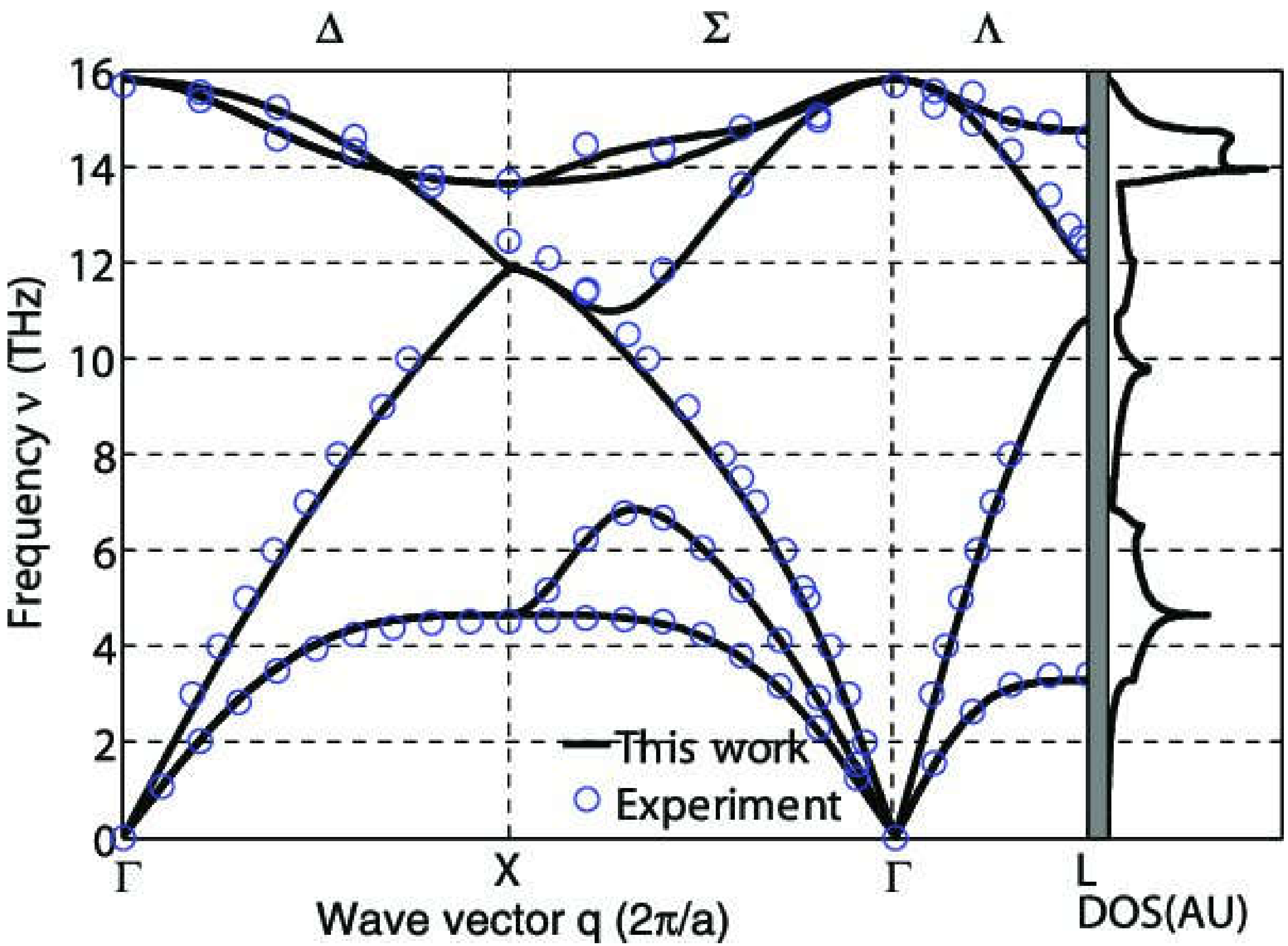
→

$$g(\omega) = \frac{dn}{d\omega} = \frac{3}{2\pi^2 v_g^3}\omega^2 = B\omega^2$$

The Debye Model (德拜模型)

Density of States (DOS) 态密度

Phonon band diagram and DOS for Silicon



A. Valentin, *et al.*, *J. Phys. Condens. Matter* **20,** 145213 (2008)

Thank you for your attention