Fundamentals of Solid State Physics

Thermal Properties

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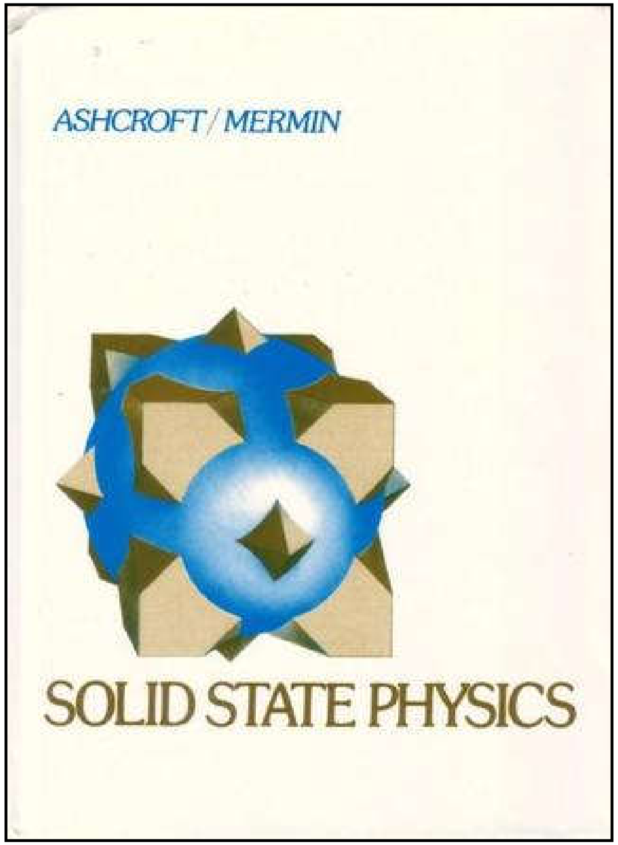
This Class

- Introduction (Week 1)
- Materials and Crystal Structures (Week 2–3)
- Electronic Properties (Week 4–12)
- Thermal Properties (Week 13)
  - Crystal vibration, phonon band
  - Thermal capacity and conductivity
- Optical Properties (Week 14)
- Magnetic Properties (Week 15)

Further Reading

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

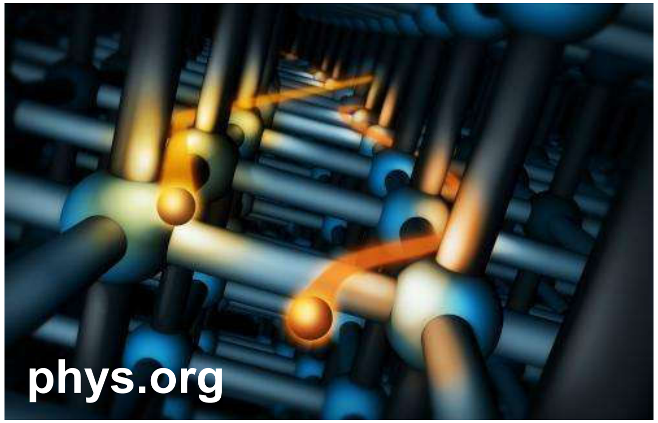


Born-Oppenheimer Approximation

- **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

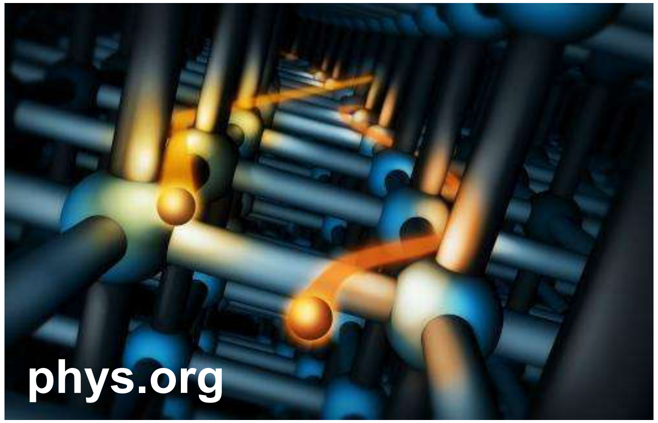
It *cannot* explain

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

We have to analyze lattice vibration

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

τ - relaxation time (s)



How to analyze Lattice Vibration?

- Born-Oppenheimer Approximation

- 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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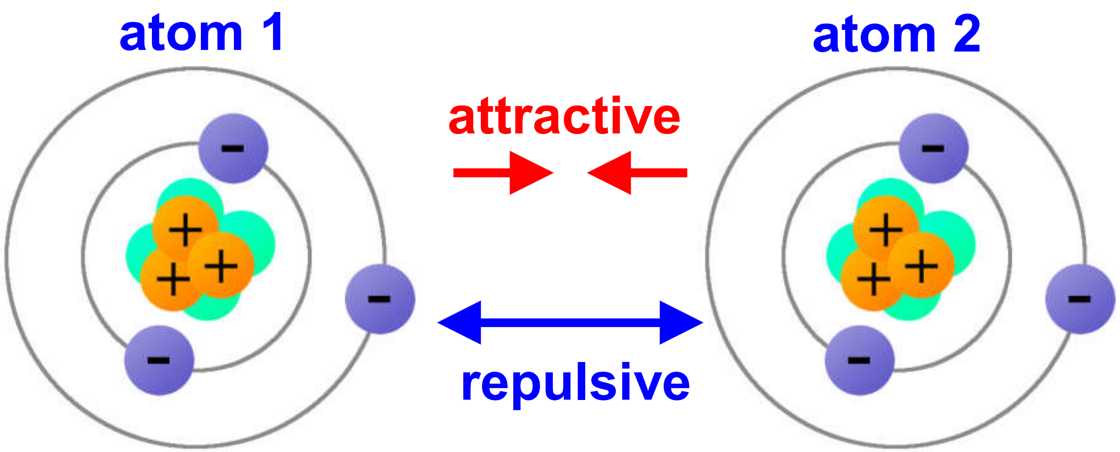
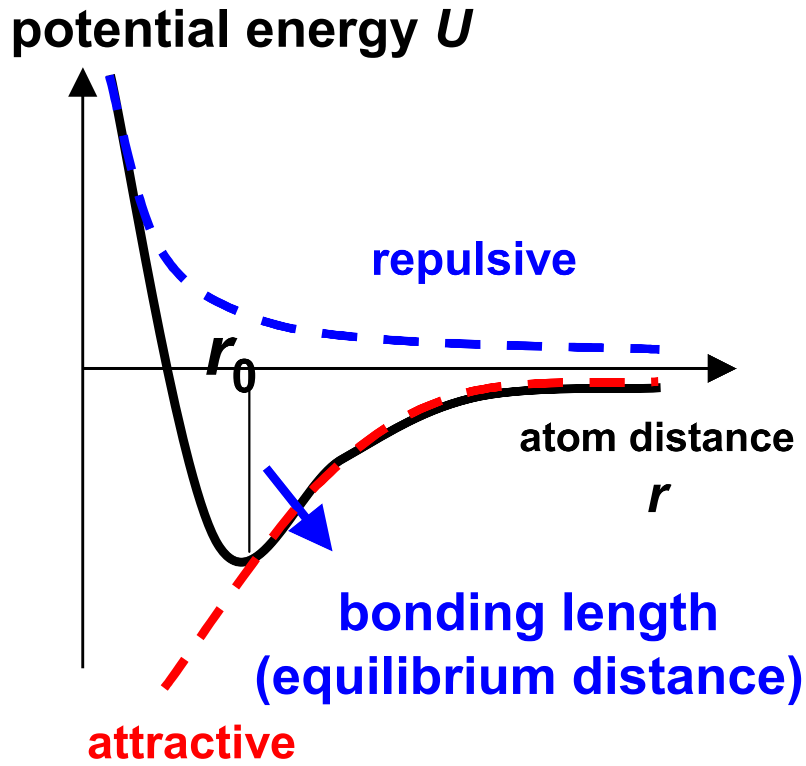
Atomic Interactions





- **Interatomic Potential *U***

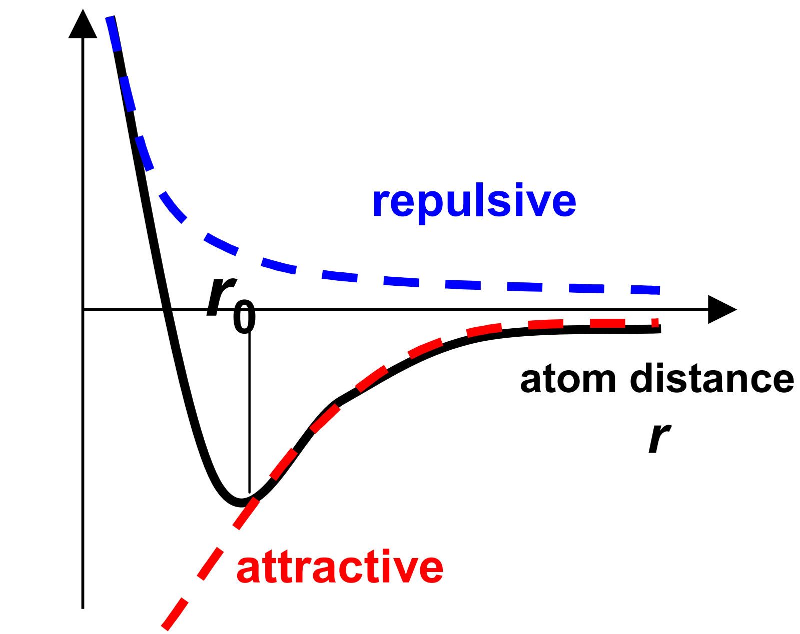
$$\boxed{U(r) = U_{\text{repulsion}}(r) - U_{\text{attaction}}(r)}$$

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

Interatomic Potential: Examples

- Lennard-Jones (L-J)

$$U(r) = \underbrace{\frac{A}{r^{12}}}_{\text{repulsive}} - \underbrace{\frac{B}{r^{6}}}_{\text{attractive}}$$



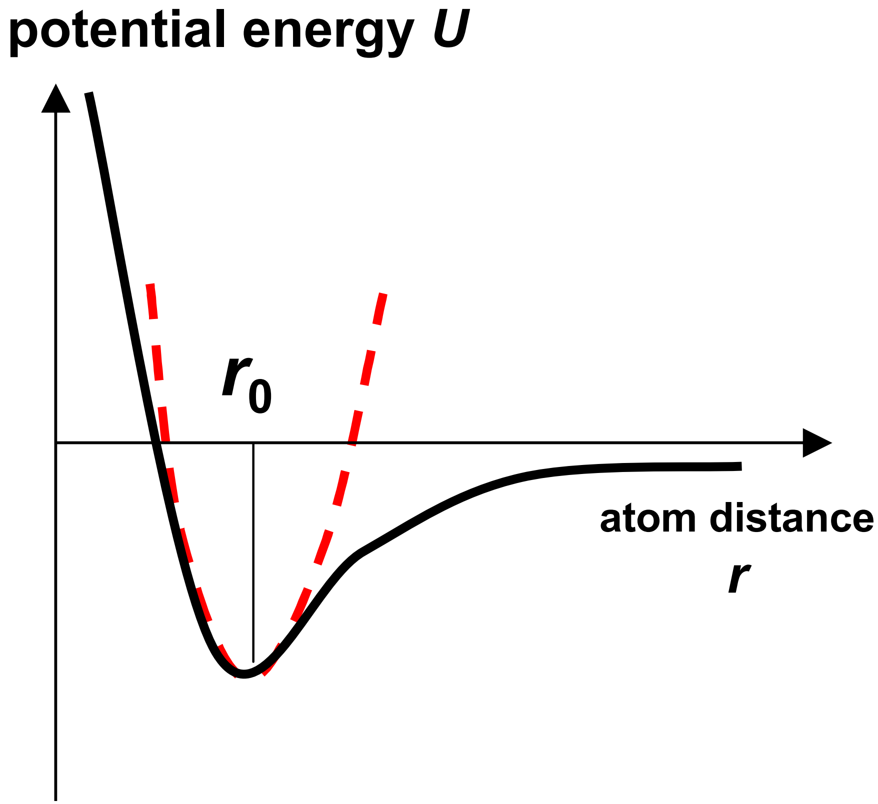
- Ionic Crystals

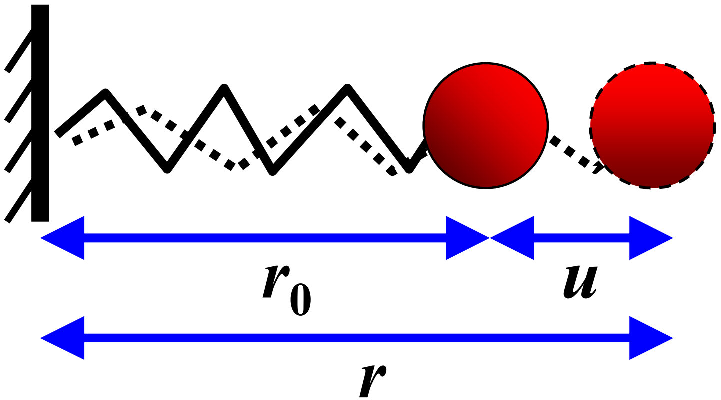
$$U(r) = \underbrace{A\exp\left(\frac{r}{\rho}\right)}_{\text{repulsive}} - \underbrace{\frac{B}{r}}_{\text{attractive}}$$

- Morse Potential

$$U(r) = D\left(\underbrace{e^{-2a(r-r_0)}}_{\text{repulsive}} - \underbrace{2e^{-a(r-r_0)}}_{\text{attractive}}\right)$$

Atomic Interactions





Harmonic Approximation (parabolic curve)

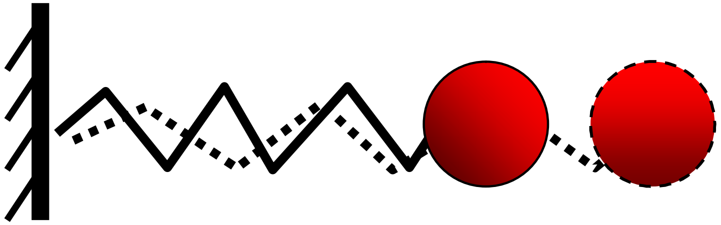
$$U(r) = U_0 + \frac{1}{2}K(r - r_0)^2$$
$$= U_0 + \frac{1}{2}K \cdot u^2$$

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

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

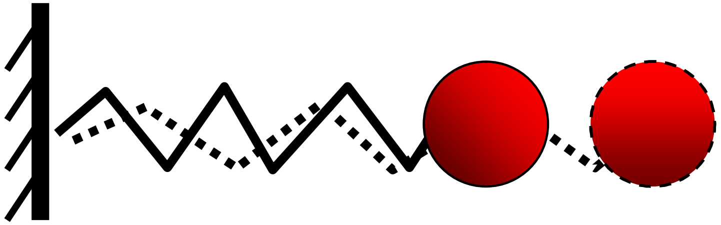
$\rightarrow$ $$m\frac{\partial^2 u}{\partial t^2} + Ku = 0$$

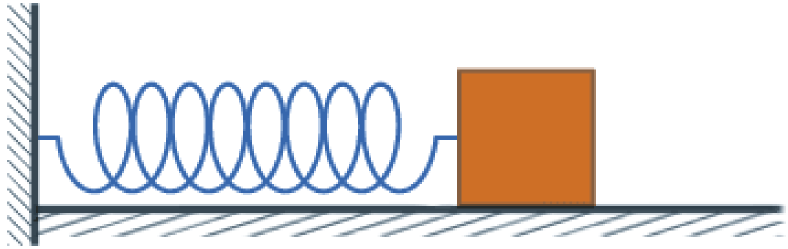
$\rightarrow$ $$u = Ae^{-i\omega t}$$

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

ω - angular frequency (rad/s)

Harmonic Oscillator 谐振子





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

Newton's Second Law

$\rightarrow$

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$\rightarrow$

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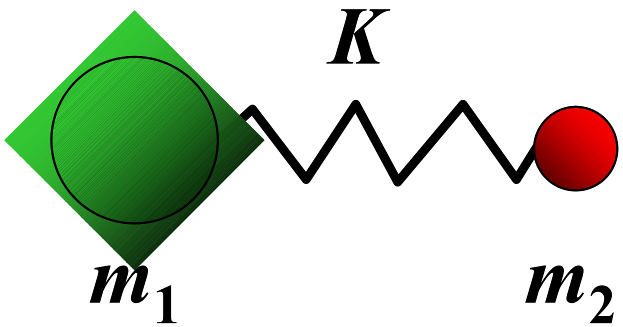
Diatomic Molecule 双原子分子

Homework 8.1

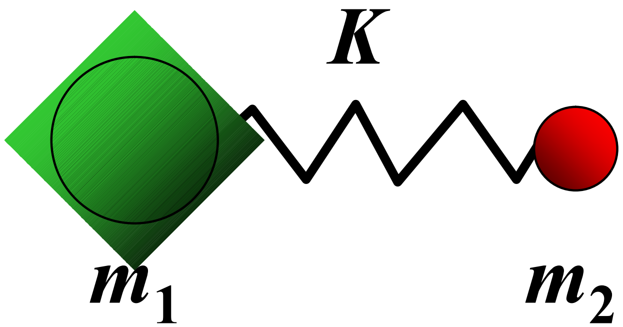


$$\omega = \sqrt{\frac{K}{m^*}} = \sqrt{\frac{m_1 + m_2}{m_1 m_2} K}$$

ω - angular frequency (rad/s)
m^* - reduced mass (kg)

Diatomic Molecule 双原子分子

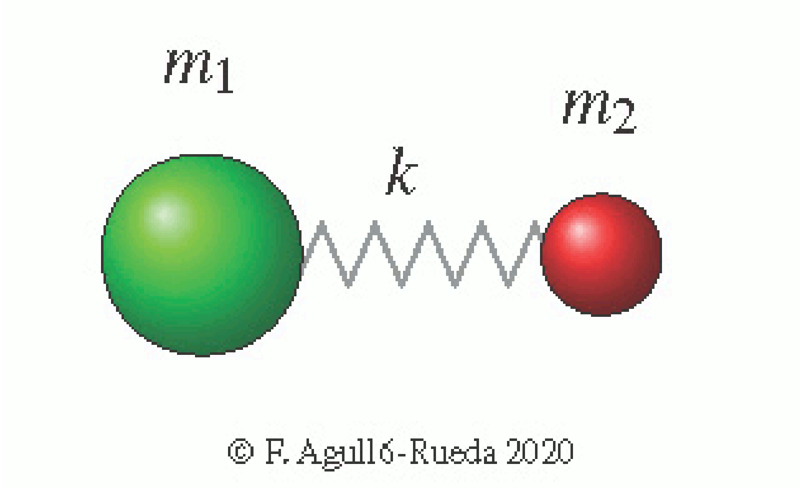
Homework 8.1



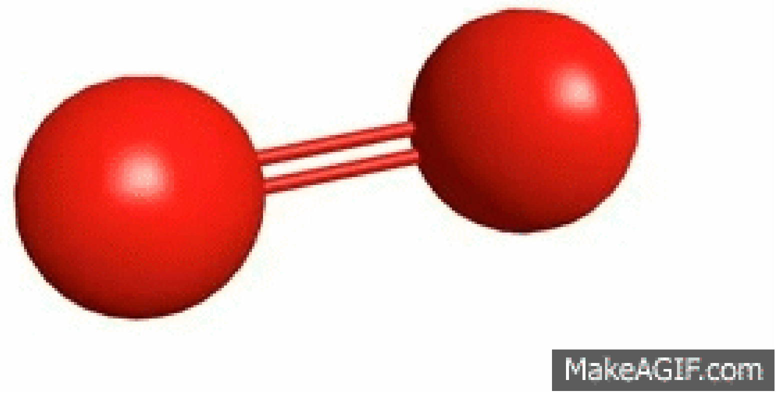
$$\omega = \sqrt{\frac{K}{m^*}} = \sqrt{\frac{m_1 + m_2}{m_1 m_2} K}$$

ω - angular frequency (rad/s)
*m** - reduced mass (kg)

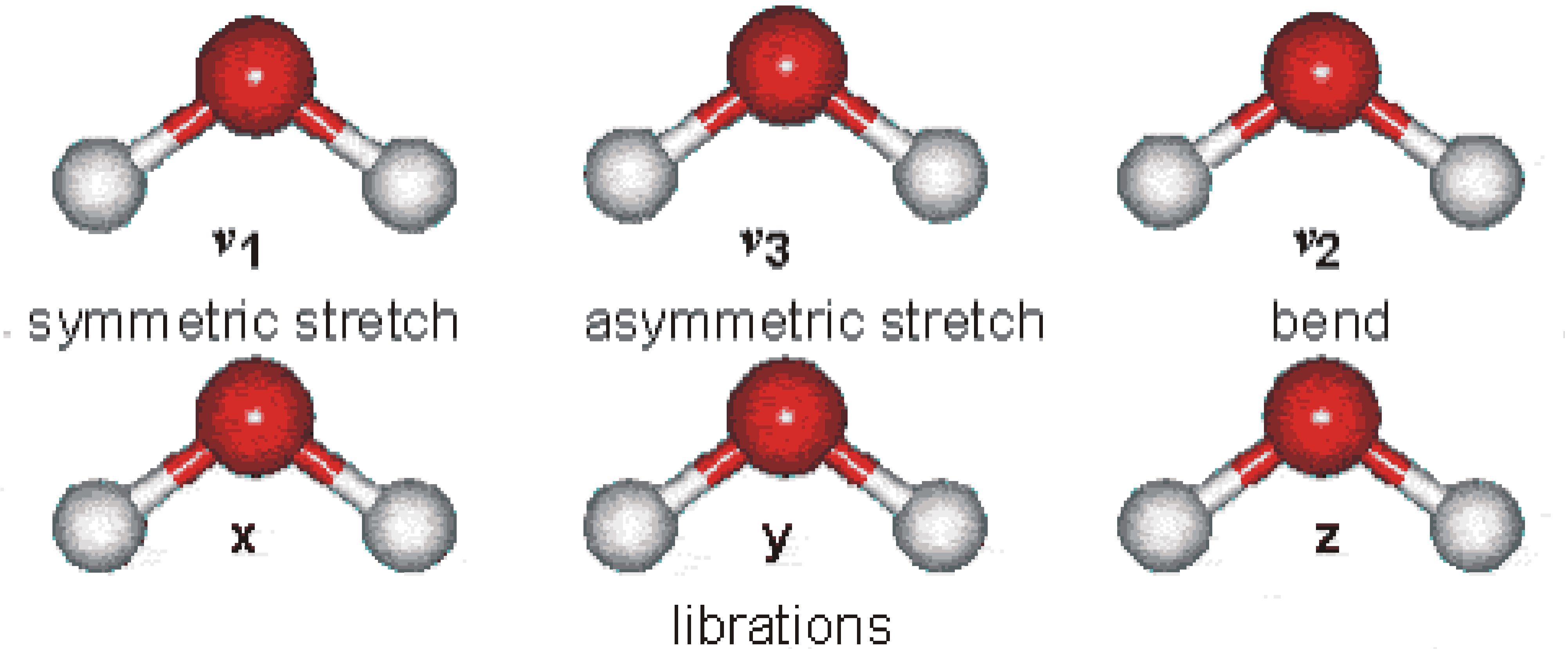
CO molecule



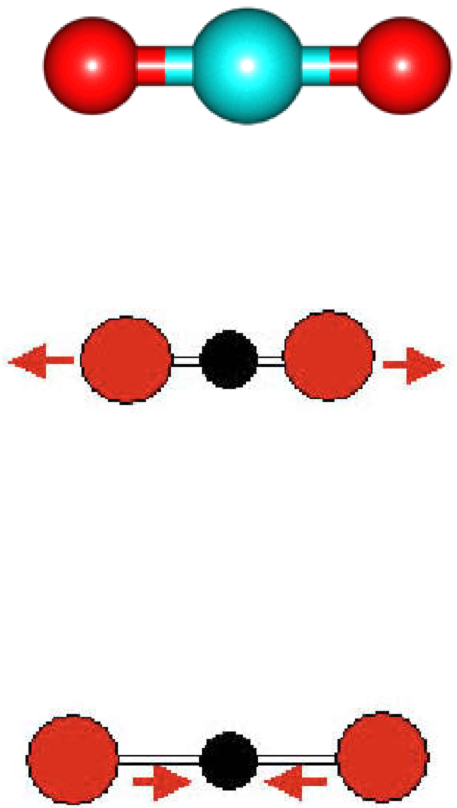
O_2 molecule



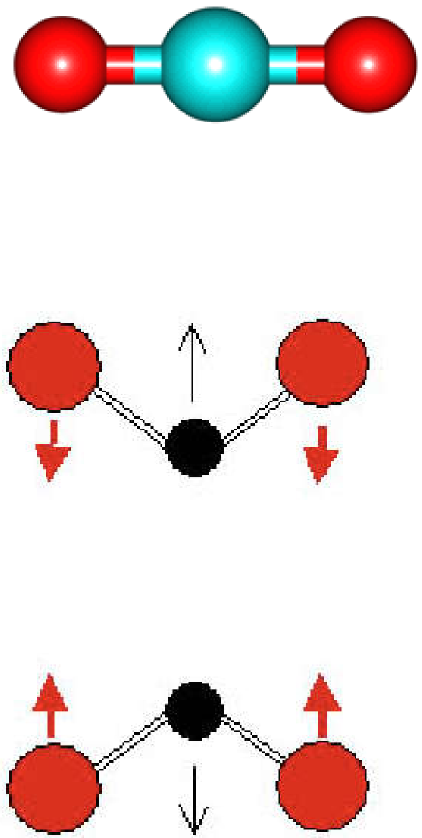
H_2O Vibration



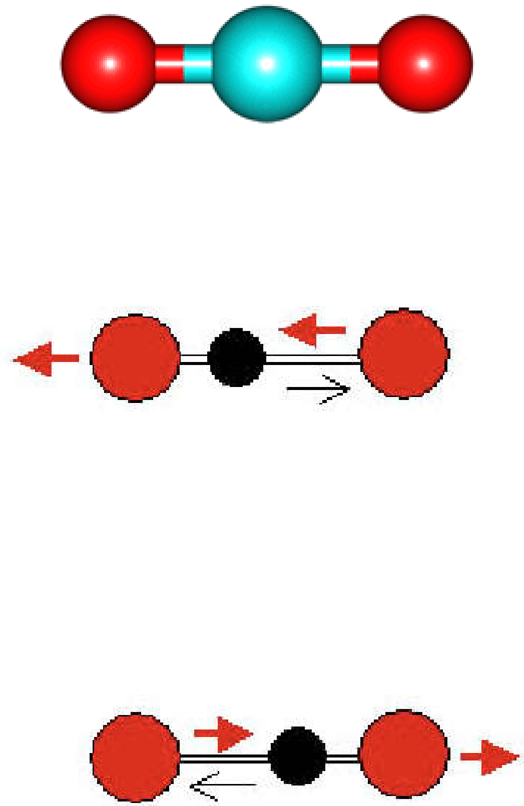
CO_2 Vibration



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



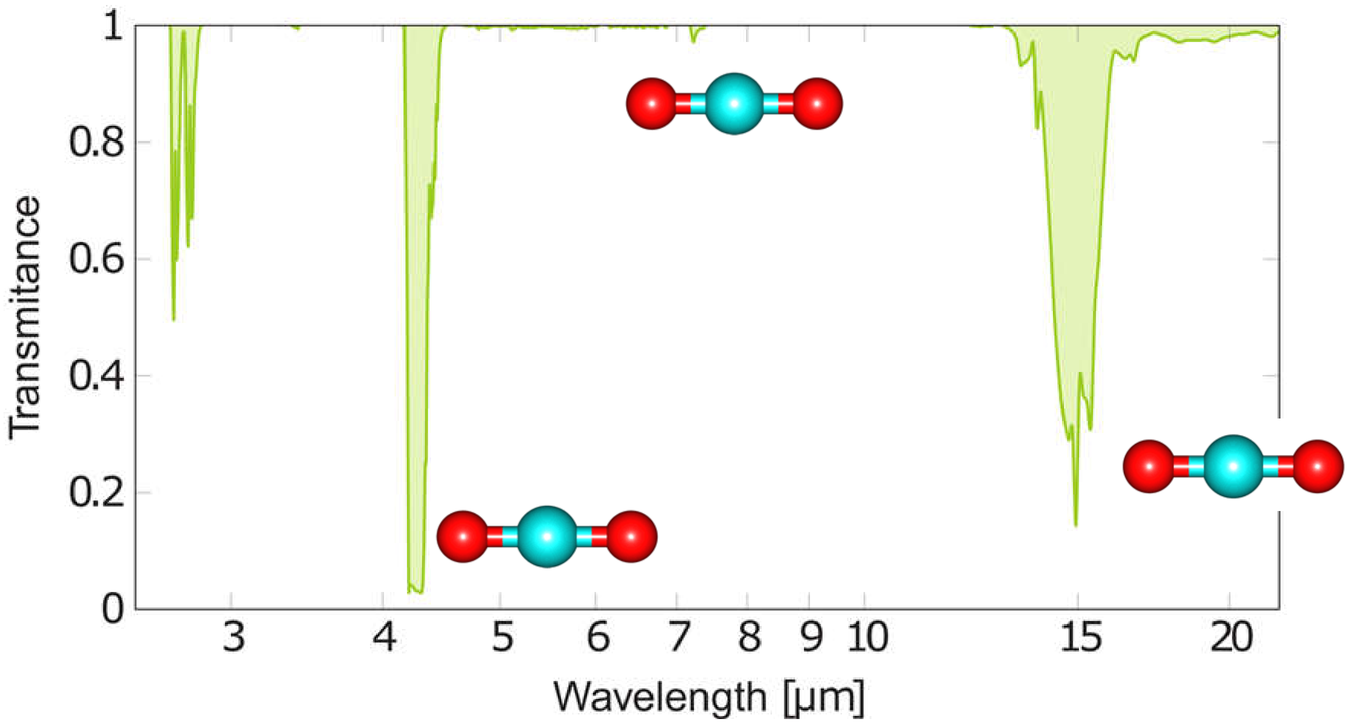
Bending
667 cm^{-1} or 15 μm



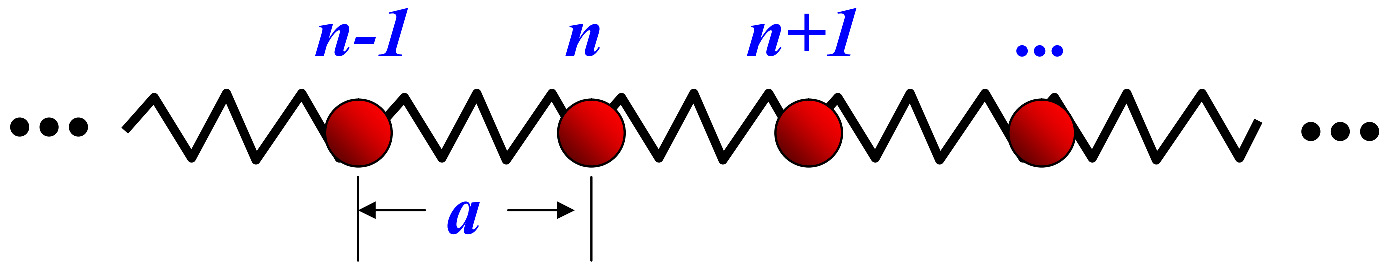
Asymmetric Stretch
2349 cm^{-1} or 4.23 μm

Molecule Vibration

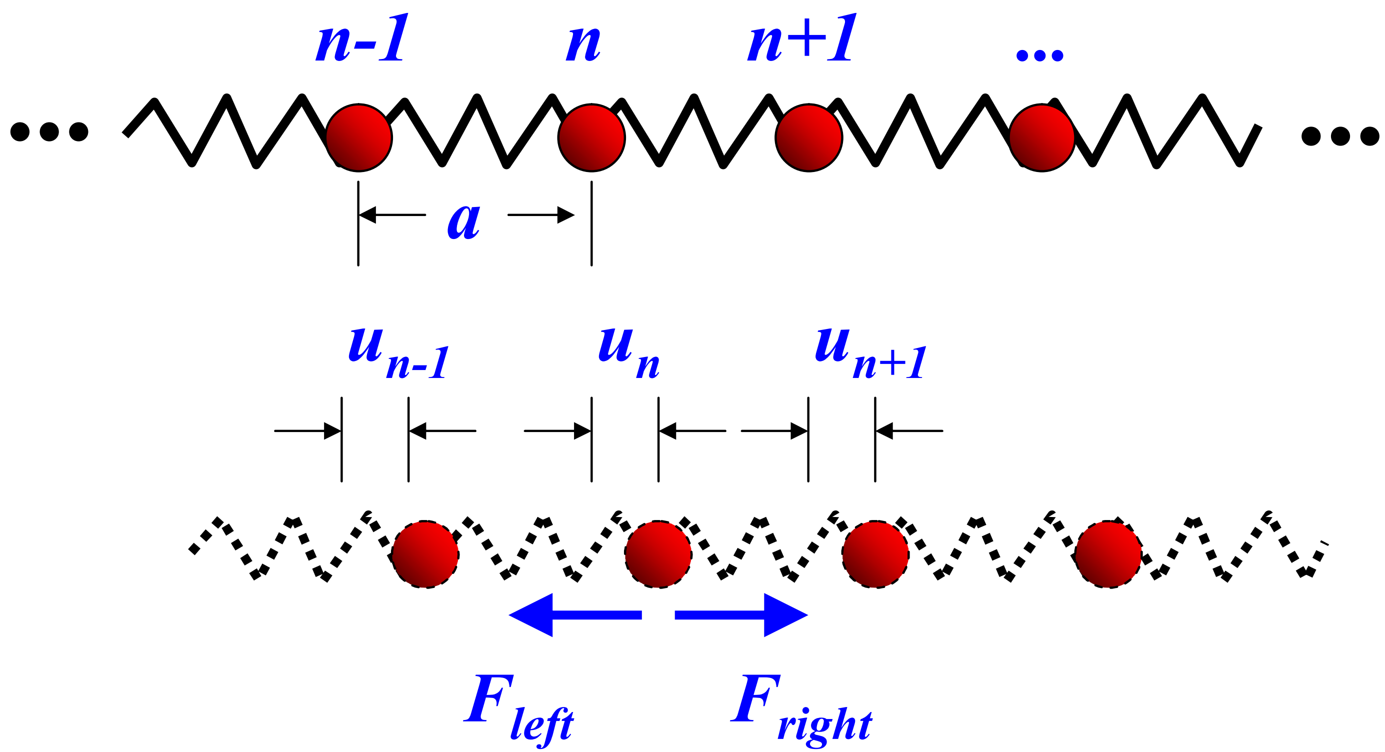
- Vibration modes of molecules can be measured by **infrared absorption spectrum**
- Infrared absorption of CO_2 causes **greenhouse effect**



1D *Monatomic* Chain 单原子链



1D *Monatomic* Chain 单原子链



$$F_{left} = K(u_n - u_{n-1})$$

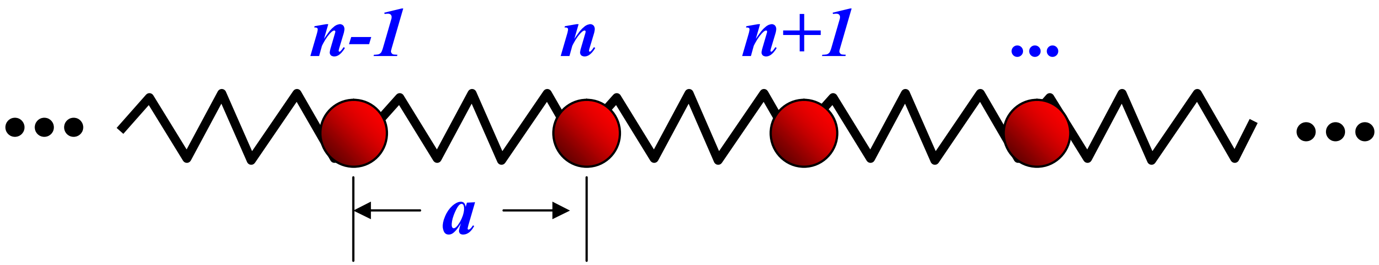
$$F_{right} = K(u_{n+1} - u_n)$$

$$F_n = F_{left} - F_{right}$$

and

$$F_n = m\frac{\partial^2 u_n}{\partial t^2}$$

1D *Monatomic* Chain 单原子链



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

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

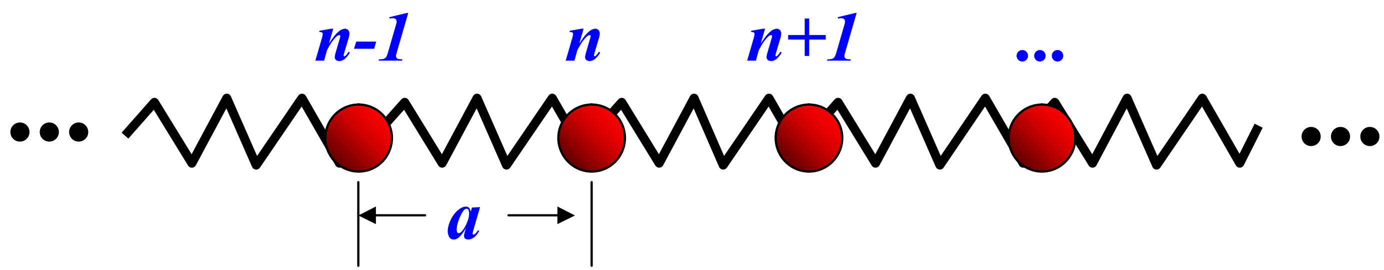
$$u_{n\pm1} = Ae^{i(kx-\omega t)}e^{\pm ika}$$

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

Wave Function

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

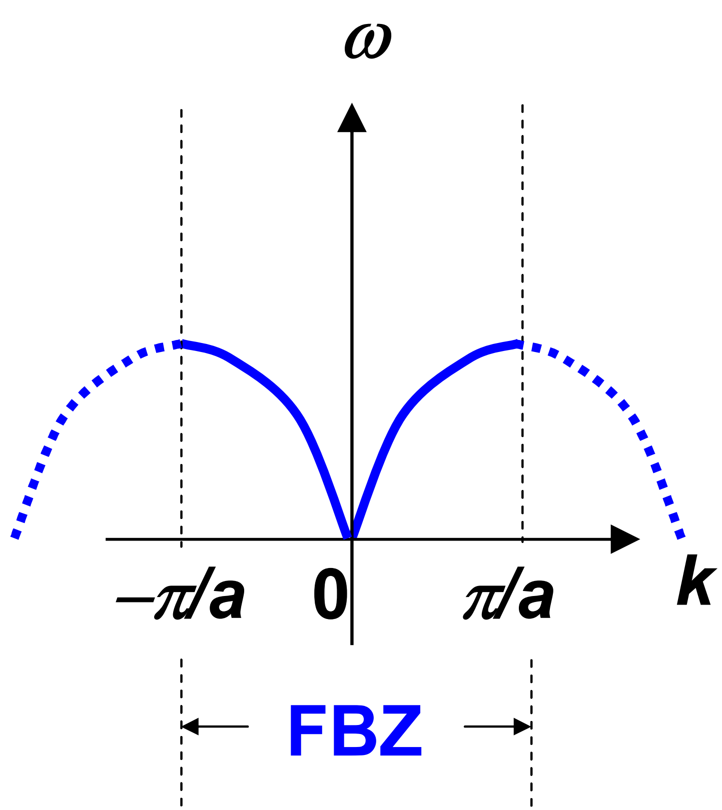
1D *Monatomic* Chain 单原子链



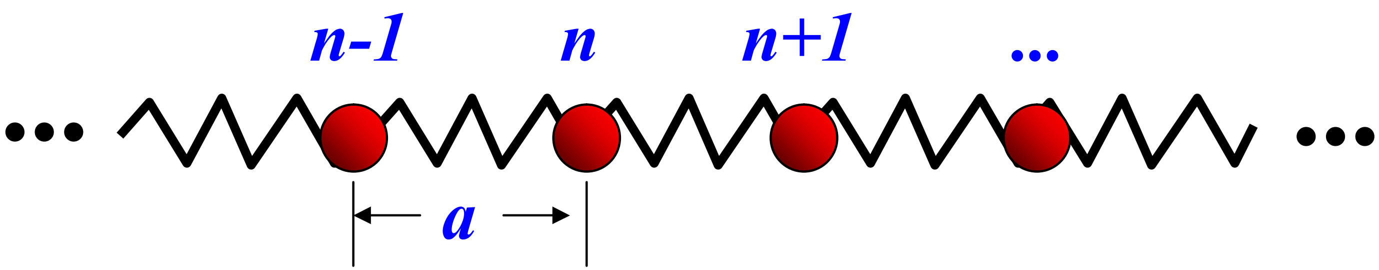
$$\omega^2 = \frac{K}{m}\left(2 - e^{-ika} - e^{+ika}\right) = \frac{4K}{m}\sin^2\left(\frac{ak}{2}\right)$$

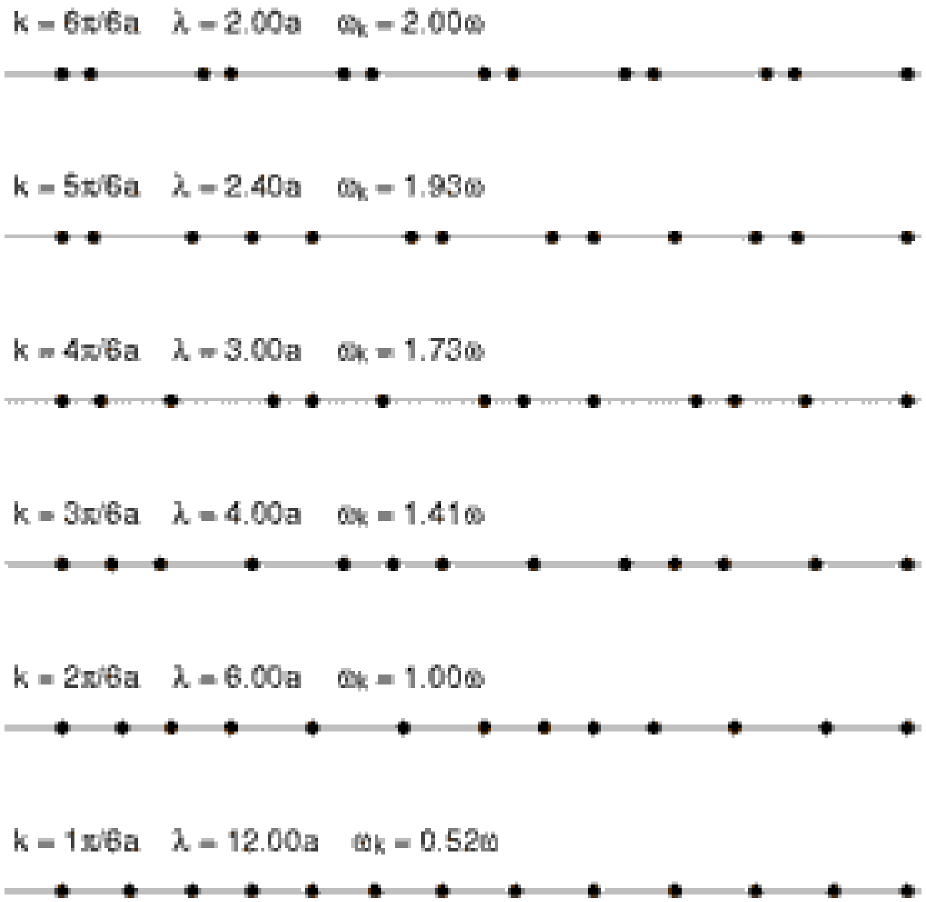
$$\omega = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{ak}{2}\right)\right|$$

ω-k diagram (dispersion curve)

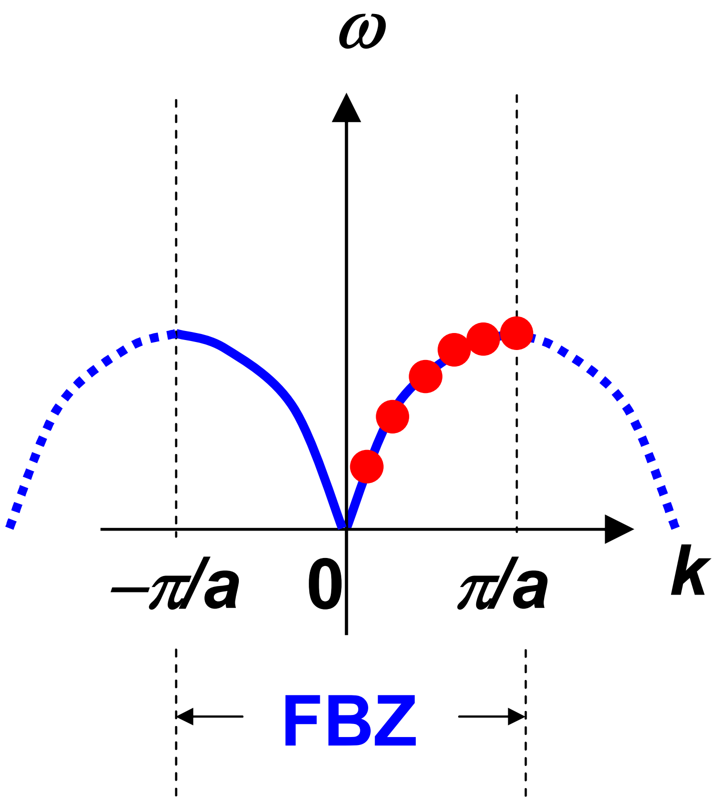


1D *Monatomic* Chain 单原子链





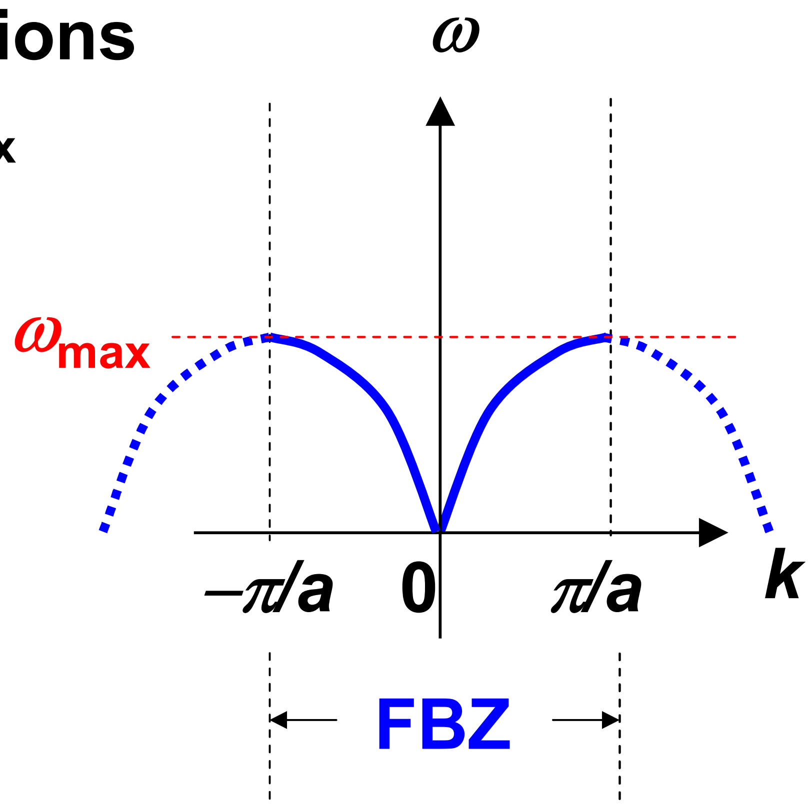
ω-*k* diagram (dispersion curve)



1D *Monatomic* Chain 单原子链

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

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



- **Phase velocity** $\boxed{v_p = \omega / k}$

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

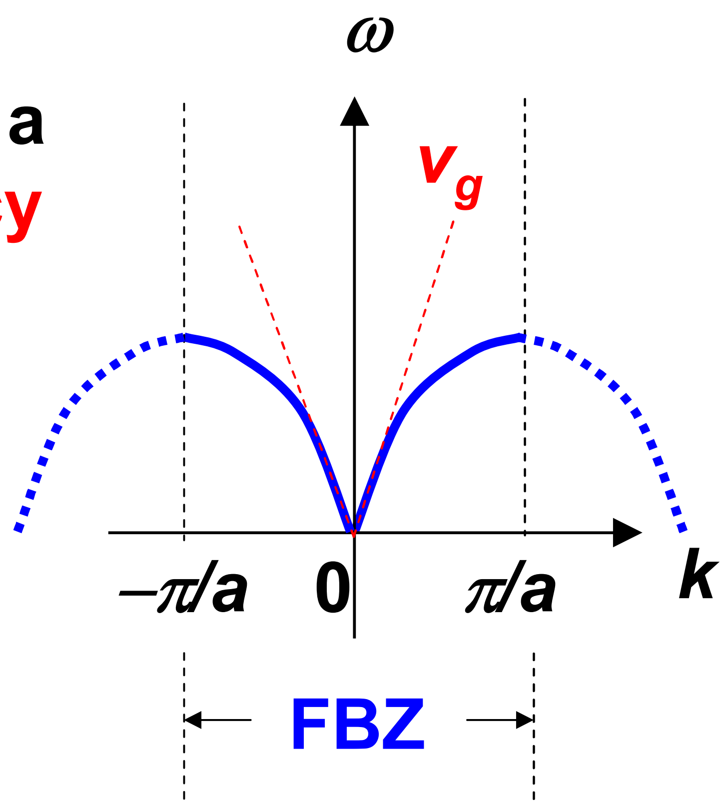
- **Standing wave (v_g = 0) at** $\boxed{k = \pm\frac{\pi}{a}}$

Speed of Sound 声速

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

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

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

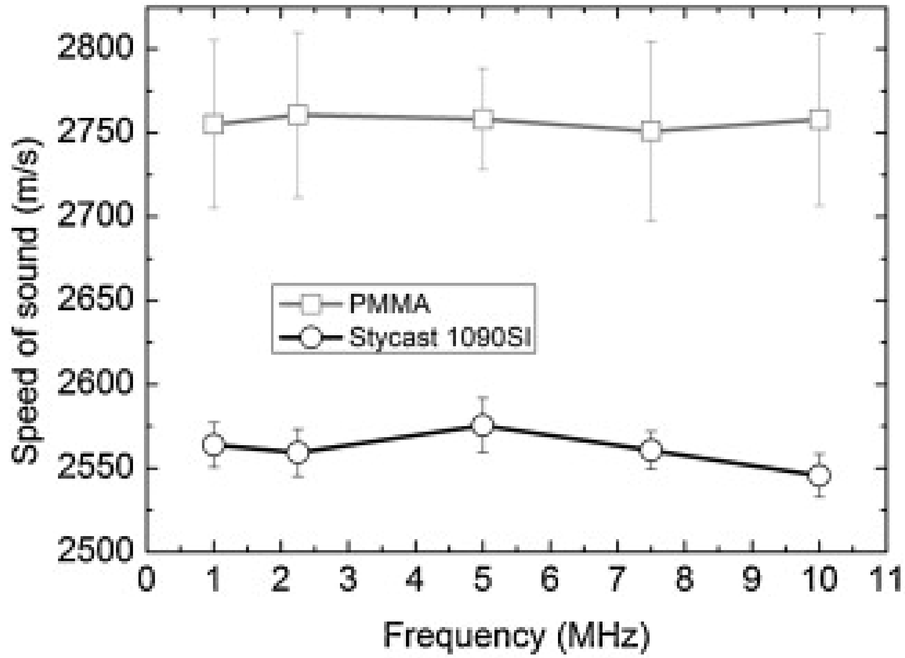


Speed of Sound 声速

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

sound speed in solids

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



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

Speed of Sound 声速

- At long wavelength limit $ka \sim 0$, group velocity is **speed of sound,** a constant **independent of frequency**

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

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

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- 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

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

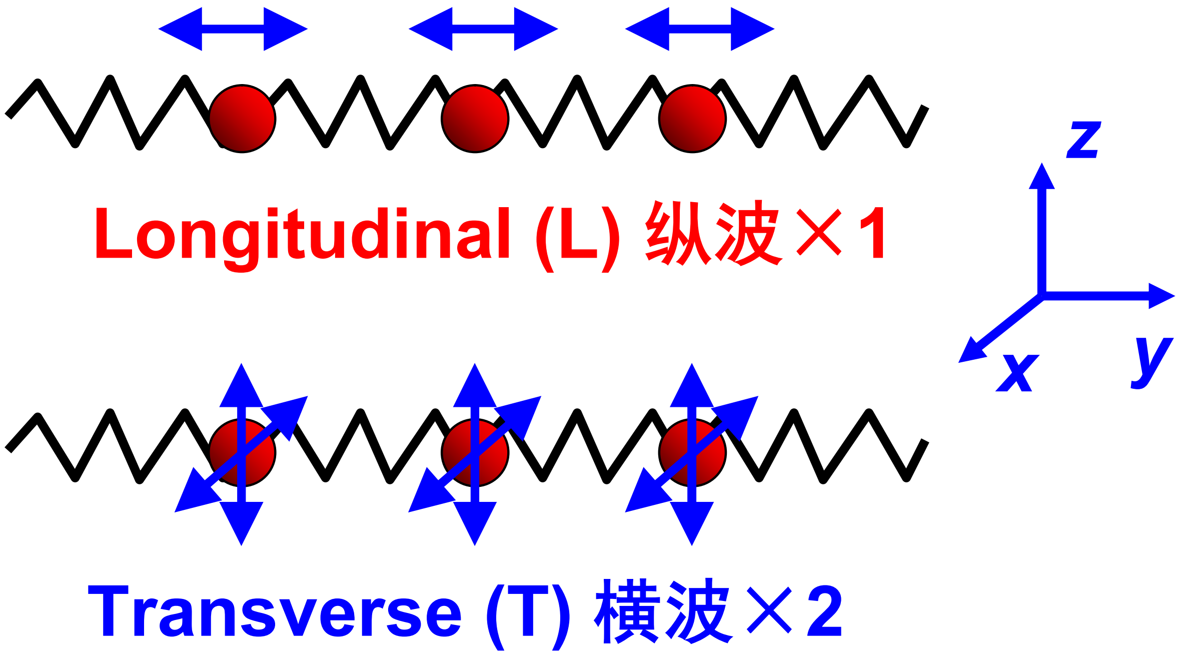
macroscopic properties

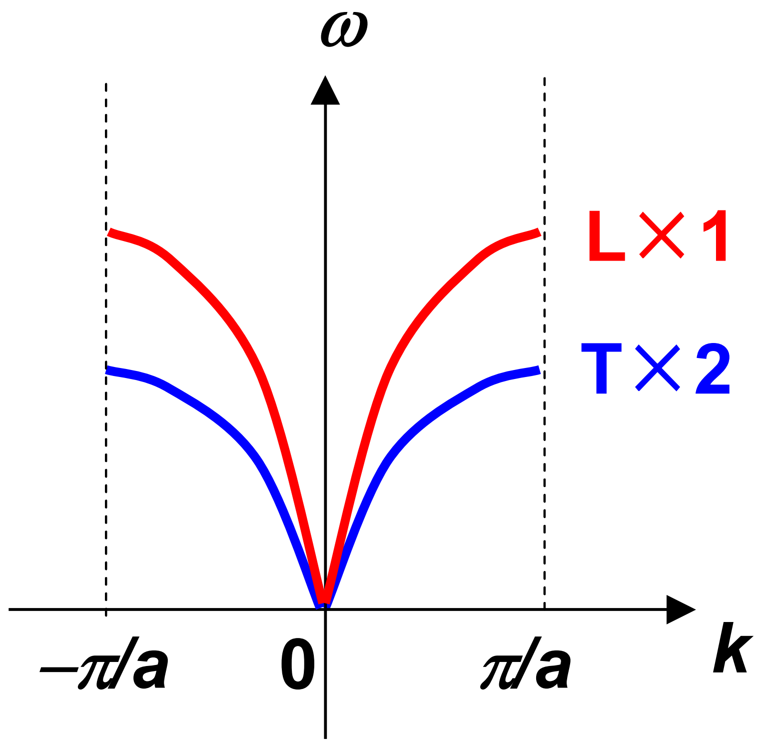
$$v_g = a\sqrt{\frac{K}{m}}$$

microscopic properties

ρ **- material density (kg/m^3)**

1D *Monatomic* Chain 单原子链



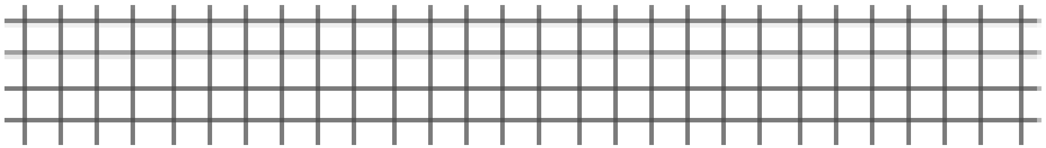


$$\omega = \sqrt{\frac{4K}{m}} \left| \sin\left(\frac{ak}{2}\right) \right|$$

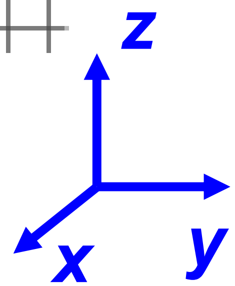
$$K_L > K_T$$

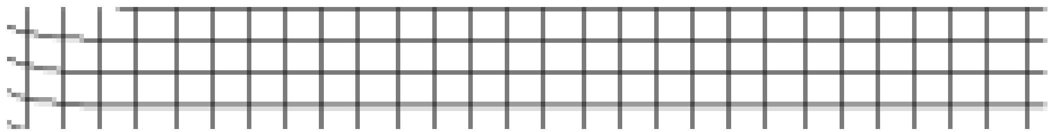
$$v_{gL} > v_{gT}$$

1D *Monatomic* Chain 单原子链

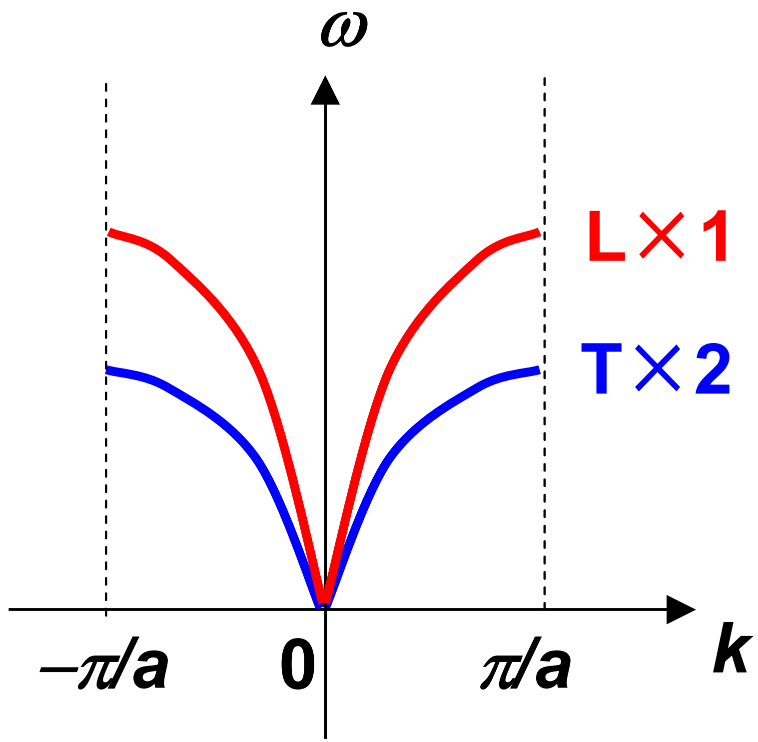


Longitudinal (L) 纵波×1





Transverse (T) 横波×2



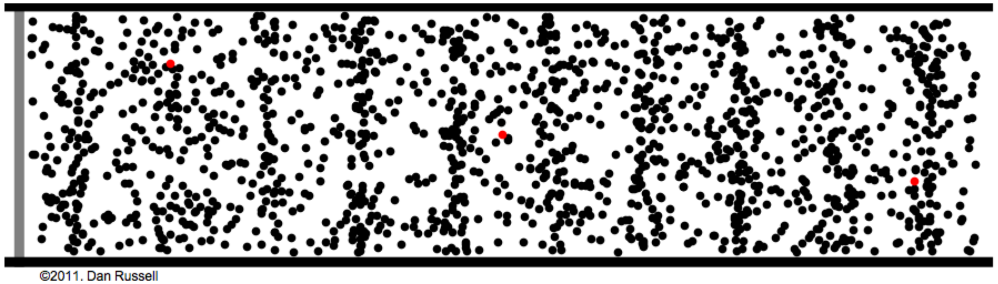
$$\omega = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{ak}{2}\right)\right|$$

$$K_L > K_T$$

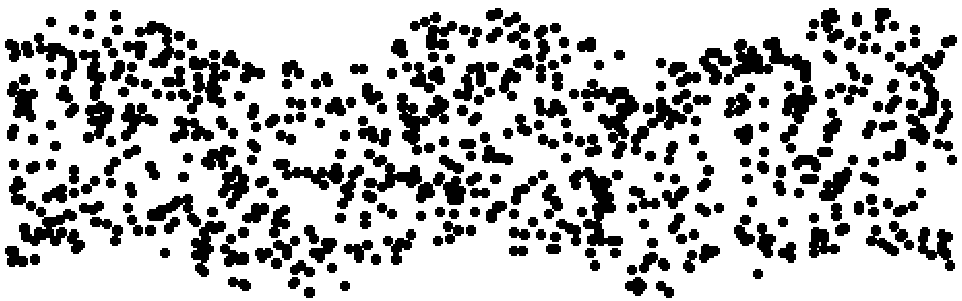
$$v_{gL} > v_{gT}$$

Seismic Waves 地震波

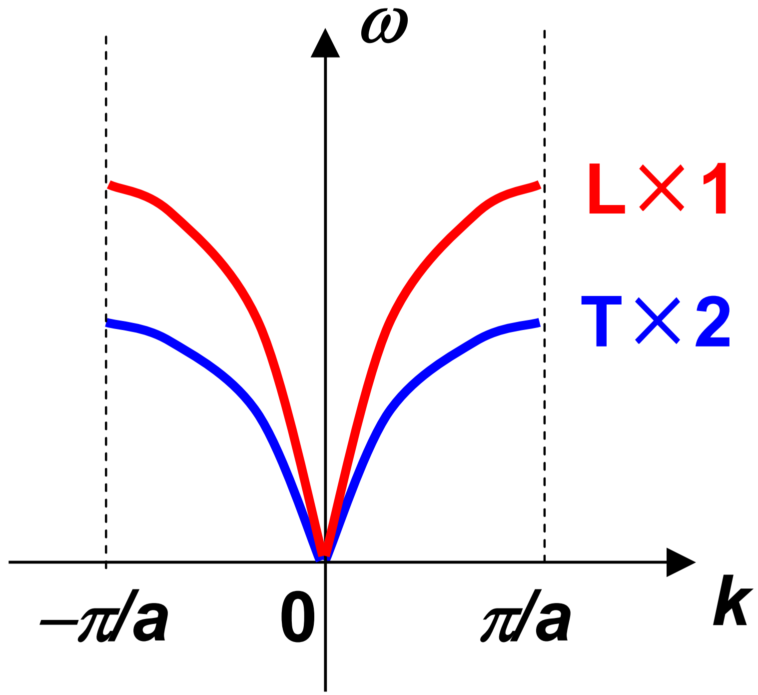
$$v_{gL} > v_{gT}$$



L wave arrives first, less damage

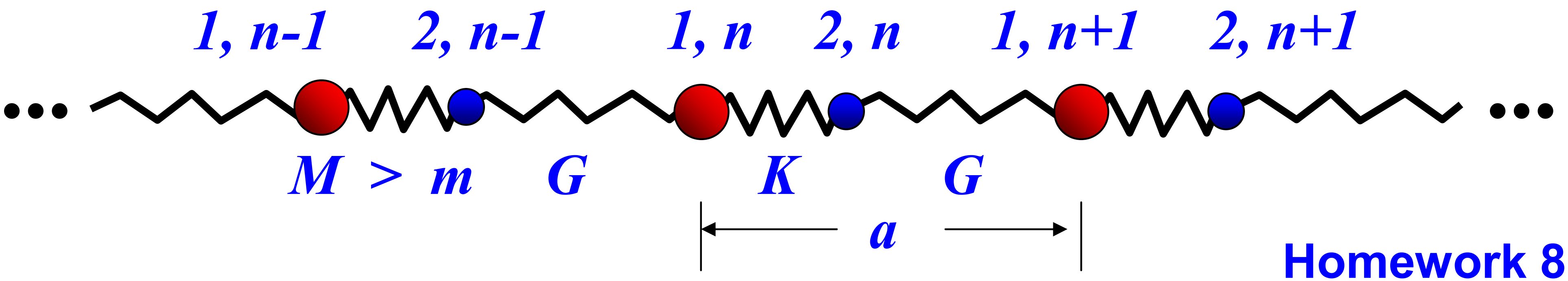


T wave arrives later, more damage!



video - earthquake

1D *Diatomic* Chain 双原子链



Homework 8.3

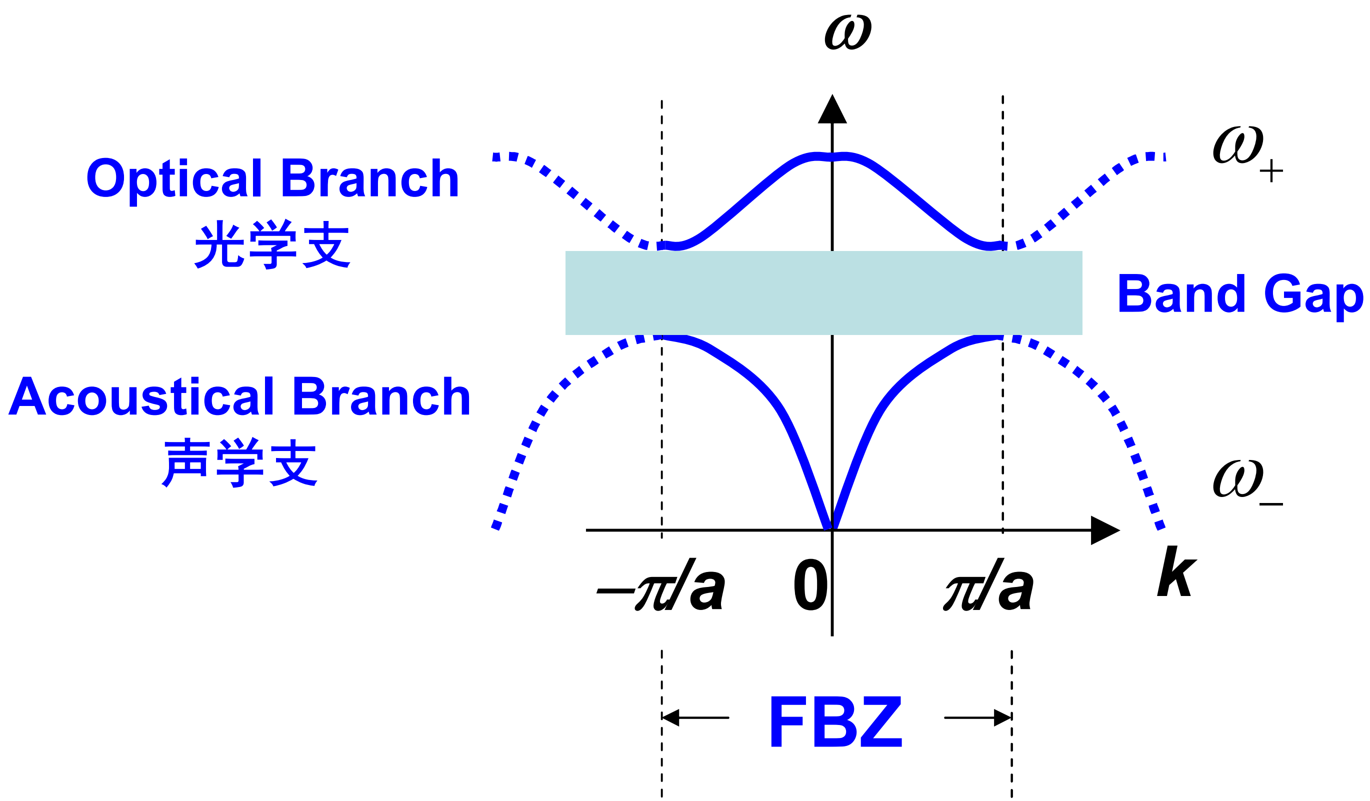
$$\begin{cases} M\dfrac{\partial^2 u_{1,n}}{\partial t^2} + K(u_{1,n} - u_{2,n}) + G(u_{1,n} - u_{2,n-1}) = 0 \\ m\dfrac{\partial^2 u_{2,n}}{\partial t^2} + K(u_{2,n} - u_{1,n}) + G(u_{2,n} - u_{1,n+1}) = 0 \end{cases}$$

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

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

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:

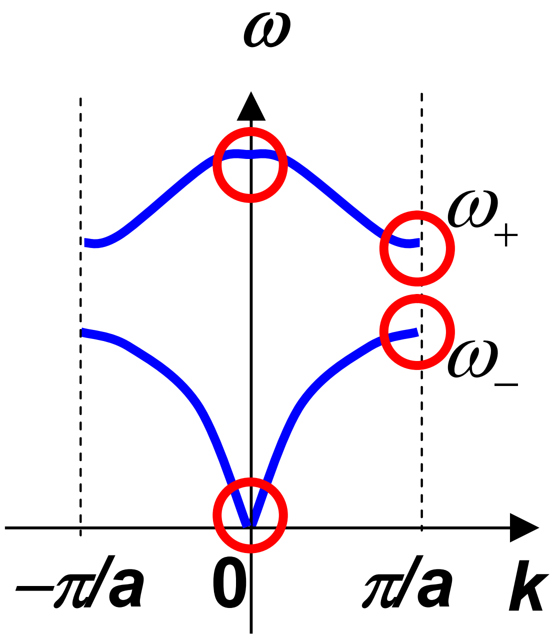
$$\omega^2 = K\frac{M+m}{Mm}\left[1 \pm \sqrt{1 - \frac{4Mm}{(M+m)^2}\sin^2\left(\frac{ak}{2}\right)}\right]$$

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

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

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

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



1D *Diatomic* Chain 双原子链

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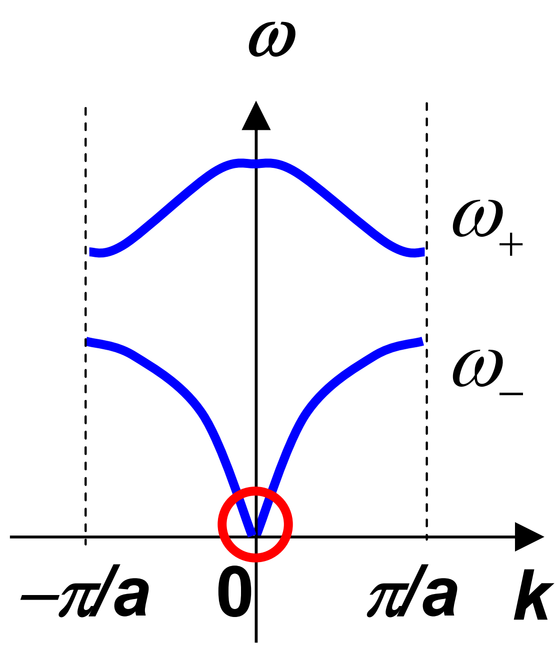
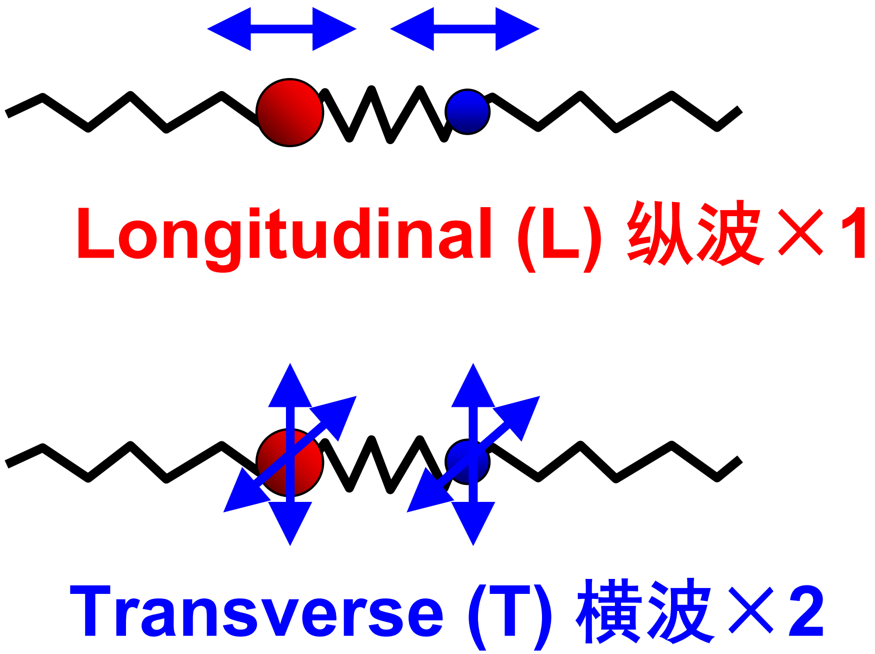
$$\omega_-(k \approx 0) = \sqrt{\frac{K}{2(M+m)}}ak$$

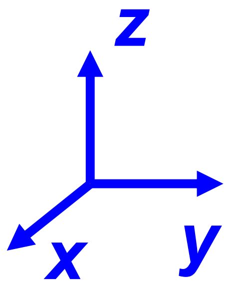
Sound Speed

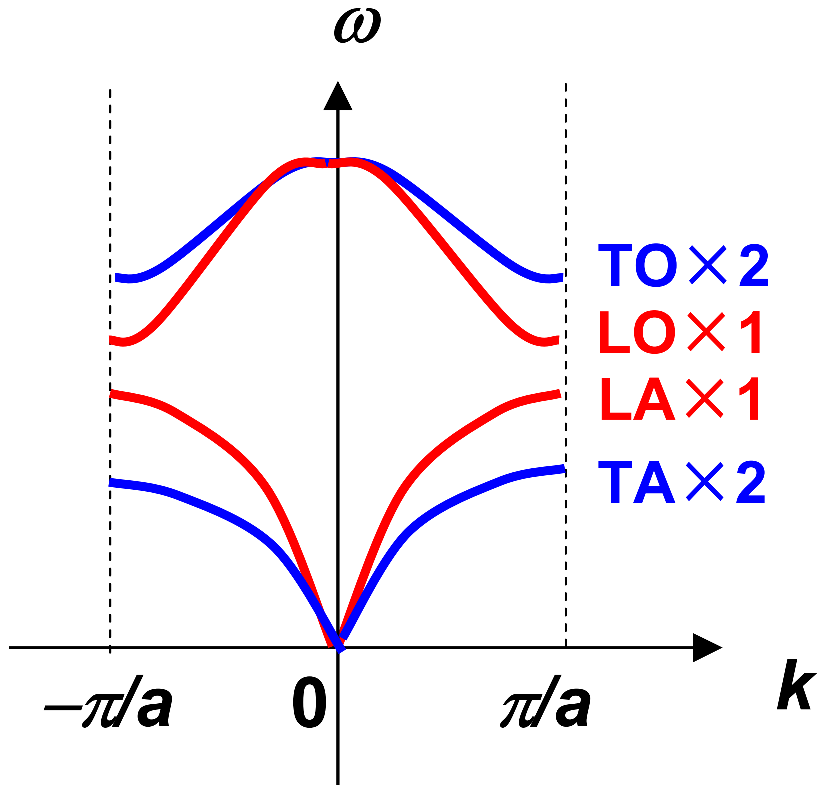
$$v_g = \partial\omega / \partial k$$
$$= a\sqrt{\frac{K}{2(M+m)}}$$



1D *Diatomic* Chain 双原子链

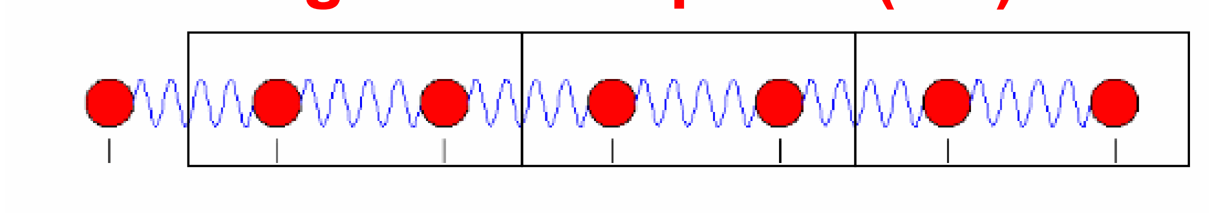




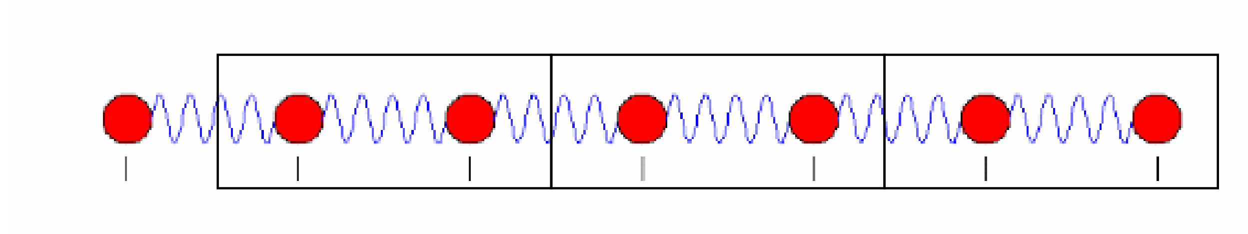


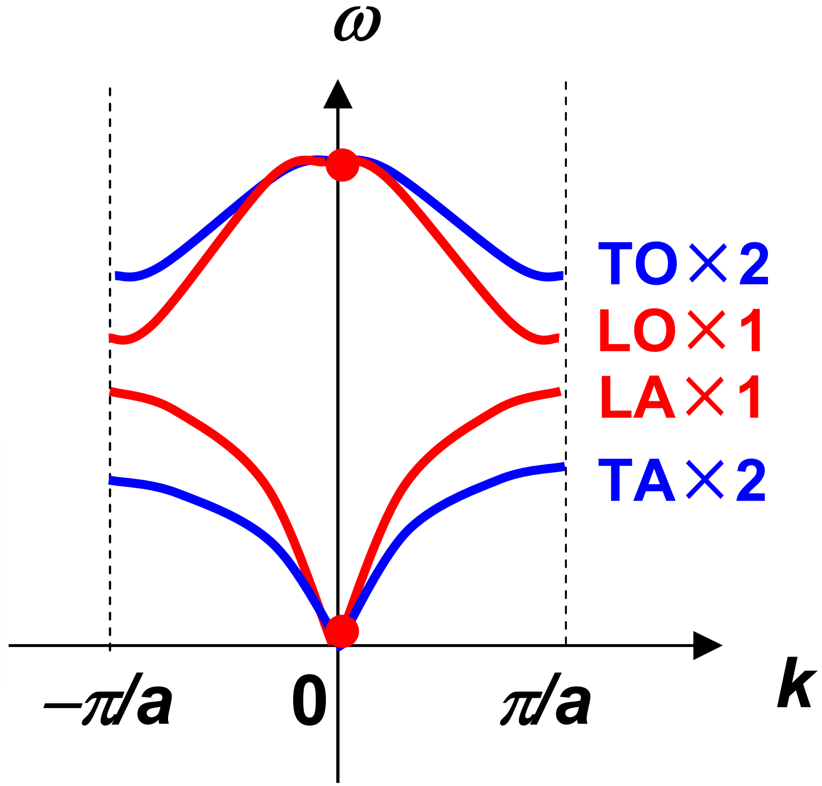
1D *Diatomic* Chain 双原子链

Longitudinal Optical (LO)



Longitudinal Acoustical (LA)



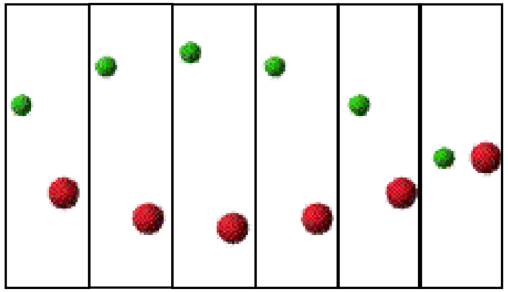


Acoustic modes are related to
the low frequency vibration across the entire crystal;
Optical modes are related to
the high frequency vibration inside the primitive cell.

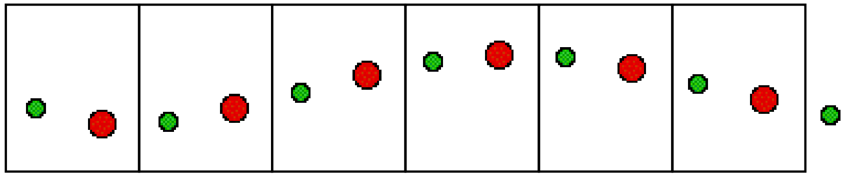
http://exafs.ucsc.edu/simulations/

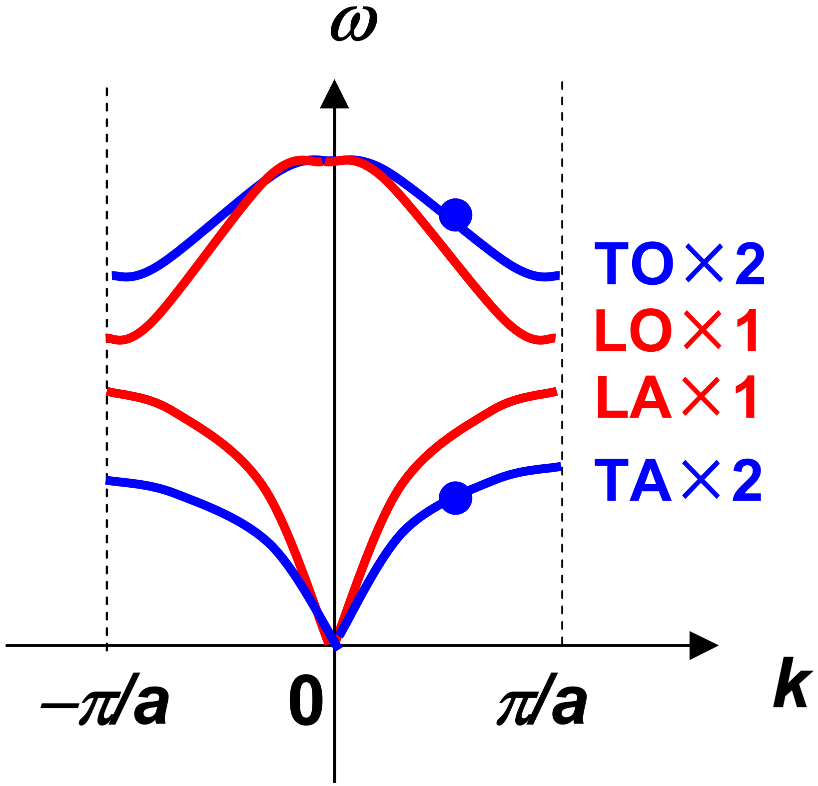
1D *Diatomic* Chain 双原子链

Transverse Optical (TO)



Transverse Acoustical (TA)





Acoustic modes are related to
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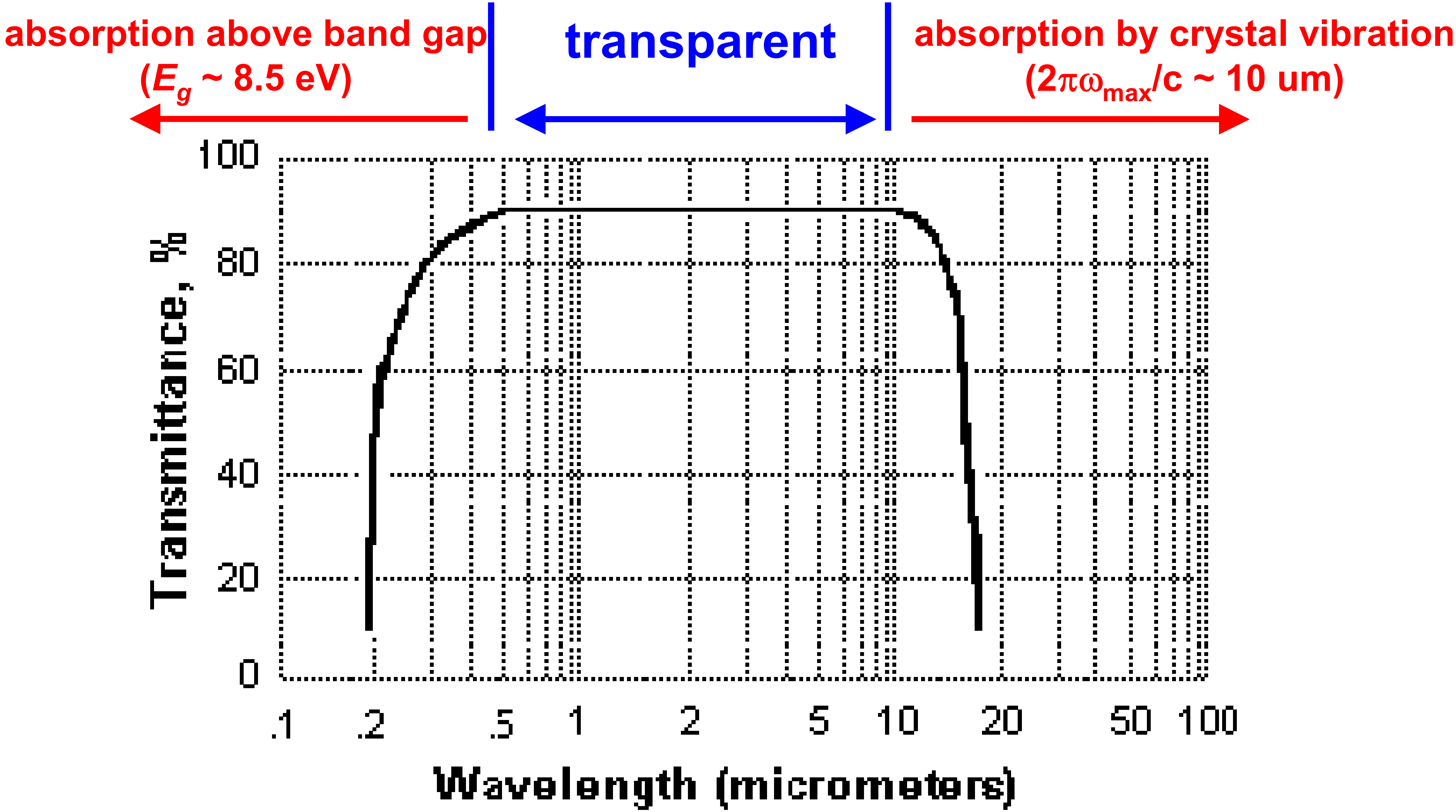
Optical modes are related to
the high frequency vibration inside the primitive cell.

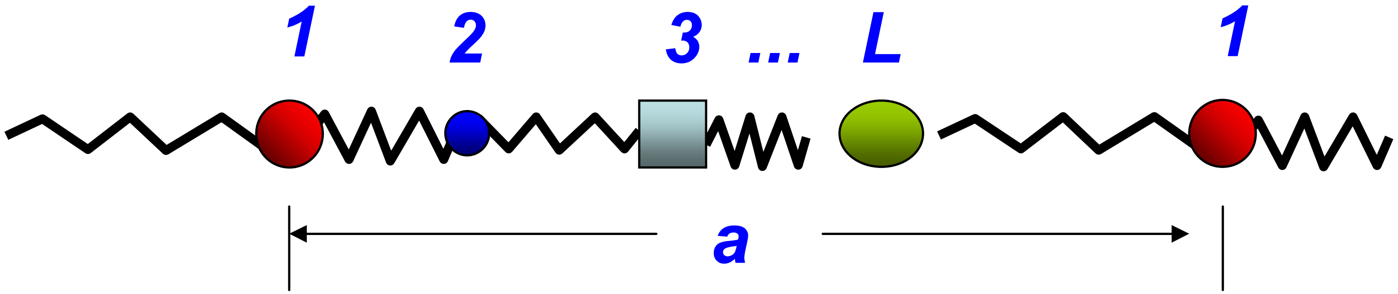
http://www.chembio.uoguelph.ca/educmat/chm729/Phonons/optmovie.htm

Optical Properties of NaCl

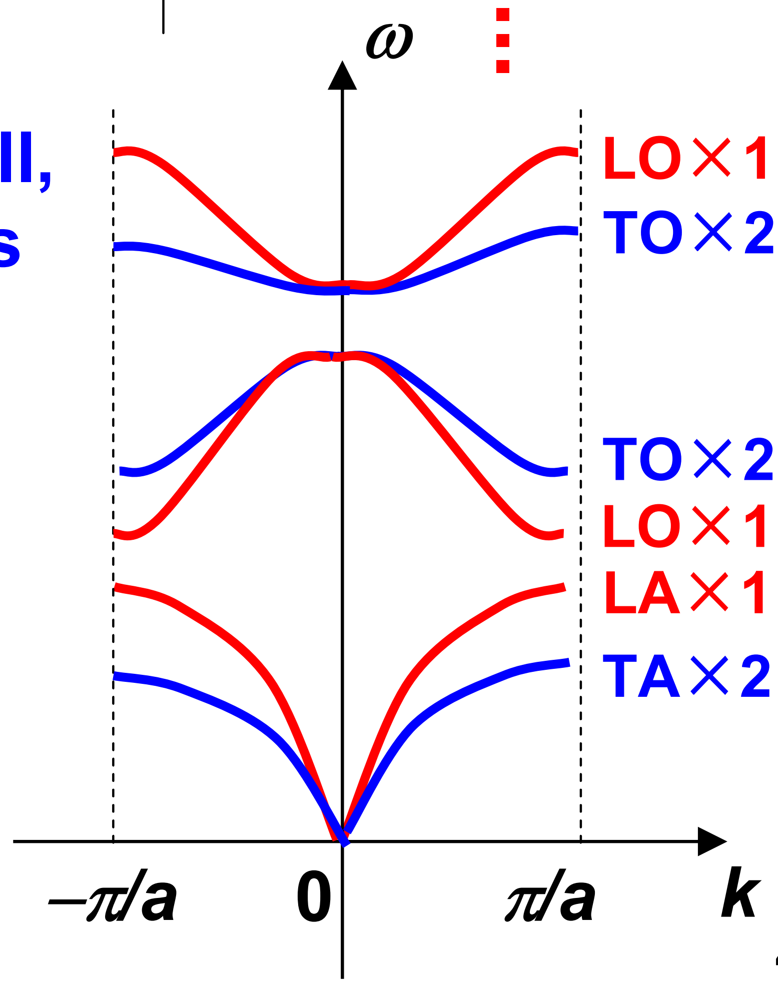


http://www.crystaltechno.com/NaCl_en.htm

1D *Multi-atomic* Chain 多原子链



If there are *L* atoms in a primitive cell, there will be more optical branches (but still finite)



There will be:

1 LA, 2 TA

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

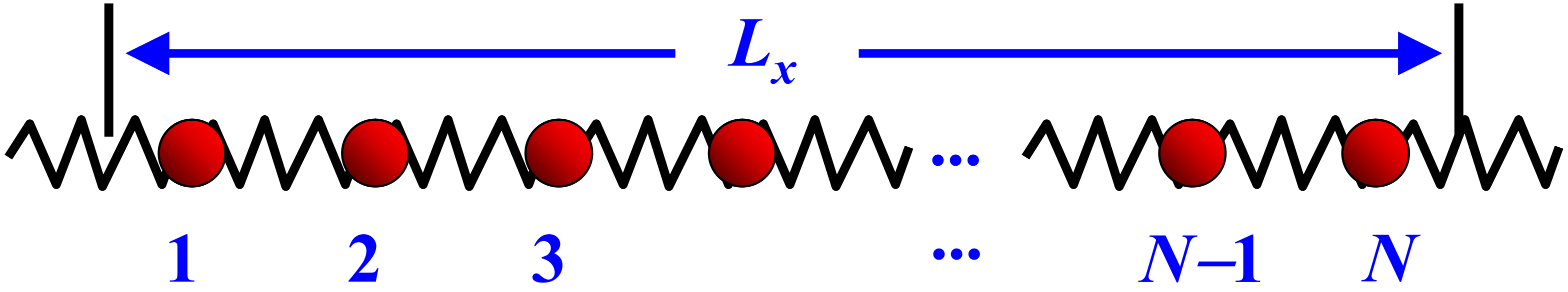
Fundamentals of Solid State Physics

Lattice Vibration
- Quantum Model

Xing Sheng 盛兴

Department of Electronic Engineering
Tsinghua University
xingsheng@tsinghua.edu.cn

Quantization of the Bands 量子化



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

Born-von Karman *periodic* boundary condition

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

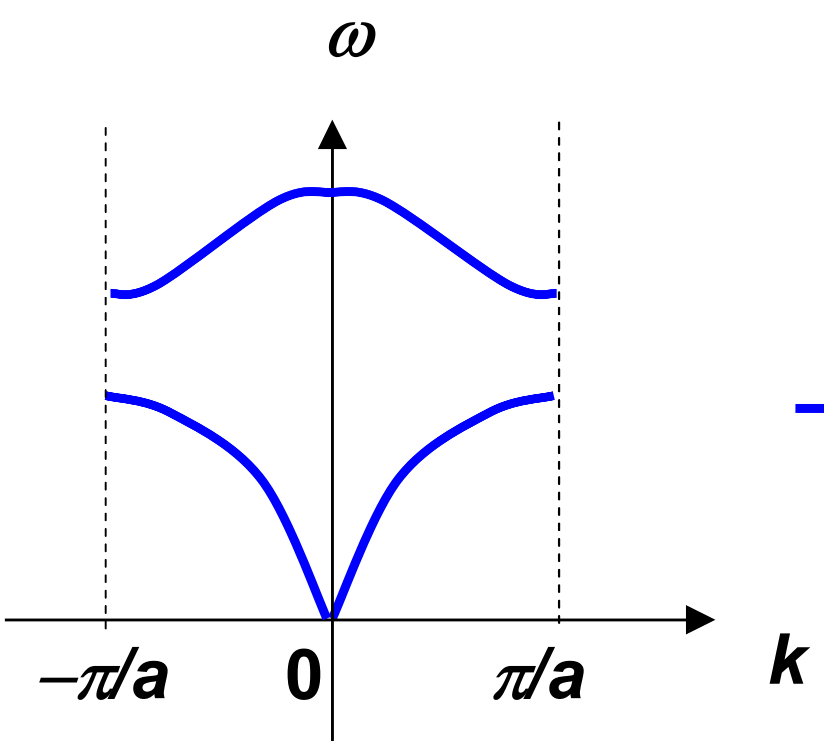
$$\rightarrow k_x = \frac{2\pi n_x}{L_x} \qquad n_x = 0, \pm 1, \pm 2, \ldots$$

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

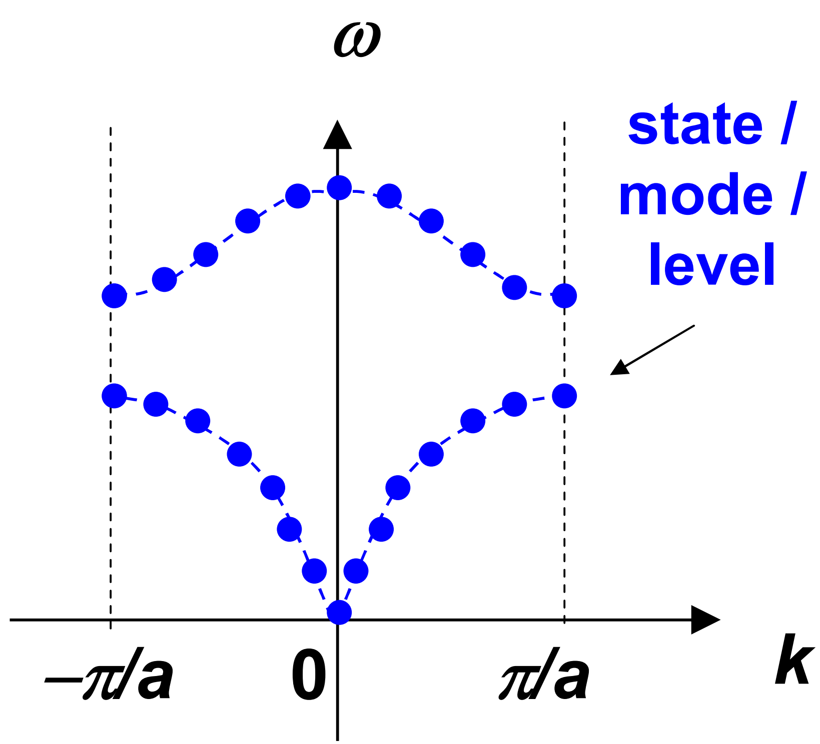
Quantization of the Bands 量子化

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

quasi-continuous



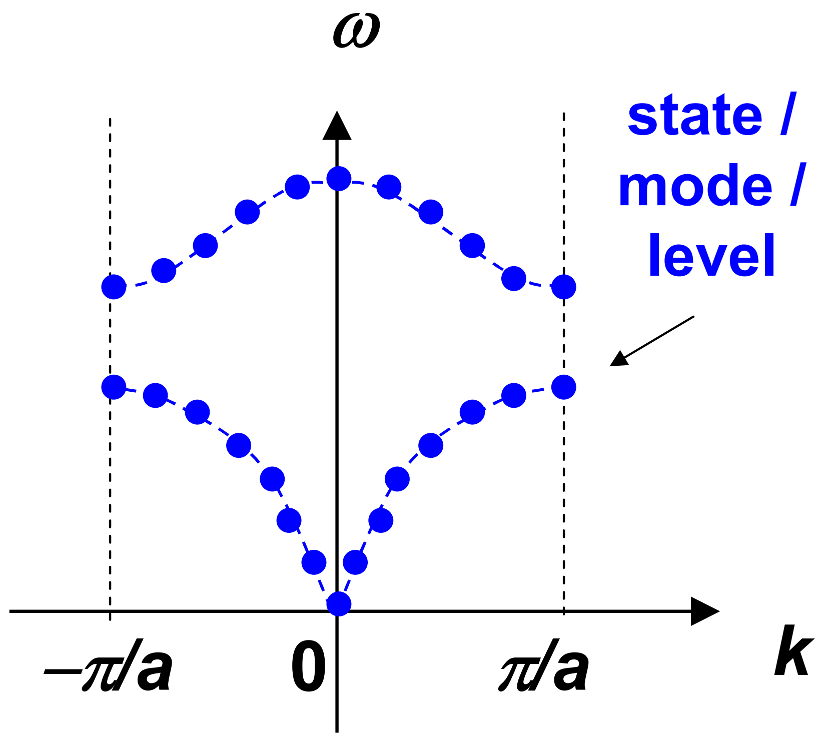
***ω-k* diagram**
(dispersion curve)



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



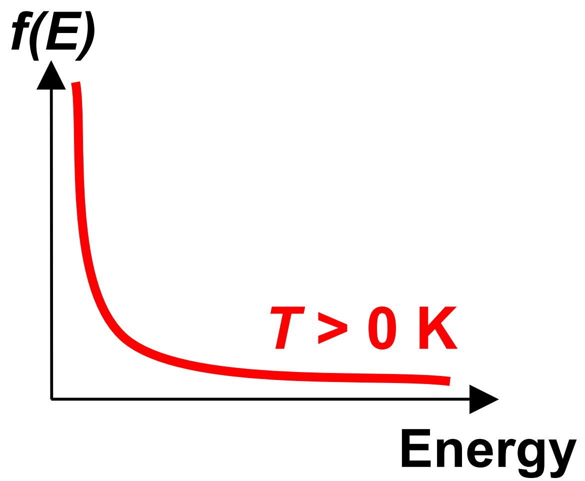
quantized state / level

Phonon 声子

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

number of phonons

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

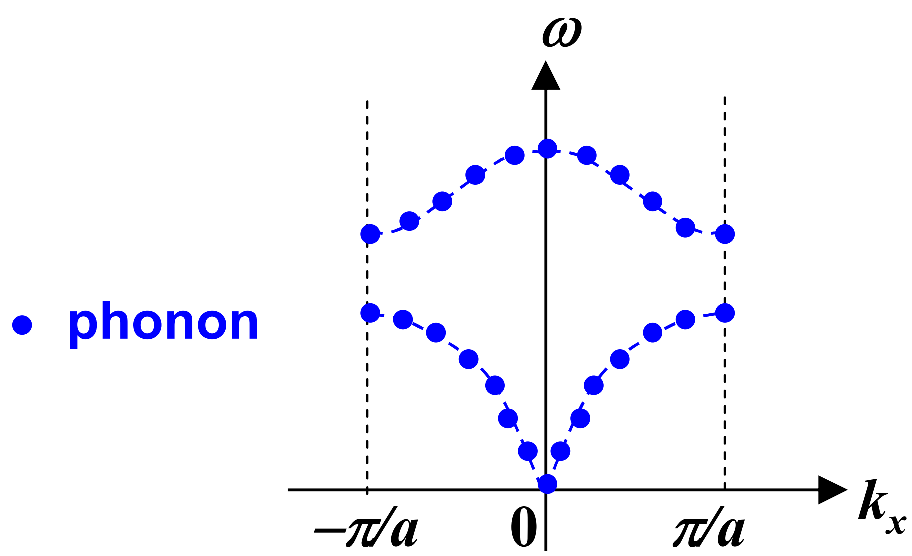


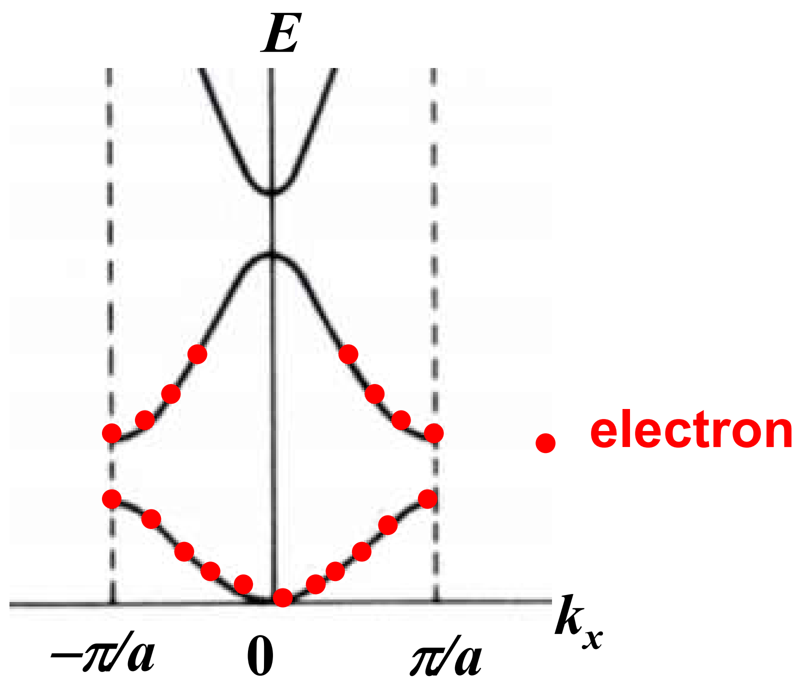
- Phonon 声子 vs. Photon 光子
  - Both of them are bosons, but
  - Phonon is a collective atom vibration, quasi-particle (准粒子)
  - Photon is a fundamental particle (基本粒子)

Phonon Band vs. Electron Band

- **Phonon Band**
  - max frequency ω_{max}
  - phonon number is not constant, depend on T
  - each state can have many phonons (Bosons)

- **Electron Band**
  - no highest energy
  - electron number is fixed
  - each state can only have one or zero electrons

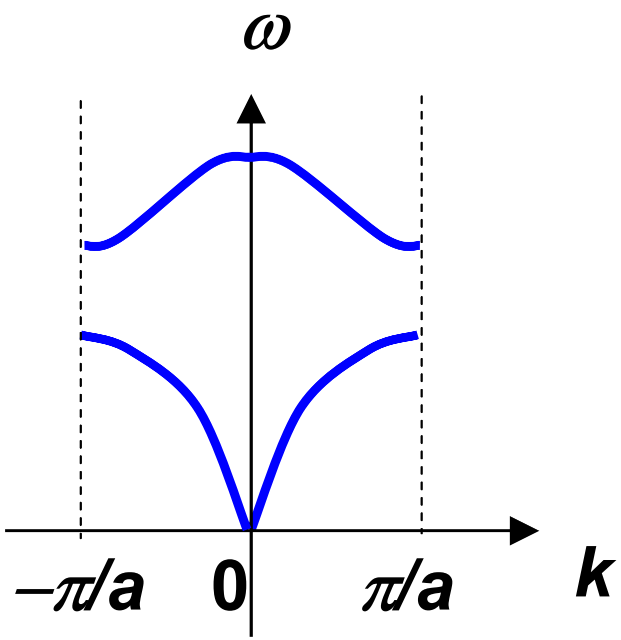




k values have the same physical meaning, related to the crystal structure

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

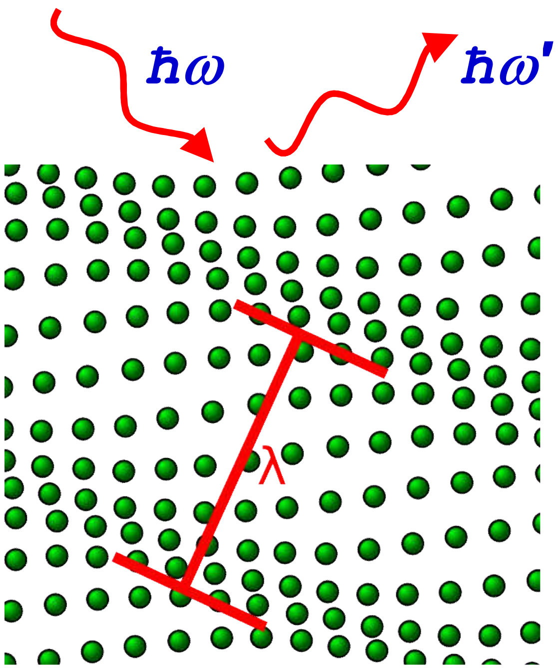
- **Optical Scattering**
  - **Photons have much smaller momentum than phonons**
  - **can only measure *k* ~ 0**

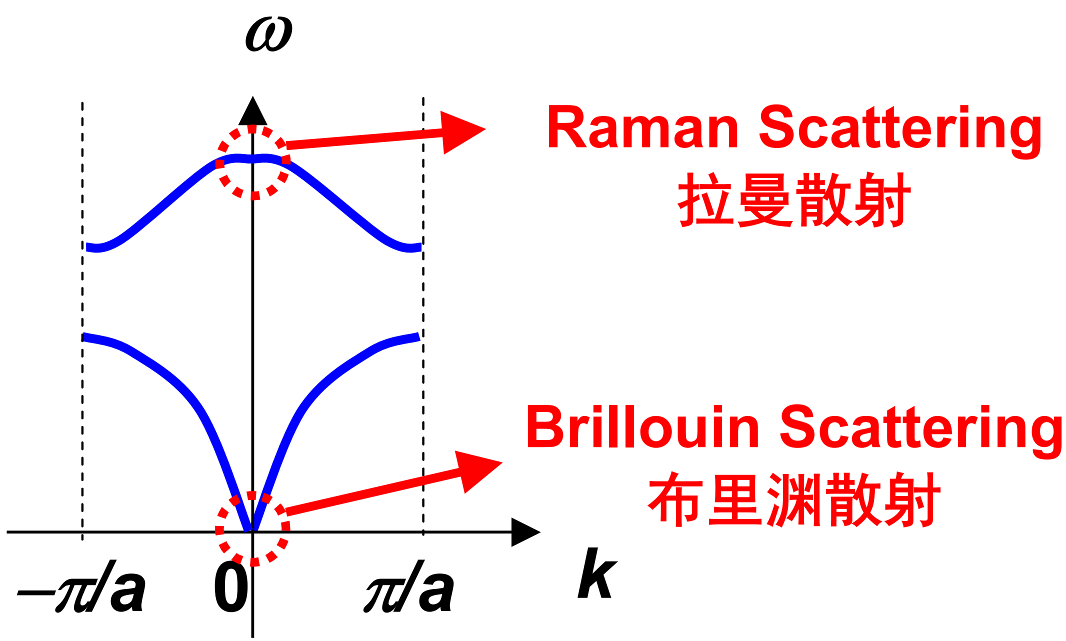
$$p = \frac{h}{\lambda} \ll \frac{h}{a}$$

$$\lambda \gg a$$

$$\Delta p = \hbar k$$

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





Measure Phonon Band Diagram

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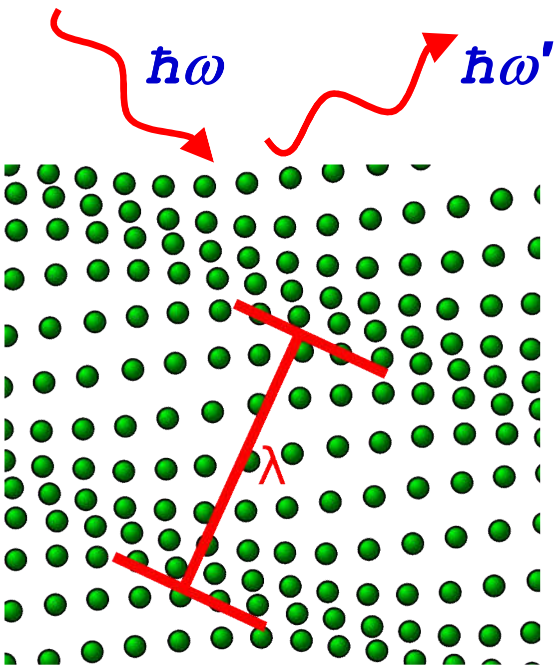
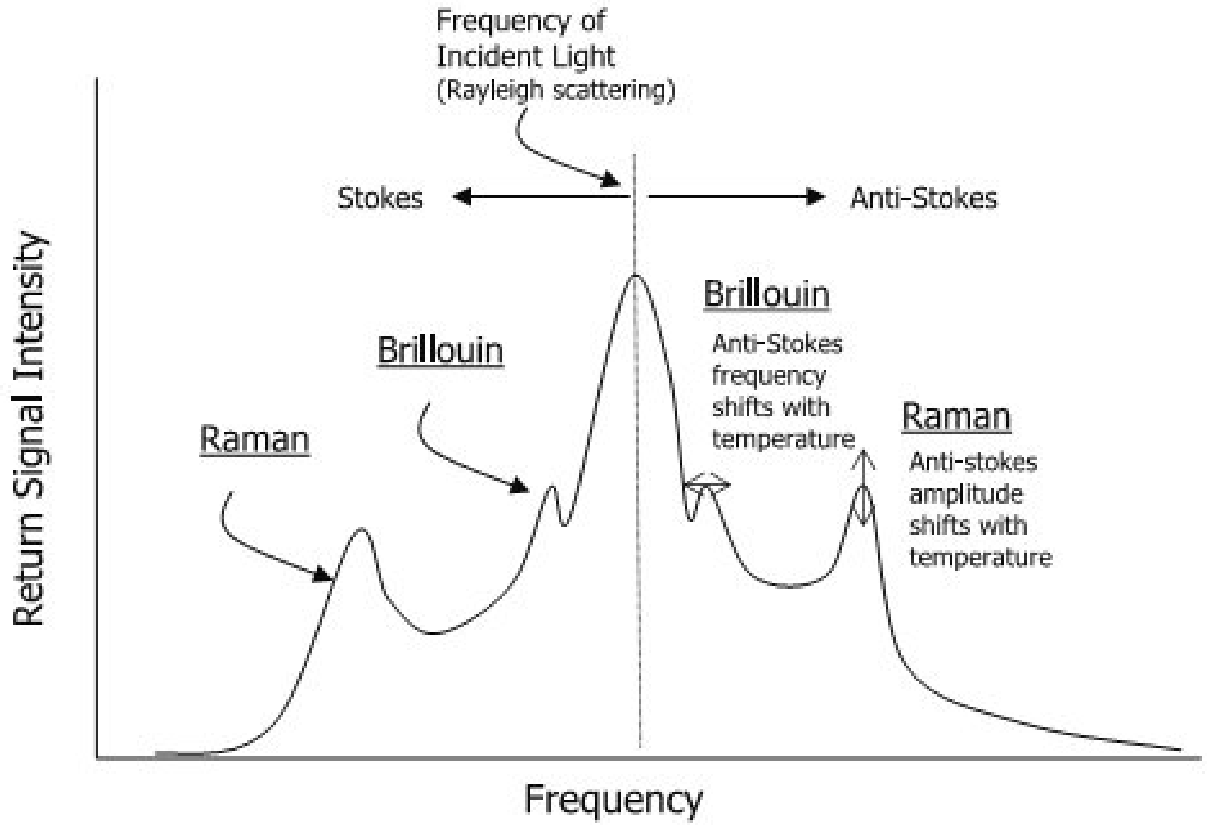


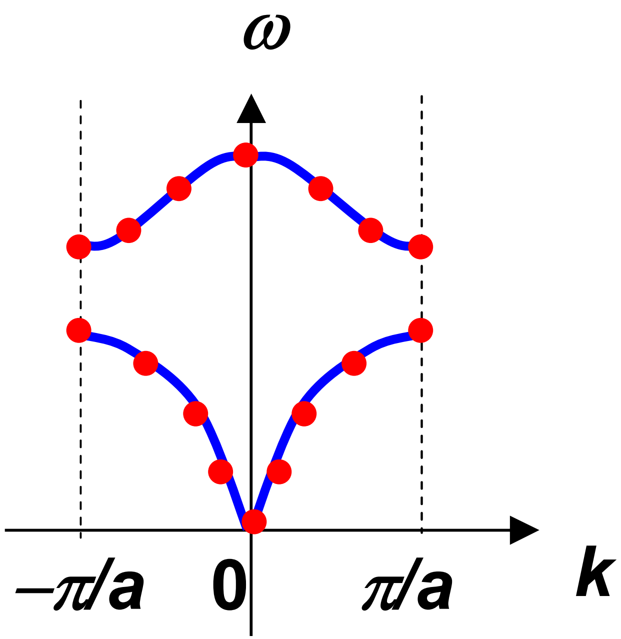


Neutron Scattering 中子散射

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

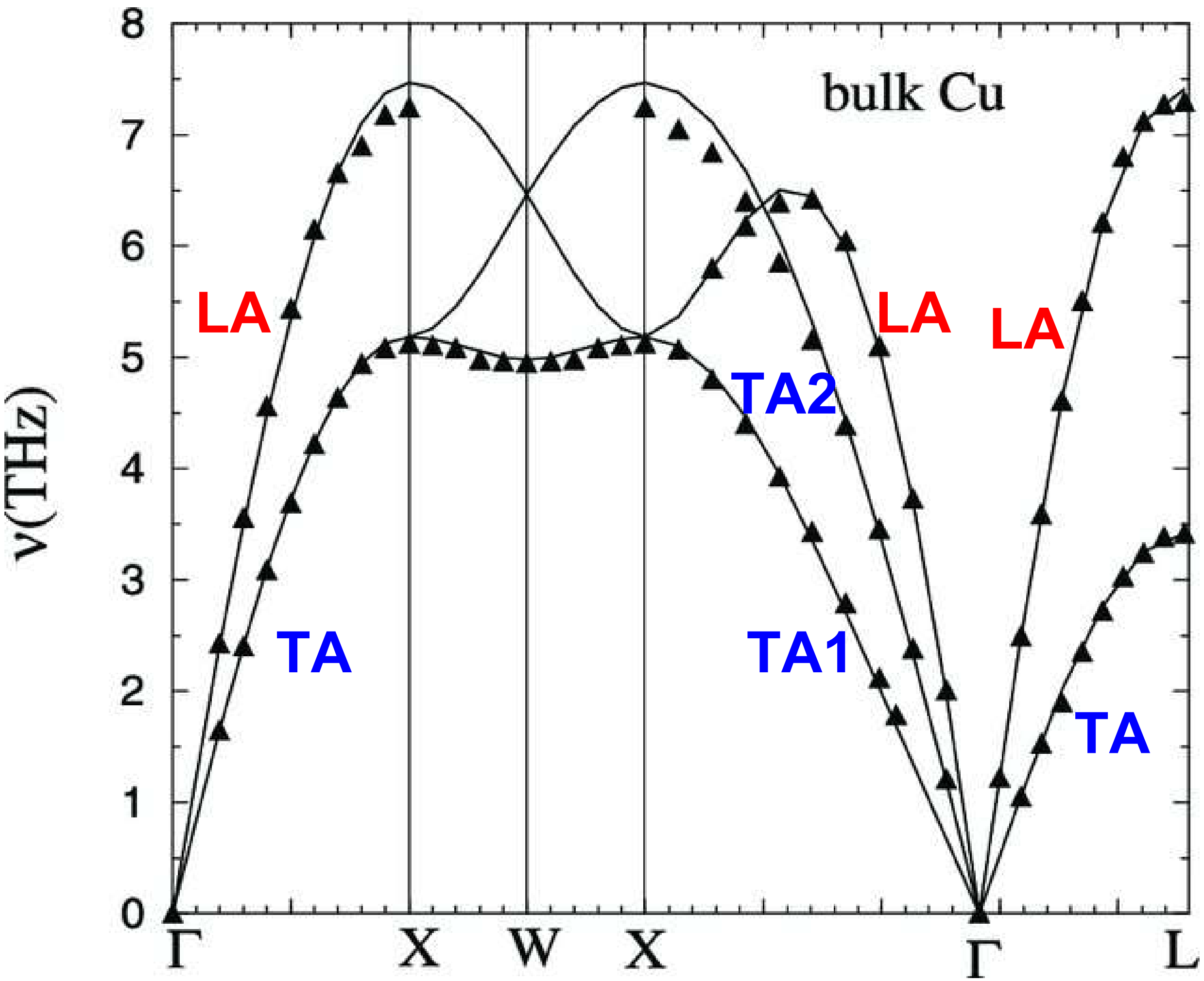
$$\boxed{\Delta p = \hbar k} \qquad \boxed{\Delta E = \hbar \omega}$$

- Need a nuclear reactor!



散裂中子源，东莞

Phonon Band Diagram - Copper



▲ **measured by neutron scattering**

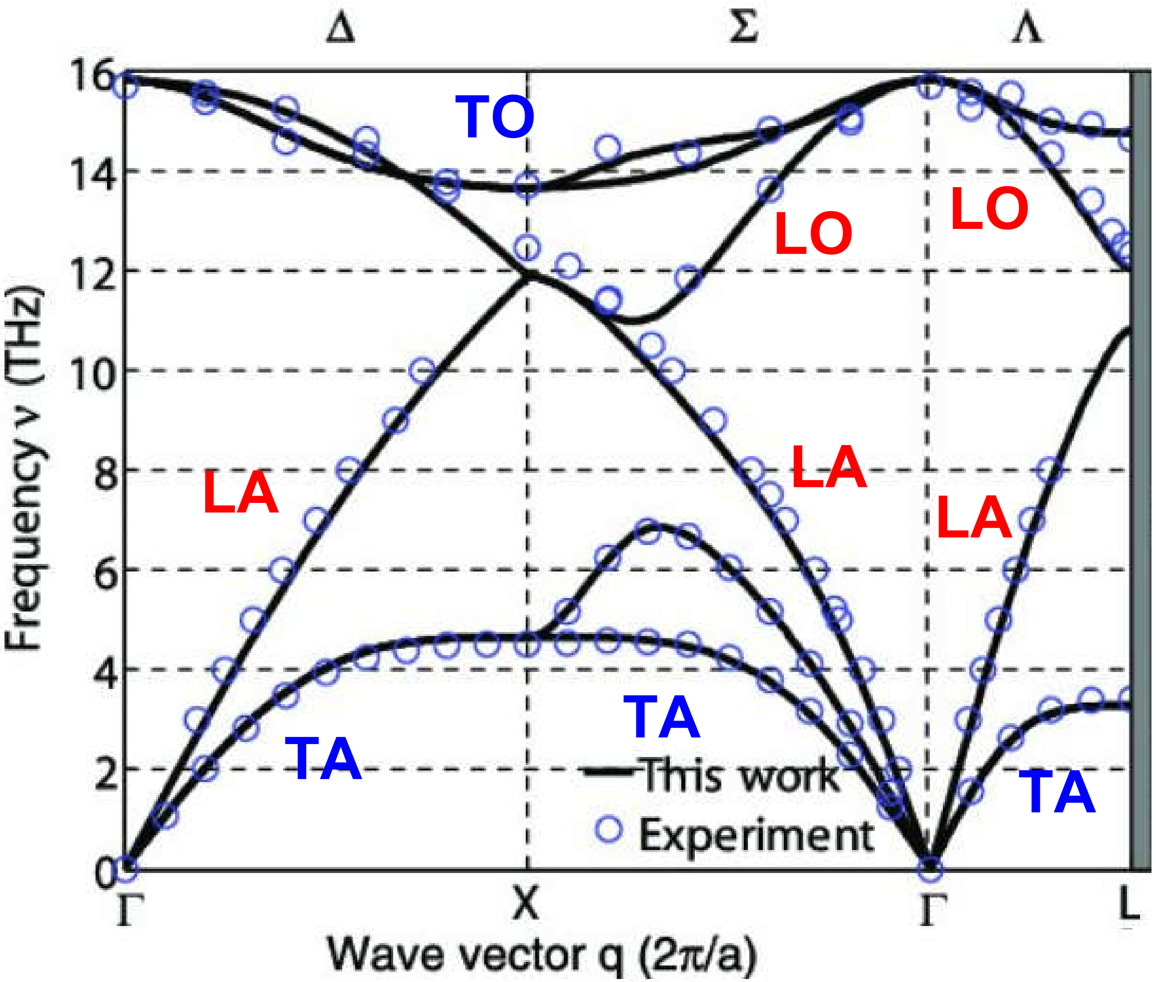
—— calculation

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

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

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

at low ω limit →

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

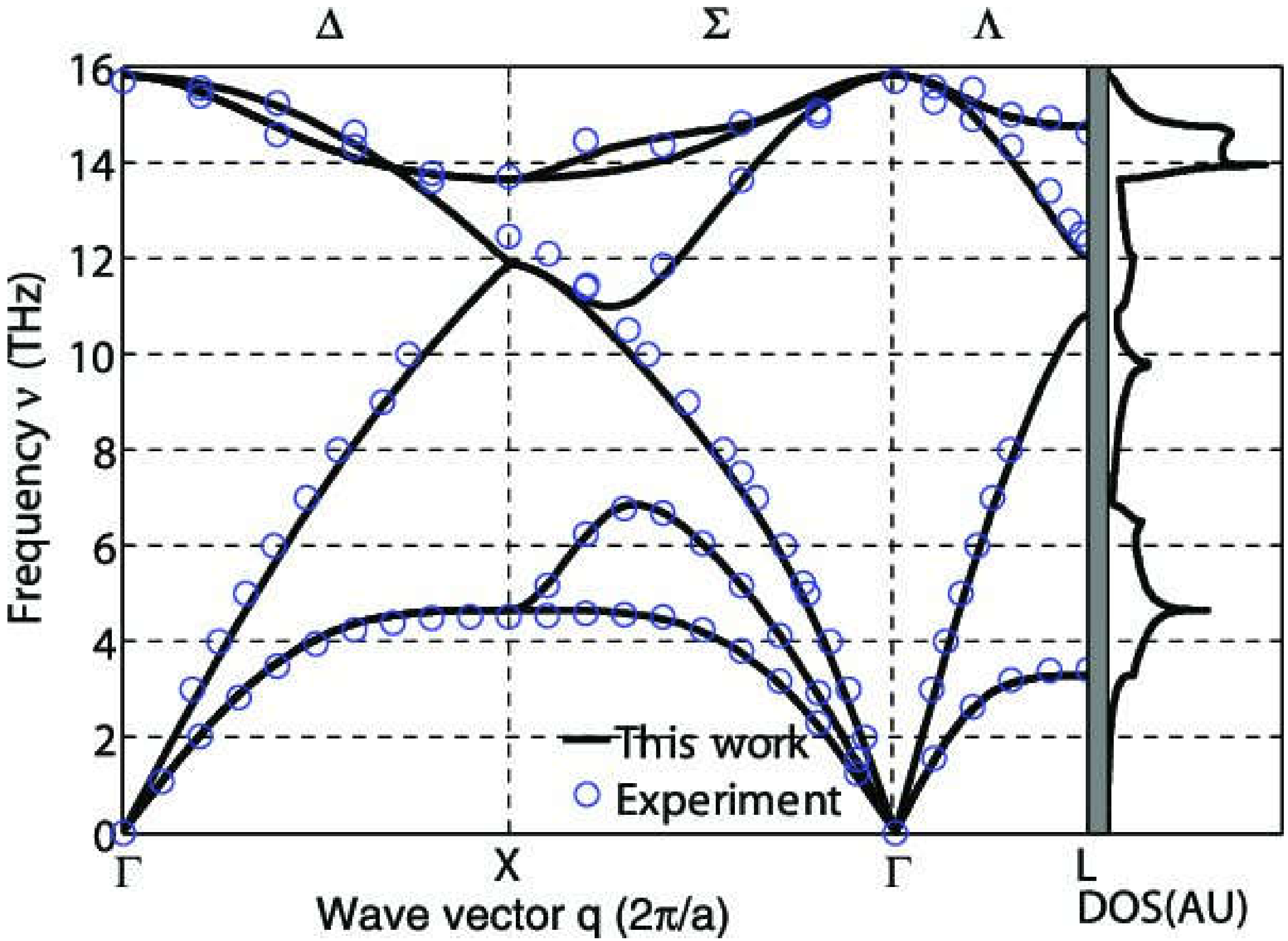
→

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

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