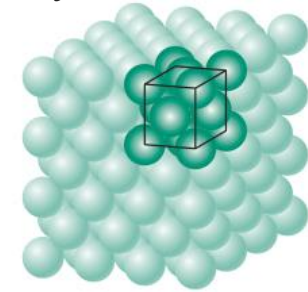


Chapter 2 Crystal Dynamics

Profile

Crystal Structure

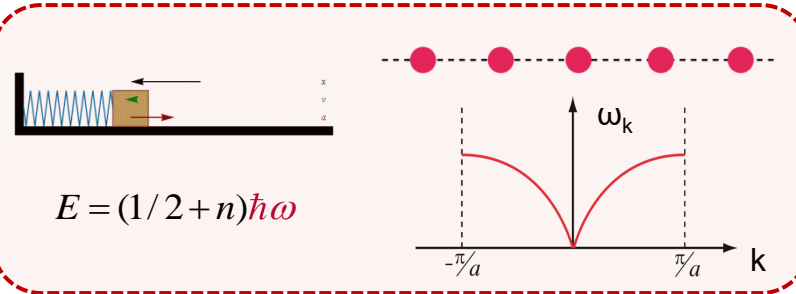


Binding

Atom

Electron

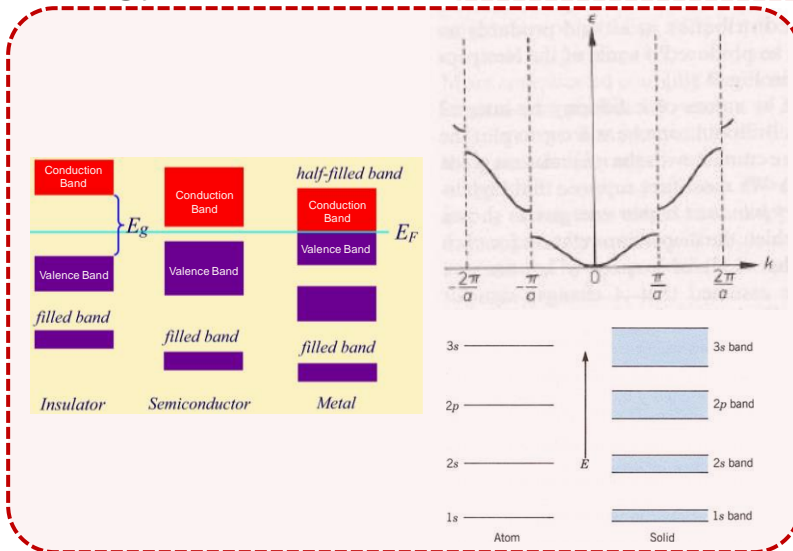
Crystal Dynamics



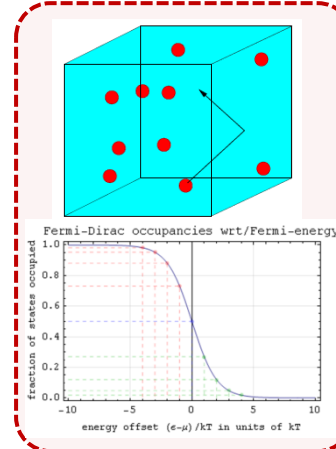
Atoms' movement

Born-Oppenheimer Approximation

Energy Bands



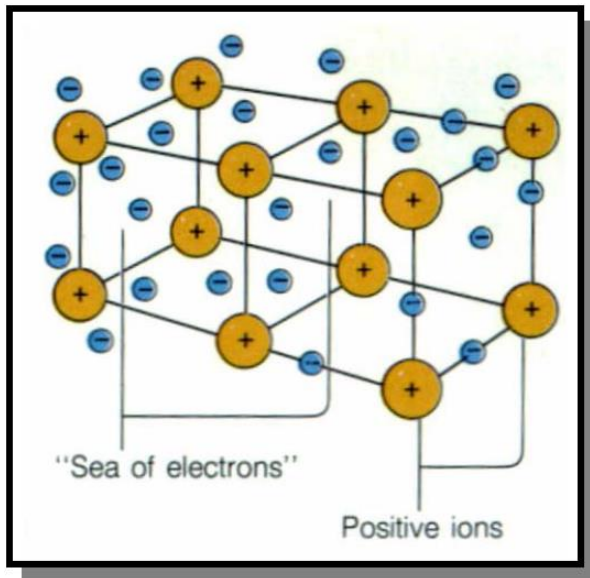
Free Electron Model



Electrons' movement

Quantum Mechanics
Classical Theory

Born-Oppenheimer Approximation



Na Crystal: $2N$ particles
 $N \sim 10^{23}$

Electrons'
movement

Atoms'
movement

Electron theory

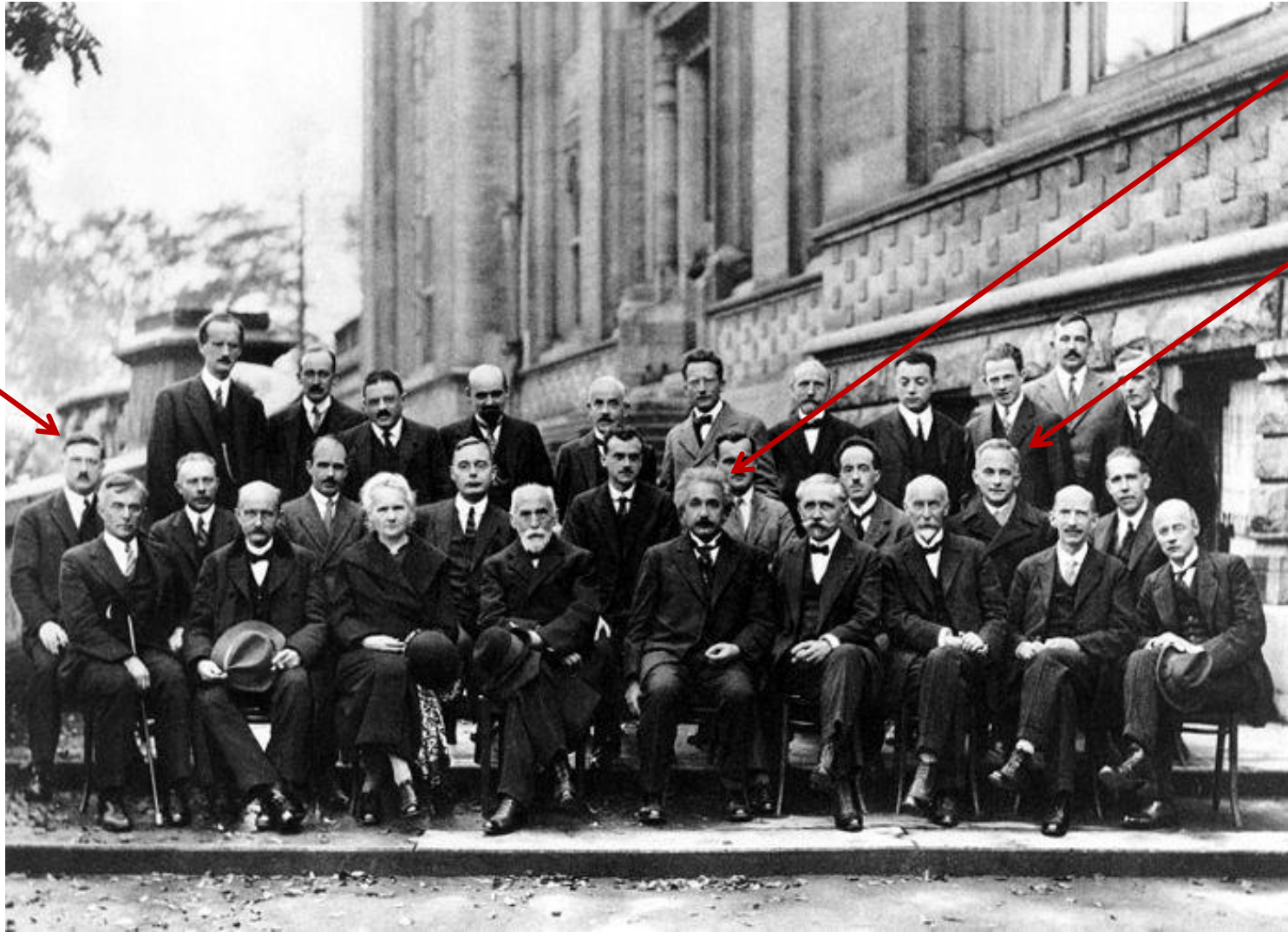
Free
electron
theory

Energy
band
theory

Crystal dynamics

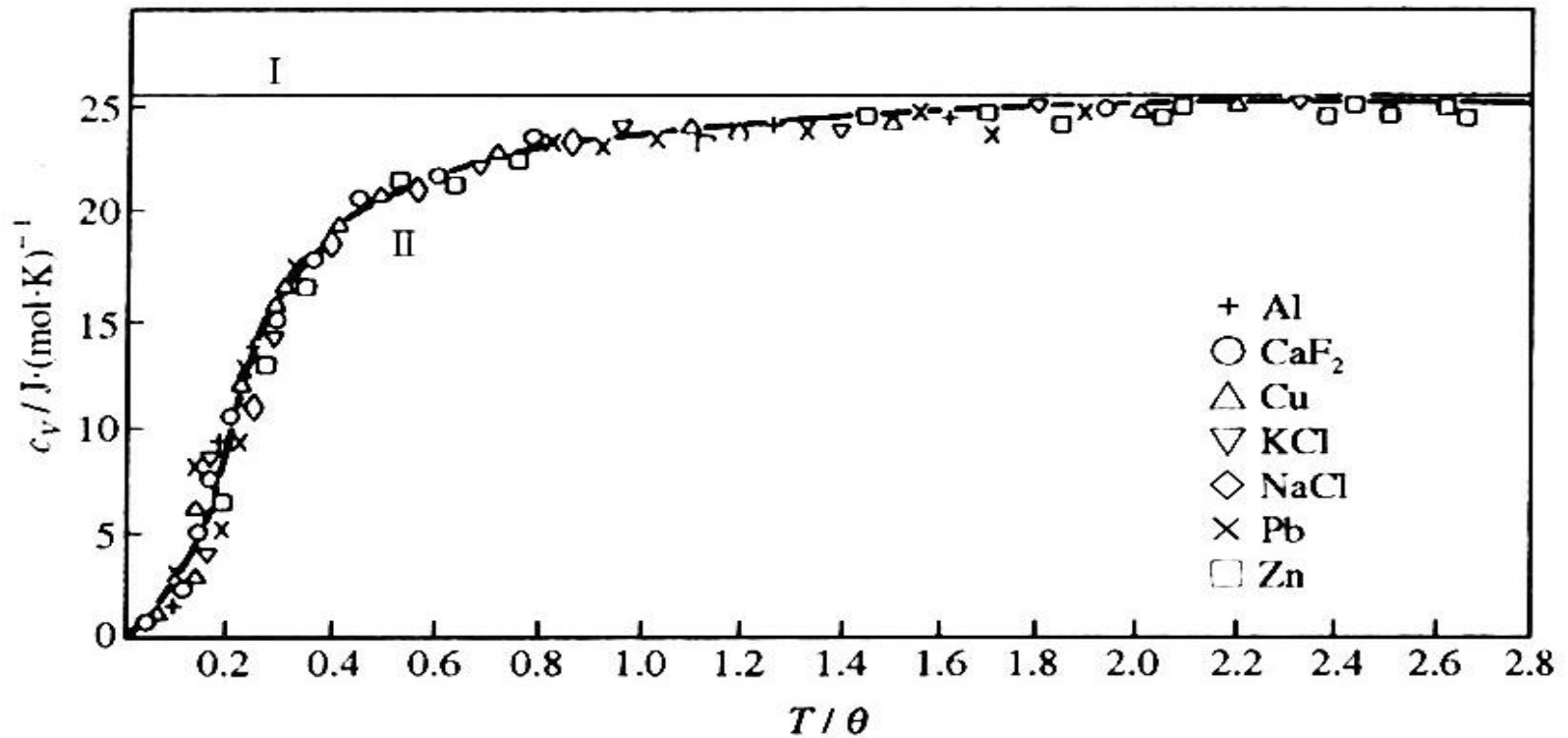
Lattice Vibration

Scientists



A. Piccard, E. Henriot, P. Ehrenfest, E. Herzen, Th. De Donder, E. Schrödinger, J.E. Verschaffelt, W. Pauli, W. Heisenberg, R.H. Fowler, L. Brillouin;
P. Debye, M. Knudsen, W.L. Bragg, H.A. Kramers, P.A.M. Dirac, A.H. Compton, L. de Broglie, M. Born, N. Bohr;
I. Langmuir, M. Planck, M. Skłodowska-Curie, H.A. Lorentz, A. Einstein, P. Langevin, Ch. E. Guye, C.T.R. Wilson, O.W. Richardson

Heat Capacity



Comparison Between Experiment and Theory

Chapter 2 Crystal Dynamics

2.1 Lattice Vibration

2.1.1 1D Monoatomic Chain

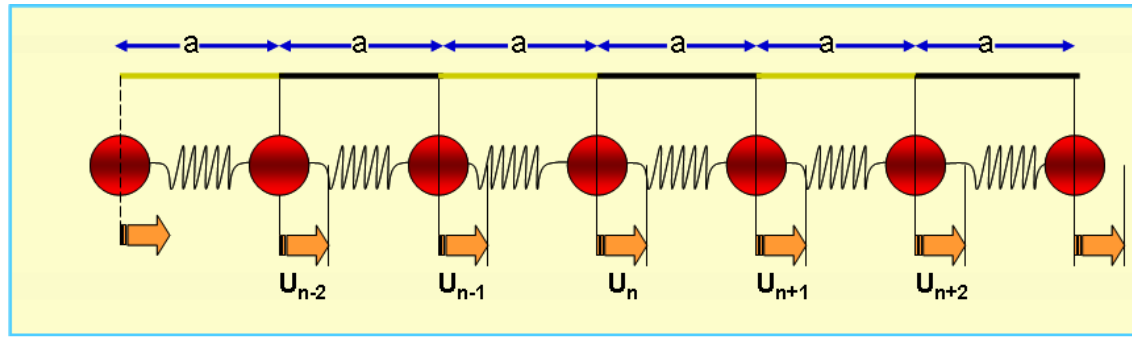
2.1.2 1D Diatomic Chain

2.1.3 3D Crystal

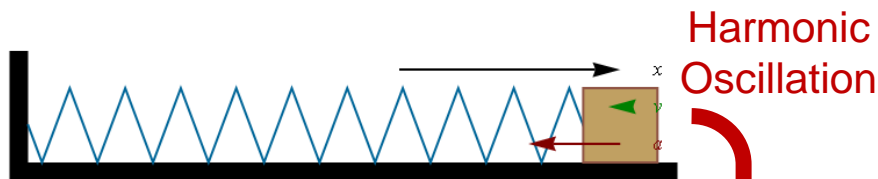
2.1.4 Quantization of Lattice Waves

2.2 Phonon Heat Capacity

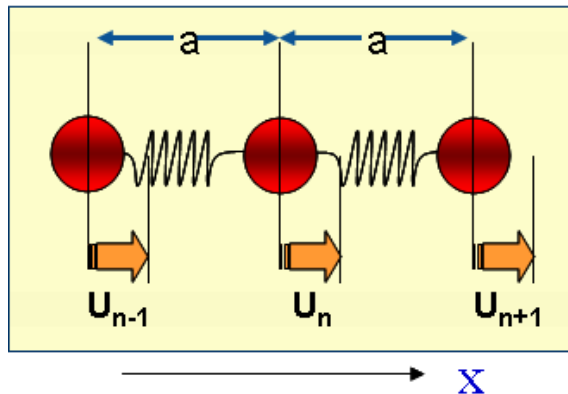
• **Equation of motion** • Periodic boundary condition • Dispersion relation • Lattice Waves



1D monoatomic chain



Harmonic
Oscillation



Nearest neighbor
interaction

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

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

Two Basic Hypotheses

Our calculations will be restricted to lattice vibrations of **small amplitude**:

Harmonic approximation (Harmonic limit): The restoring force on each atom is approximately proportional to its displacement.

$$F = -\beta x$$

--Hook's Law

Spring!

Nearest-neighbor limit: To calculate the forces simply, only **nearest-neighbor interactions** of atoms be considered.

How to calculate β ?

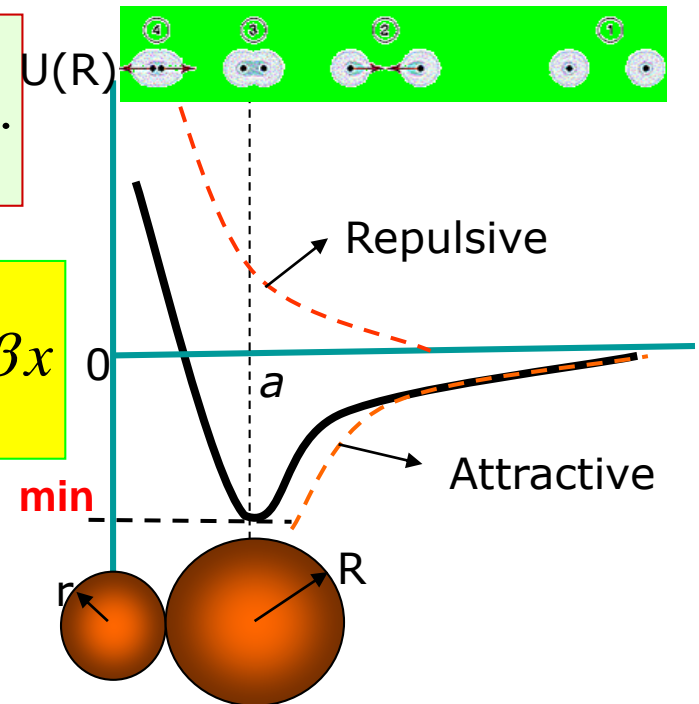
Atomic potential $U(r)$ can be written in Taylor's series:

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

$$F = -\frac{dU(r)}{dr} = -\left[\frac{d^2U(r)}{dr^2} \right]_{r=a} \cdot (r-a) = -\beta x$$

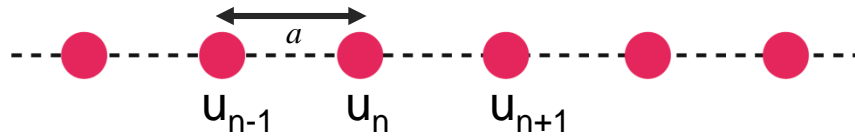


$$\beta = \left(\frac{d^2U}{dr^2} \right)_{r=a}$$

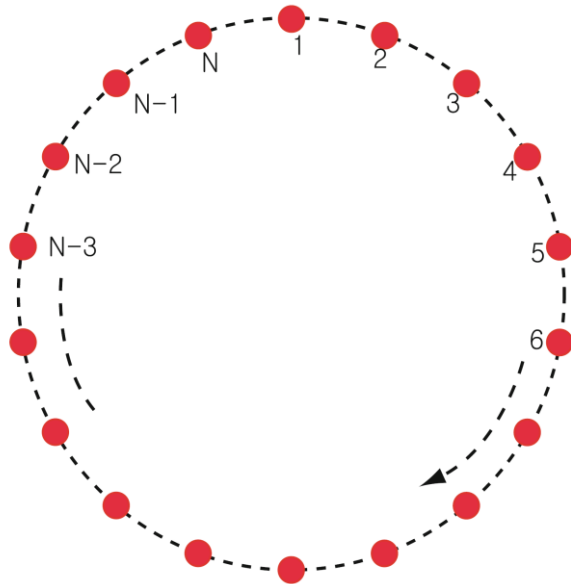


β is the force constant between nearest-neighbor atoms. It will differ for longitudinal and transverse waves in 3D space.

· **Equation of motion** · Periodic boundary condition · Dispersion relation · Lattice Waves



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



$$u_{N+1} = u_1$$

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

Born-Karman boundary condition
Periodic boundary condition

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

$$-m\omega^2 Ae^{i(kna - \omega t)}$$

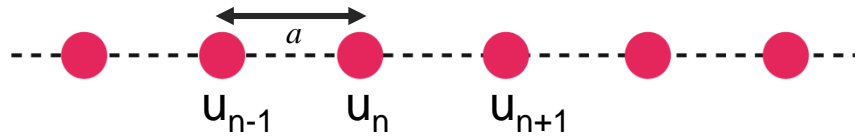
$$= \beta \left(Ae^{i(kna + ka - \omega t)} - 2Ae^{i(kna - \omega t)} + Ae^{i(kna - ka - \omega t)} \right)$$

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

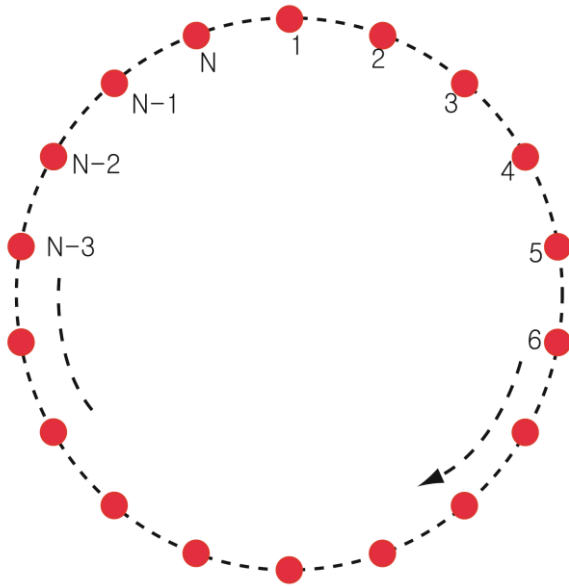
$$m\omega^2 = 2\beta(1 - \cos ka)$$

$$\omega = 2\sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right|$$

• Equation of motion • **Periodic boundary condition** • Dispersion relation • Lattice Waves



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



$$u_{N+1} = u_1$$

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

Born-Karman boundary condition
Periodic boundary condition

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

$$\omega = 2\sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right|$$

$$e^{i(nka - \omega t)} = e^{[i(N+n)ak - \omega t]}$$

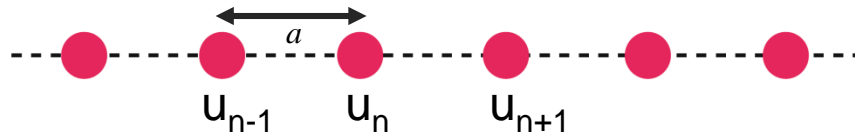
$$e^{iNka} = 1$$

$$Nka = 2\pi m$$

$$k = \frac{2\pi}{Na} m$$

$$m = 0, \pm 1, \pm 2, \dots$$

· Equation of motion · Periodic boundary condition · **Dispersion relation** · Lattice Waves



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

$$u_n = A e^{i(nak - \omega t)} \quad u_{N+1} = u_1$$

$$\omega = 2 \sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right|$$

$$k = \frac{2\pi}{Na} m \quad m = 0, \pm 1, \pm 2, \dots$$

$$k = 6\pi/6a \quad \lambda = 2.00a \quad \omega_k = 2.00\omega$$



$$k = 5\pi/6a \quad \lambda = 2.40a \quad \omega_k = 1.93\omega$$



$$k = 4\pi/6a \quad \lambda = 3.00a \quad \omega_k = 1.73\omega$$



$$k = 3\pi/6a \quad \lambda = 4.00a \quad \omega_k = 1.41\omega$$



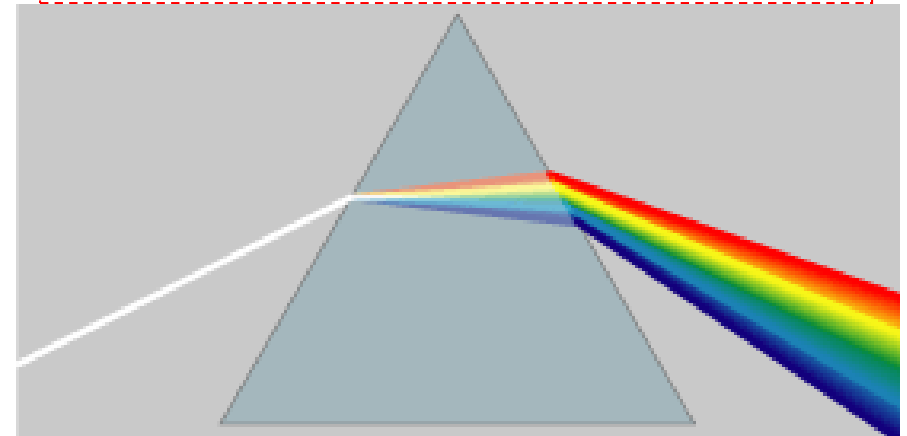
$$k = 2\pi/6a \quad \lambda = 6.00a \quad \omega_k = 1.00\omega$$



$$k = \pi/6a \quad \lambda = 12.00a \quad \omega_k = 0.52\omega$$

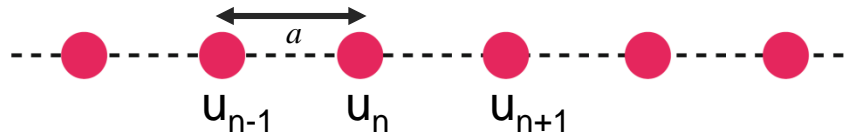


Lattice Wave



Dispersion relation

• Equation of motion • Periodic boundary condition • Dispersion relation • **Lattice Waves**



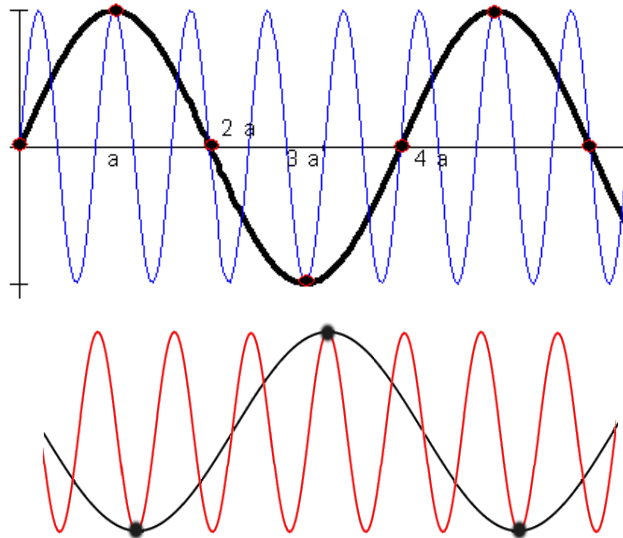
$$m \ddot{u}_n = \beta(u_{n+1} - 2u_n + u_{n-1})$$

Independent Lattice Wave

$$\omega(k) = \omega(k + G) \quad G = m \cdot \frac{2\pi}{a} \hat{i}$$

$$k_1 = \frac{\pi}{2a} = \frac{2\pi}{\lambda_1} \quad \lambda_1 = 4a$$

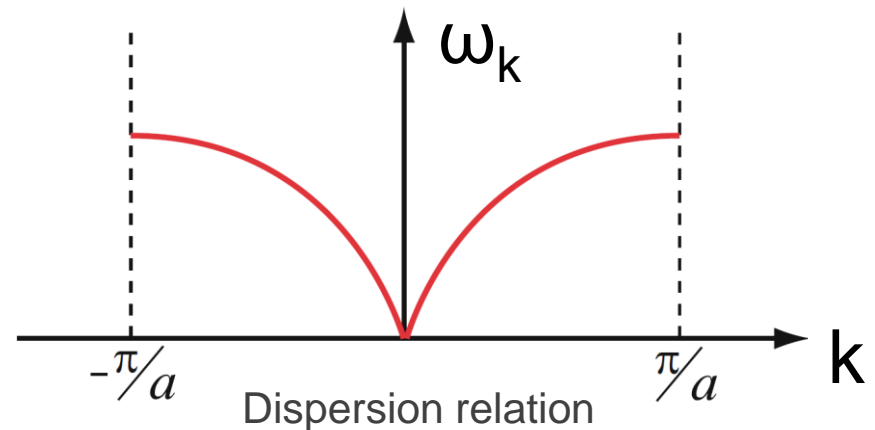
$$k_2 = \frac{5\pi}{2a} = \frac{2\pi}{\lambda_2} \quad k_2 - k_1 = \frac{2\pi}{a} \quad \lambda_2 = \frac{4}{5}a$$



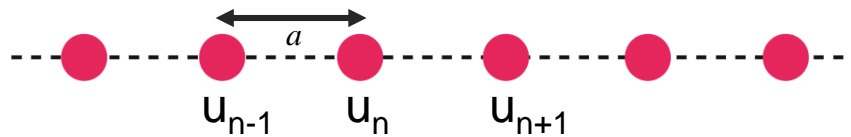
$$u_n = A e^{i(nak - \omega t)} \quad u_{N+1} = u_1$$

$$\omega = 2 \sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right|$$

$$k = \frac{2\pi}{Na} m \quad m = 0, \pm 1, \pm 2, \dots$$



• Equation of motion • Periodic boundary condition • Dispersion relation • **Lattice Waves**



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

Independent Lattice Wave

$$\omega(k) = \omega(k + G) \quad G = m \cdot \frac{2\pi}{a} \hat{i}$$

$$k_1 = \frac{\pi}{2a} = \frac{2\pi}{\lambda_1} \quad \lambda_1 = 4a$$

$$k_2 = \frac{5\pi}{2a} = \frac{2\pi}{\lambda_2} \quad k_2 - k_1 = \frac{2\pi}{a} \quad \lambda_2 = \frac{4}{5}a$$

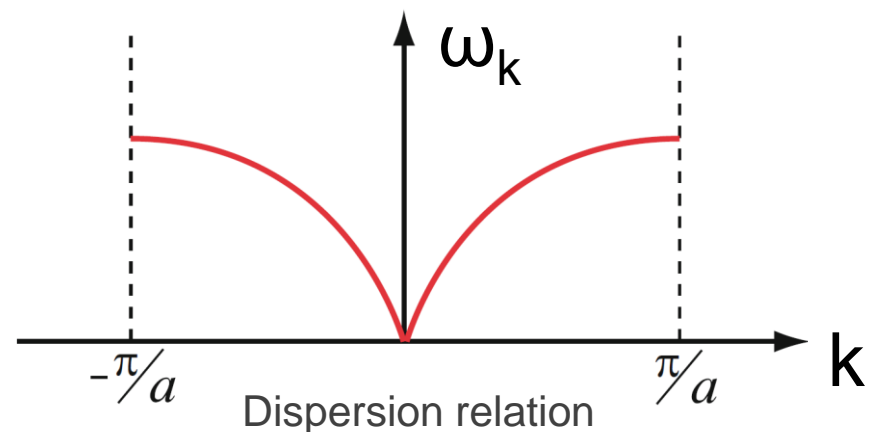
The movement of atoms with k or $k+G$ is the same.

All independent vibrations are described by k inside BZ.

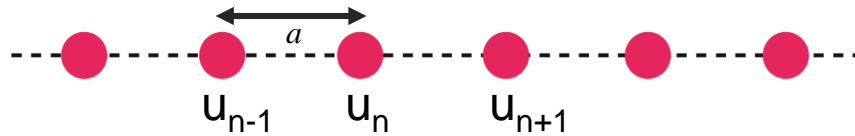
$$u_n = A e^{i(nak - \omega t)} \quad u_{N+1} = u_1$$

$$\omega = 2 \sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right|$$

$$k = \frac{2\pi}{Na} m \quad m = 0, \pm 1, \pm 2, \dots$$



· Equation of motion · Periodic boundary condition · Dispersion relation · **Lattice Waves**



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

$$k = 6\pi/6a \quad \lambda = 2.00a \quad \omega_k = 2.00\omega$$



$$k = 5\pi/6a \quad \lambda = 2.40a \quad \omega_k = 1.93\omega$$



$$k = 4\pi/6a \quad \lambda = 3.00a \quad \omega_k = 1.73\omega$$



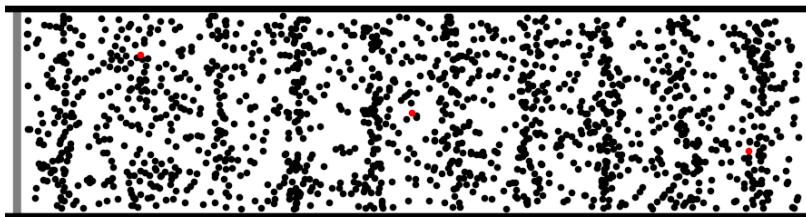
$$k = 3\pi/6a \quad \lambda = 4.00a \quad \omega_k = 1.41\omega$$



$$k = 2\pi/6a \quad \lambda = 6.00a \quad \omega_k = 1.00\omega$$



$$k = 1\pi/6a \quad \lambda = 12.00a \quad \omega_k = 0.52\omega$$



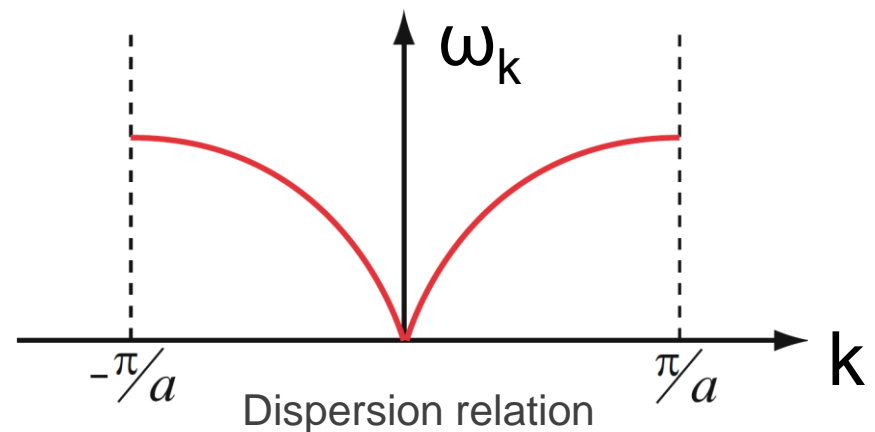
©2011, Dan Russell

Lattice Wave

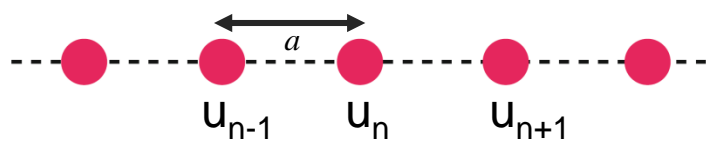
$$u_n = Ae^{i(nak - \omega t)} \quad u_{N+1} = u_1$$

$$\omega = 2\sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right|$$

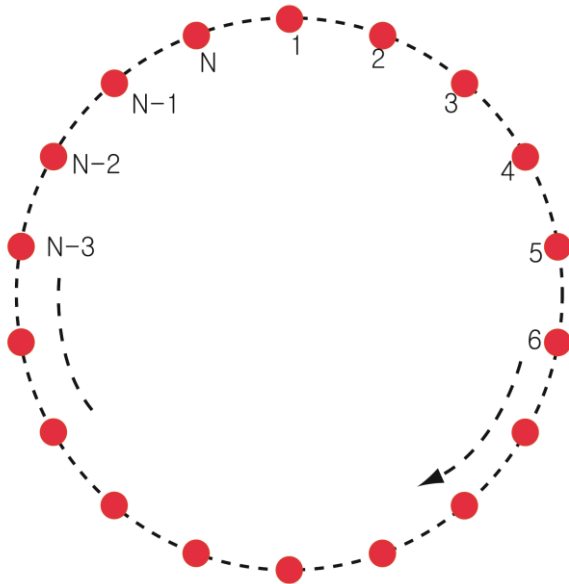
$$k = \frac{2\pi}{Na} m \quad m = 0, \pm 1, \pm 2, \dots$$



• Equation of motion • Periodic boundary condition • Dispersion relation • **Lattice Waves**



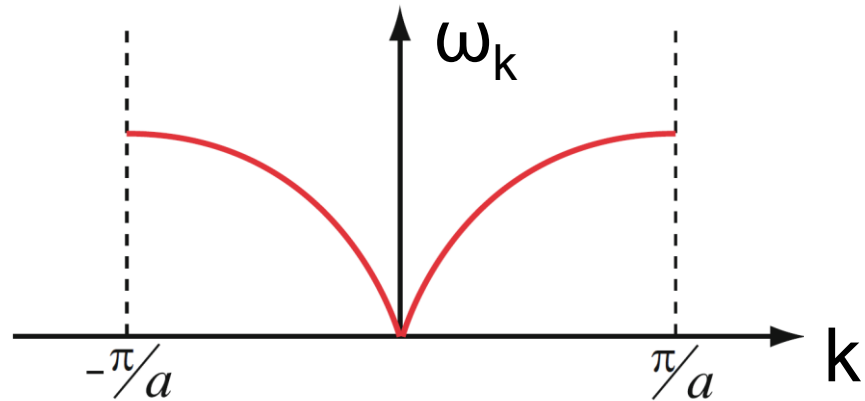
$$\omega = 2\sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right| \quad k = \frac{2\pi}{Na} m \quad m = 0, \pm 1, \pm 2, \dots$$



$$u_{N+1} = u_1$$

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

Born-Karman boundary condition
Periodic boundary condition



$$-\frac{\pi}{a} \leq k < \frac{\pi}{a} \quad -\frac{\pi}{a} \leq \frac{2\pi}{Na} m < \frac{\pi}{a} \quad -\frac{N}{2} \leq m < \frac{N}{2}$$

Total number of degrees of freedom

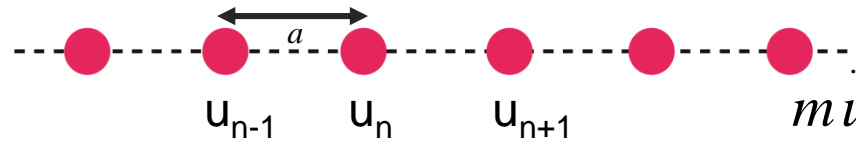
=

Number of independent lattice wave

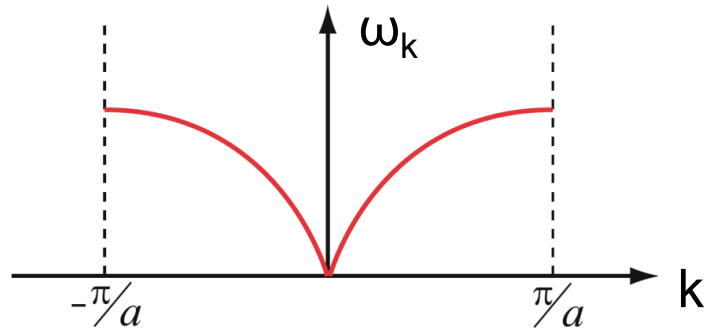
N

• Equation of motion • Periodic boundary condition • Dispersion relation • Lattice Waves

A summary here:



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



$$\omega = 2\sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right| \quad k = \frac{2\pi}{Na} m$$

$$k = 6\pi/6a \quad \lambda = 2.00a \quad \omega_k = 2.00\omega$$



$$k = 5\pi/6a \quad \lambda = 2.40a \quad \omega_k = 1.93\omega$$



$$k = 4\pi/6a \quad \lambda = 3.00a \quad \omega_k = 1.73\omega$$



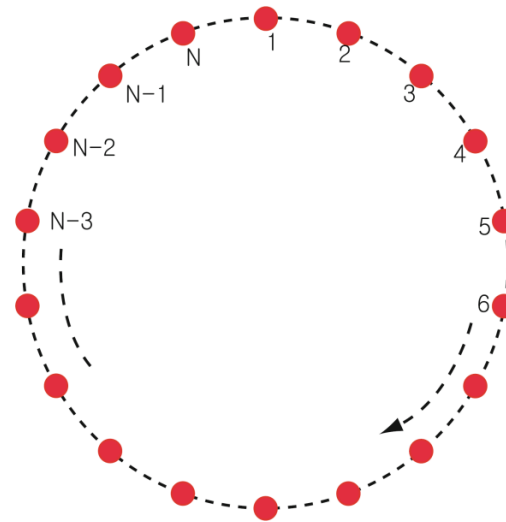
$$k = 3\pi/6a \quad \lambda = 4.00a \quad \omega_k = 1.41\omega$$



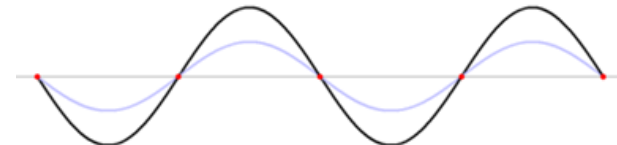
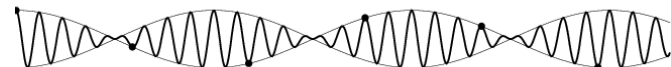
$$k = 2\pi/6a \quad \lambda = 6.00a \quad \omega_k = 1.00\omega$$



$$k = \pi/6a \quad \lambda = 12.00a \quad \omega_k = 0.52\omega$$



Total number of
degrees of freedom
=
Number of
independent lattice
wave



Chapter 2 Crystal Dynamics

2.1 Lattice Vibration

2.1.1 1D Monoatomic Chain

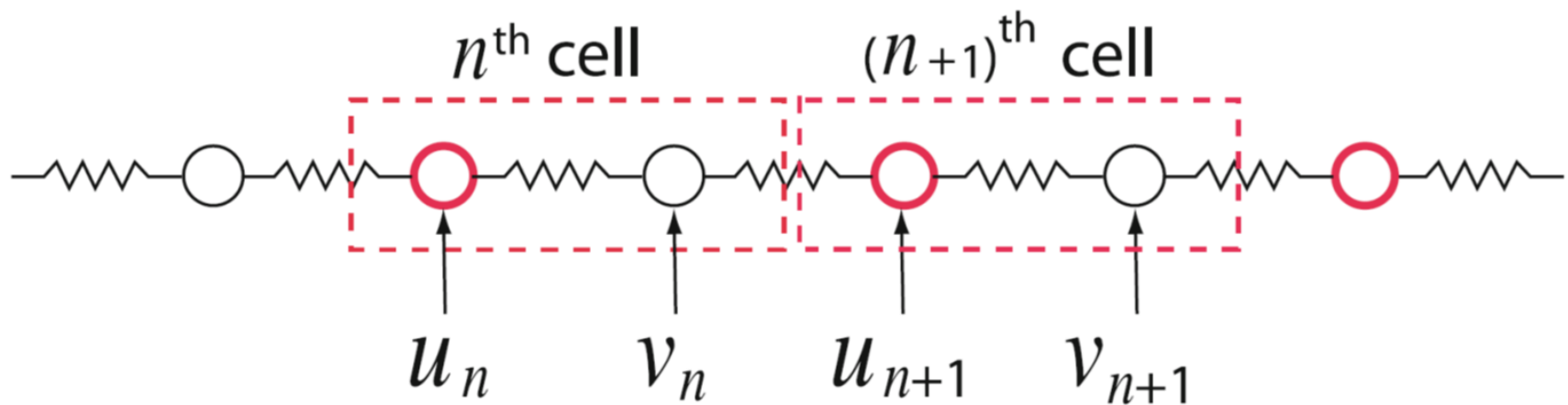
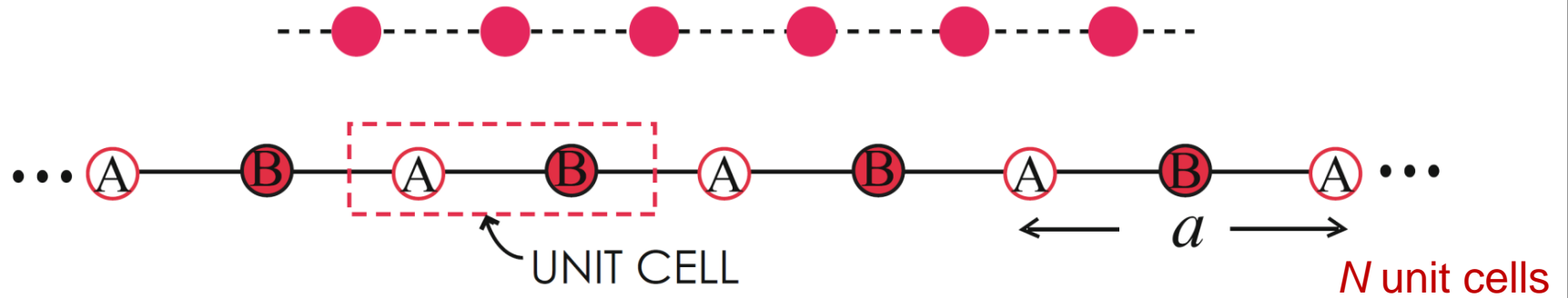
2.1.2 1D Diatomic Chain

2.1.3 3D Crystal

2.1.4 Quantization of Lattice Waves

2.2 Phonon Heat Capacity

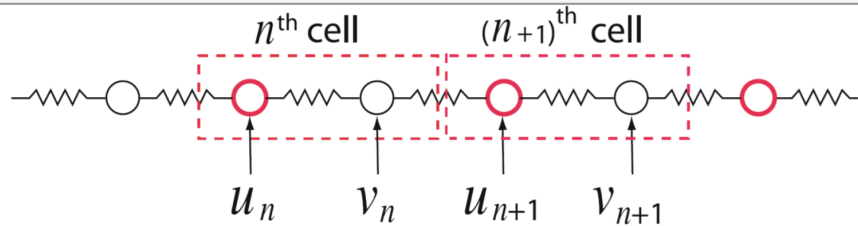
• Equation of motion • Dispersion relation • Lattice Waves



$$M\ddot{u}_n = \beta(v_n + v_{n-1} - 2u_n)$$

$$m\ddot{v}_n = \beta(u_n + u_{n+1} - 2v_n)$$

• Equation of motion • Dispersion relation • Lattice Waves



$$M\ddot{u}_n = \beta(v_n + v_{n-1} - 2u_n)$$

$$m\ddot{v}_n = \beta(u_n + u_{n+1} - 2v_n)$$

$$u_{N+1} = u_1$$

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

$$v_n = Be^{i[(n+1/2)ak - \omega t]}$$

$$v_{N+n} = v_n$$

$$\begin{aligned} (2\beta - M\omega^2)A - 2\beta \cos\left(\frac{1}{2}ak\right)B &= 0 \\ -2\beta \cos\left(\frac{1}{2}ak\right)A + (2\beta - m\omega^2)B &= 0 \end{aligned} \quad \left| \begin{array}{cc} 2\beta - M\omega^2 & -2\beta \cos\left(\frac{1}{2}ak\right) \\ -2\beta \cos\left(\frac{1}{2}ak\right) & 2\beta - m\omega^2 \end{array} \right| = 0$$

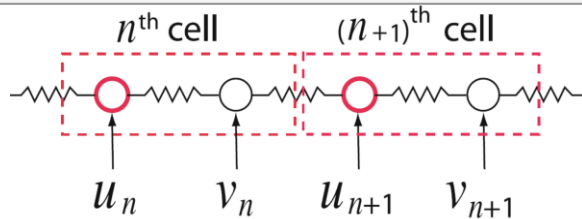
$$\omega_{\pm}^2 = \frac{\beta(M+m)}{Mm} \left\{ 1 \pm \sqrt{1 - \frac{4Mm}{(M+m)^2} \sin^2\left(\frac{1}{2}ak\right)} \right\}$$

$$\omega_{\pm}^2 = \frac{\beta}{Mm} [(M+m) \pm \sqrt{M^2 + m^2 + 2Mm \cos(ak)}]$$

$$k = \frac{2\pi}{Na} m$$

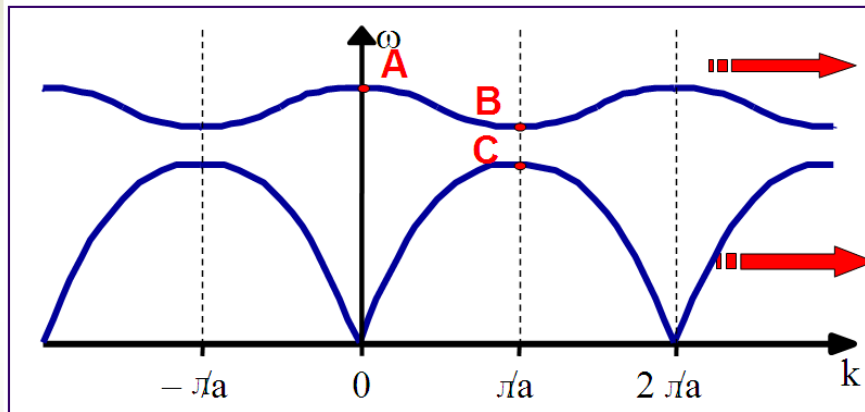
$$m = 0, \pm 1, \pm 2, \dots$$

• Equation of motion • **Dispersion relation** • Lattice Waves



$$\omega_{\pm}^2 = \frac{\beta}{Mm} [(M + m) \pm \sqrt{M^2 + m^2 + 2Mm \cos(ak)}]$$

$$\omega_+^2 = \frac{\beta}{Mm} [(M + m) + \sqrt{M^2 + m^2 + 2Mm \cos(ak)}] \quad \omega_-^2 = \frac{\beta}{Mm} [(M + m) - \sqrt{M^2 + m^2 + 2Mm \cos(ak)}]$$



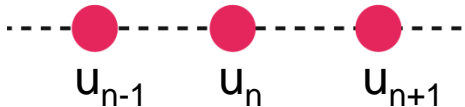
Optical Branch

Upper branch is due to the “+” sign of the root.

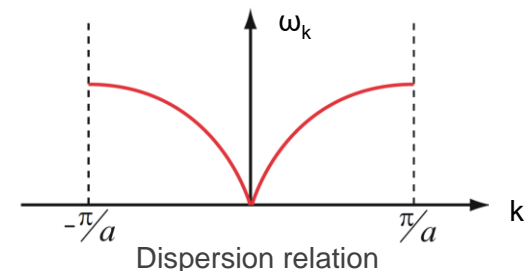
Acoustical Branch

Lower branch is due to the “-” sign of the root.

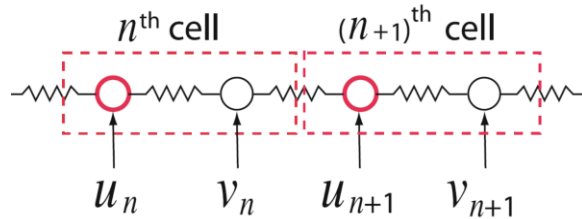
Compare with 1D Monoatomic Chain



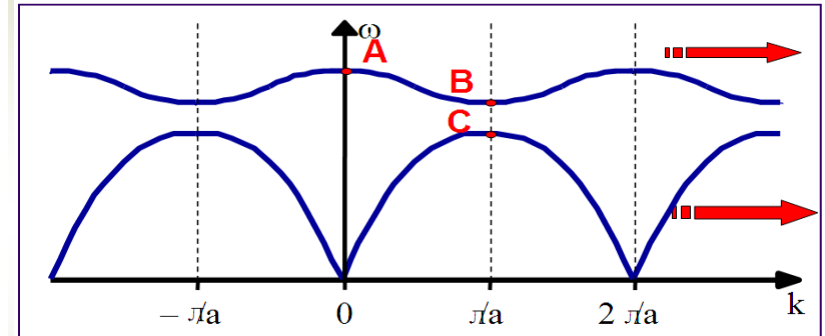
$$\omega = 2\sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right|$$



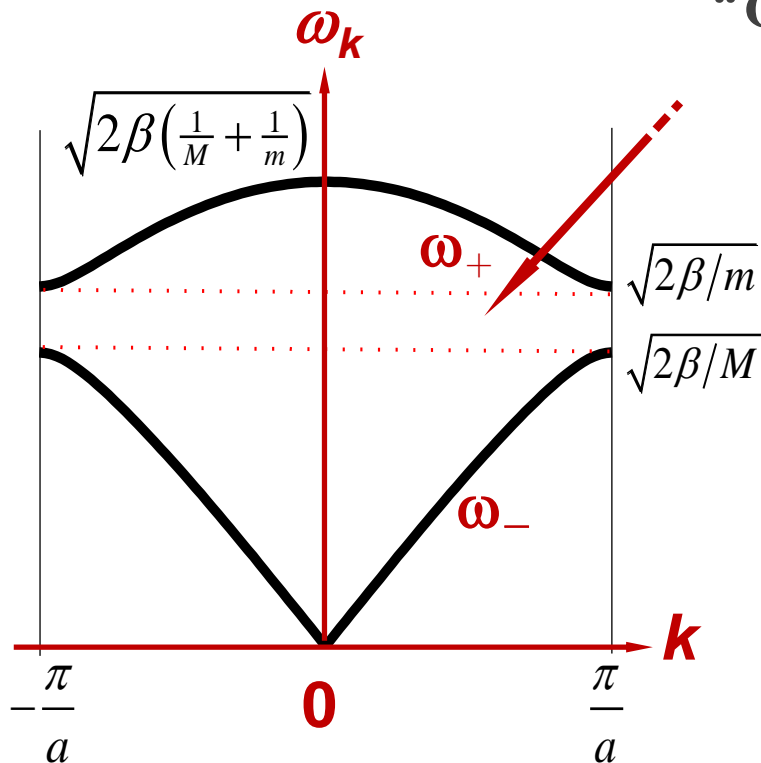
• Equation of motion • **Dispersion relation** • Lattice Waves



$$\omega_{\pm}^2 = \frac{\beta}{Mm} [(M+m) \pm \sqrt{M^2 + m^2 + 2Mm \cos(ak)}]$$

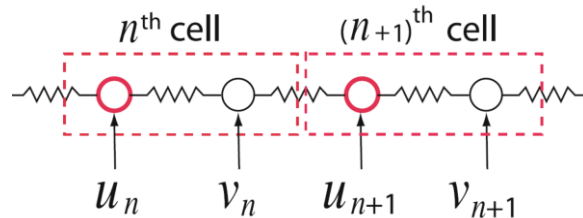


“Gap” means that no vibrations can occur!

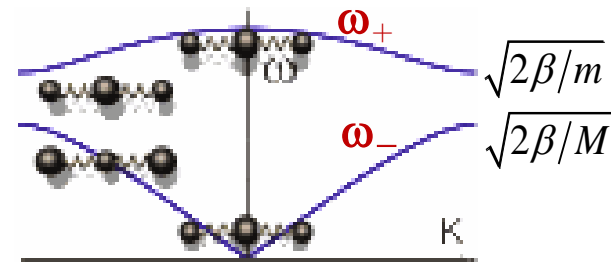


| | ω_+ | ω_- |
|---------------------|--|---------------------------|
| $k = 0$ | $\sqrt{2\beta \left(\frac{1}{M} + \frac{1}{m} \right)}$ | 0 |
| $k = \frac{\pi}{a}$ | $\sqrt{\frac{2\beta}{m}}$ | $\sqrt{\frac{2\beta}{M}}$ |

• Equation of motion • **Dispersion relation** • Lattice Waves



$$\omega_{\pm}^2 = \frac{\beta}{Mm} [(M+m) \pm \sqrt{M^2 + m^2 + 2Mm \cos(ak)}]$$



$$M\ddot{u}_n = \beta(v_n + v_{n-1} - 2u_n)$$

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

$$m\ddot{v}_n = \beta(u_n + u_{n+1} - 2v_n)$$

$$v_n = Be^{i[(n+1/2)ak - \omega t]} = B'e^{i(nak - \omega t)}$$

$$(2\beta - M\omega^2)A - \beta(1 + e^{-iak})B' = 0$$

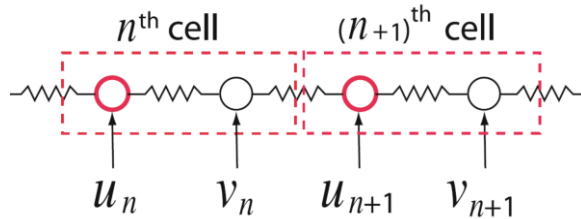
$$-\beta(1 + e^{-iak})A + (2\beta - m\omega^2)B' = 0$$

$$\frac{u_n}{v_n} = \frac{A}{B'} = \frac{\beta(1 + e^{-iak})}{2\beta - M\omega_{\pm}^2} = \frac{2\beta - m\omega_{\pm}^2}{\beta(1 + e^{-iak})}$$

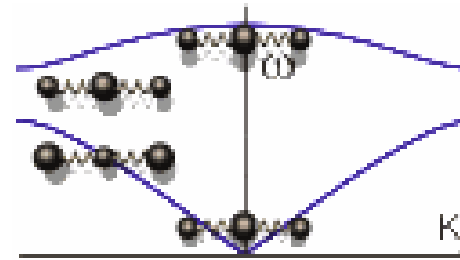
$$\left(\frac{u_n}{v_n}\right)_+ = \left(\frac{A}{B'}\right)_+ < 0$$

$$\left(\frac{u_n}{v_n}\right)_- = \left(\frac{A}{B'}\right)_- > 0$$

• Equation of motion • **Dispersion relation** • Lattice Waves



$$\omega_{\pm}^2 = \frac{\beta}{Mm} [(M+m) \pm \sqrt{M^2 + m^2 + 2Mm \cos(ak)}]$$



$$\left(\frac{u_n}{v_n} \right)_+ = \left(\frac{A}{B'} \right)_+ < 0$$

$$\left(\frac{u_n}{v_n} \right)_- = \left(\frac{A}{B'} \right)_- > 0$$

$$\frac{u_n}{v_n} = \frac{A}{B'} = \frac{\beta(1 + e^{-iak})}{2\beta - M\omega_{\pm}^2} = \frac{2\beta - m\omega_{\pm}^2}{\beta(1 + e^{-iak})}$$

$k=0$

$$\left[\left(\frac{u_n}{v_n} \right)_+ \right]_{k=0} = -\frac{m}{M} \quad \left[\left(\frac{u_n}{v_n} \right)_- \right]_{k=0} = 1$$

$k = \pm \pi/a$

$$\left[\left(\frac{u_n}{v_n} \right)_+ \right]_{k=\pm \frac{\pi}{a}} = 0 \quad \left[\left(\frac{u_n}{v_n} \right)_- \right]_{k=\pm \frac{\pi}{a}} = \infty$$

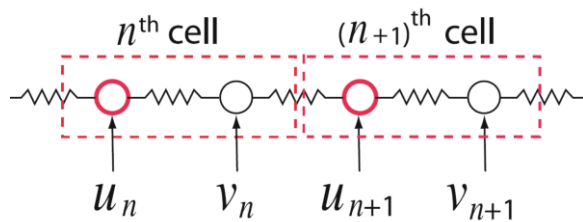
$k \rightarrow 0$

$$\begin{aligned} \omega_{\pm}^2 &= \frac{\beta(M+m)}{Mm} \left\{ 1 \pm \sqrt{1 - \frac{4Mm}{(M+m)^2} \sin^2\left(\frac{1}{2}ak\right)} \right\} \\ &\approx \frac{\beta(M+m)}{Mm} \left[1 \pm \sqrt{1 - \frac{4Mm}{(M+m)^2} \left(\frac{1}{2}ak\right)^2} \right] \\ &\approx \frac{\beta(M+m)}{Mm} \cdot \frac{2Mm}{(M+m)^2} \left(\frac{1}{2}ak\right)^2 \\ &= \frac{2\beta}{M+m} \left(\frac{1}{2}ak\right)^2 \quad (1-x)^{1/2} \xrightarrow{x \rightarrow 0} 1 - (x/2) \end{aligned}$$

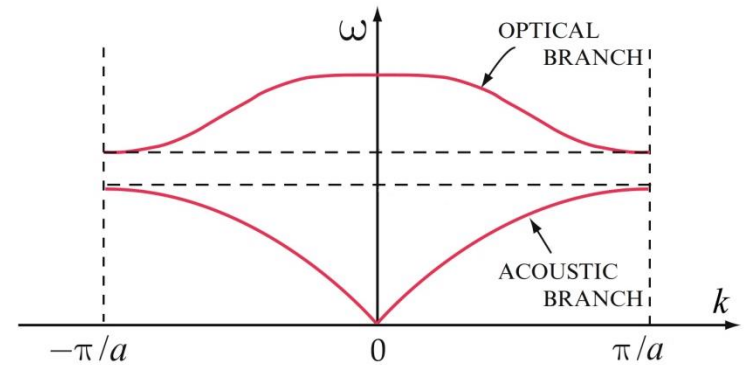
$$\omega_{\pm} \approx \frac{1}{2}a \sqrt{\frac{2\beta}{M+m}} \cdot k \propto k$$

$$v_k = \frac{1}{2}a \sqrt{\frac{2\beta}{M+m}}$$

• Equation of motion • Dispersion relation • **Lattice Waves**



$$\omega_{\pm}^2 = \frac{\beta}{Mm} [(M+m) \pm \sqrt{M^2 + m^2 + 2Mm \cos(ak)}]$$



$$k = \frac{2\pi}{Na} m \quad m = 0, \pm 1, \pm 2, \dots$$

$$-\frac{\pi}{a} \leq k < \frac{\pi}{a} \quad -\frac{\pi}{a} \leq \frac{2\pi}{Na} m < \frac{\pi}{a}$$

$$-\frac{N}{2} \leq m < \frac{N}{2}$$

Total number of degrees of freedom
=
Number of independent lattice wave

一维双原子链

| | |
|---------|----------------|
| 原胞数 | N |
| 晶格振动波矢数 | N |
| 原胞内原子数 | 2 |
| 总自由度数 | 2N |
| 独立格波数 | 2N |
| 分支 | 2 |
| 分支情况 | 1支声学波 1支光学波 |

Chapter 2 Crystal Dynamics

2.1 Lattice Vibration

2.1.1 1D Monoatomic Chain

2.1.2 1D Diatomic Chain

2.1.3 3D Crystal

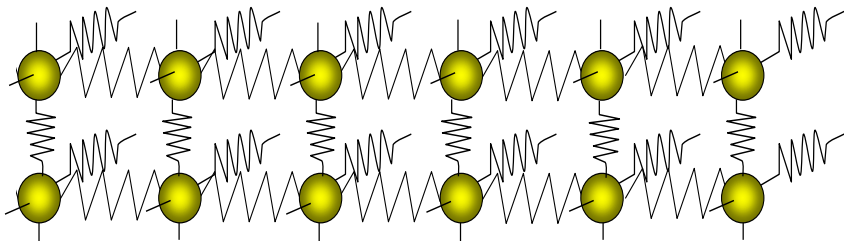
2.1.4 Quantization of Lattice Waves

2.2 Phonon Heat Capacity

· **Lattice Waves** · Dispersion relation / Phonon spectrum

| | 原胞数 | 晶格振动波矢数 | 原胞内原子数 | 总自由度数 | 独立格波数 | 分支数 | 分支情况 |
|---------------------|-----|---------|--------|-------|-------|-----|-----------------------------|
| 一维单原子链 | N | N | 1 | N | N | 1 | 1支声学波 |
| 一维双原子链 | N | N | 2 | $2N$ | $2N$ | 2 | 1支声学波 1支光学波 |
| 一维P原子链 | N | N | P | PN | PN | P | 1支声学波 P-1支光学波 |
| 三维单原子链 (三维单原子晶体) | N | N | 1 | $3N$ | $3N$ | 3 | 3支声学波 (1纵2横) |
| 三维P原子链 (三维晶体) | N | N | P | $3PN$ | $3PN$ | 3P | 3支声学波 (1纵2横) 3P-3支光学波 |

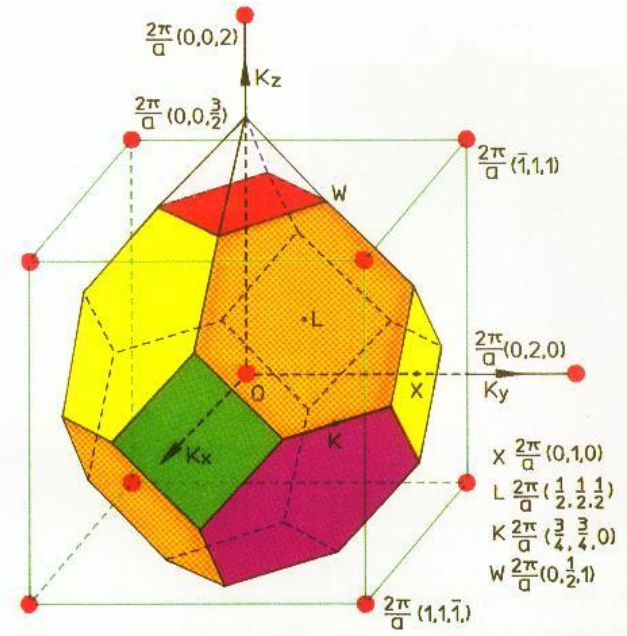
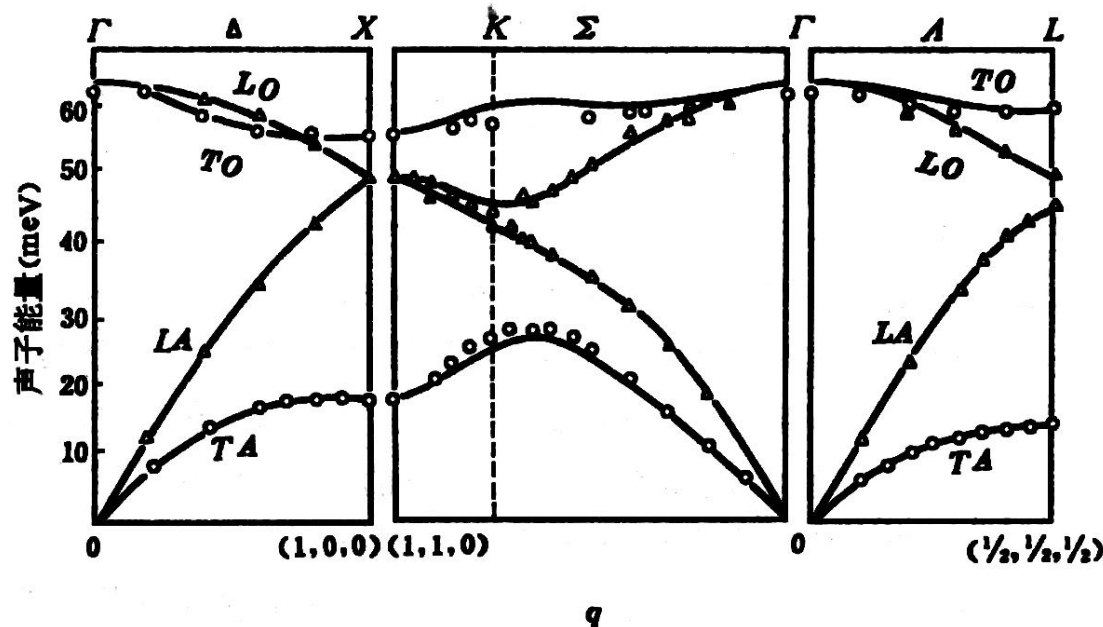
Three dimensional crystal



Total number of degrees of freedom
=
Number of independent lattice wave

· Lattice Waves · Dispersion relation / Phonon spectrum

ω_k of Si Crystal



2 atoms per primitive cell \longrightarrow 3×2 vibration branches

Optic 3(p-1) : LO (longitudinal), TO_1 (transverse), TO_1 (transverse)

Acoustic (3) : LA (longitudinal), TA_1 (transverse), TA_2 (transverse)

Chapter 2 Crystal Dynamics

2.1 Lattice Vibration

2.1.1 1D Monoatomic Chain

2.1.2 1D Diatomic Chain

2.1.3 3D Crystal

2.1.4 Quantization of Lattice Waves

2.2 Phonon Heat Capacity

Density of k distribution in k space

Volume of 1st BZ

$$v_b = \frac{(2\pi)^3}{v_a}$$

Density of k distribution in k space (3D)

$$\rho(k) = \frac{N}{\frac{(2\pi)^3}{v_a}} = \frac{V}{(2\pi)^3}$$

1D

$$\rho(k) = \frac{Na}{2\pi} = \frac{L}{2\pi}$$

2D

$$\rho(k) = \frac{S}{(2\pi)^2}$$

Equivalence between a vibration mode and a harmonic oscillator

We care about $C_v = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta E}{\Delta T} \right)_v = \left(\frac{\partial E}{\partial T} \right)_v$

where $E = T_k + U_k = \frac{1}{2} m \sum \dot{u}_n^2 + \frac{1}{2} \beta \sum (u_{n-1} - u_n)^2$ for

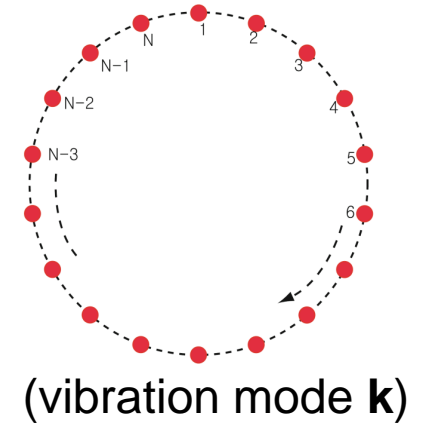
Cause $u_n = A e^{-i(\omega t - k n a)}$ (vibration mode \mathbf{k})

then $T_k = \frac{1}{2} m \sum_{n=1}^N \dot{u}_n^2 = \frac{1}{2} m \omega^2 e^{-2i\omega t} \sum_{n=1}^N e^{2ikna}$

Cause $-\frac{\partial U_k}{\partial u_n} = \beta(u_{n-1} + u_{n+1} - 2u_n)$

then $U_k = \frac{1}{2} \beta \sum_{n=1}^N (2u_n^2 - u_n u_{n+1} - u_n u_{n-1}) = 2\beta \sin^2\left(\frac{ka}{2}\right) e^{-2i\omega t} \sum_{n=1}^N e^{2ikna}$

With the dispersion relation $\omega = 2\sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right|$ we have $U_k = \frac{1}{2} m \omega^2 e^{-2i\omega t} \sum_{n=1}^N e^{2ikna}$



Introducing generalized coordinates $q_k = \sqrt{m} \sum_{n=1}^N e^{-i(\omega t - k n a)}$

and generalized momentum $p_k = \frac{dq_k}{dt} = -i\omega \sqrt{m} \sum_{n=1}^N e^{-i(\omega t - k n a)}$

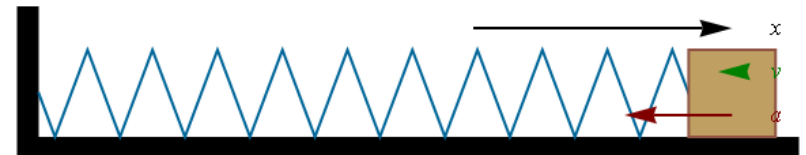
We can have $U_k = \frac{1}{2} \omega^2 q_k^2$ and $T_k = \frac{1}{2} p_k^2$

Then the energy of crystal corresponding to vibration mode **k** will be

$$E_k = T_k + U_k = \frac{1}{2} p_k^2 + \frac{1}{2} \omega^2 q_k^2$$

which is the energy of a harmonic oscillator with displacement q_k , momentum p_k and vibration frequency ω .

This tells us the **equivalence** between **the energy of a vibration mode** and the **energy of a harmonic oscillator**. Crystal lattice vibration energy of a monoatomic chain contain N atoms can be expressed as the summation of the energy of N harmonic oscillators.



A monoatomic chain

$$U_k = \frac{1}{2} \omega^2 q_k^2 \quad T_k = \frac{1}{2} p_k^2 \quad E_k = T_k + U_k = \frac{1}{2} p_k^2 + \frac{1}{2} \omega^2 q_k^2$$

Crystal lattice vibration energy of a monoatomic chain contain N atoms can be expressed as the summation of the energy of N harmonic oscillators.

A 3D monoatomic crystal

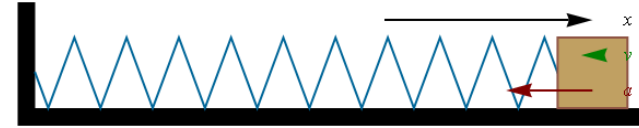
$$U = \frac{1}{2} \sum_{k=1}^{3N} \omega_k^2 q_k^2 \quad T = \frac{1}{2} \sum_{k=1}^{3N} p_k^2 \quad E = T + U = \frac{1}{2} \sum_{k=1}^{3N} (p_k^2 + \omega_k^2 q_k^2)$$

Crystal lattice vibration energy of a 3D monoatomic crystal contain N atoms can be expressed as the summation of the energy of 3N harmonic oscillator, whose frequencies are just the frequencies of the 3N independent vibration modes.

• Density of k distribution • **Equivalence** • Phonon • Lattice vibration energy • Density of states

Harmonic Oscillator

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right) \psi(x) = E \psi(x)$$



$$E = nh\nu?$$

$$\xi = \sqrt{\frac{m\omega}{\hbar}} x \quad \lambda = \frac{2E}{\hbar\omega}$$

$$\frac{d^2}{d\xi^2} \psi(\xi) + (\lambda - \xi^2) \psi(\xi) = 0$$

$$\frac{d^2}{d\xi^2} \psi - \xi^2 \psi = 0 \quad \lambda \ll \xi^2$$

$$\psi = e^{\pm \frac{1}{2} \xi^2} \longrightarrow \psi = e^{-\frac{1}{2} \xi^2} \quad \text{Only this solution is accepted}$$

$$\frac{d^2}{d\xi^2} e^{-\frac{1}{2} \xi^2} + (\lambda - \xi^2) e^{-\frac{1}{2} \xi^2} = -(1 - \xi^2) e^{-\frac{1}{2} \xi^2} + (\lambda - \xi^2) e^{-\frac{1}{2} \xi^2} = 0$$

$$\lambda = 1 \quad \psi_0 = e^{-\frac{1}{2} \xi^2} \quad E = \frac{1}{2} \lambda \hbar \omega = \frac{1}{2} \hbar \omega$$

$$(\psi_0'')' + [(1 - \xi^2) \psi_0]' \equiv 0$$

$$\downarrow \quad \psi_0' = -\xi e^{-\frac{1}{2} \xi^2} = -\xi \psi_0$$

$$\frac{d^2}{d\xi^2} \psi_0' + (3 - \xi^2) \psi_0' \equiv 0$$

$$\lambda = 3 \quad \psi_1 = \psi_0' = -\xi e^{-\frac{1}{2} \xi^2}$$

$$E = \frac{1}{2} \lambda \hbar \omega = \frac{3}{2} \hbar \omega$$

$$\lambda = 5 \quad \psi_2 = (2\xi^2 - 1) e^{-\frac{1}{2} \xi^2}$$

$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega \quad (n = 0, 1, 2, \dots)$$

Crystal lattice vibration energy of a 3D monoatomic crystal contain N atoms can be expressed as the summation of the energy of 3N **harmonic oscillator, whose frequencies are just the frequencies of the 3N independent vibration modes.**

Energy of a harmonic oscillator with angular frequency ω

$$E = (n + 1/2)\hbar\omega = (n + 1/2)h\nu$$

Energy of a vibration mode or a lattice wave with angular frequency $\omega_j(\mathbf{k})$

$$E_j(\mathbf{k}) = (\mathbf{n}_j(\mathbf{k}) + 1/2)\hbar\omega_j(\mathbf{k}) \quad n_j(\mathbf{k})=0,1,2,\dots$$

Total Energy of lattice vibration of a crystal with N unit cells, each cell having P atoms

$$E = \sum_{j=1}^{3P} \sum_{k=1}^N E_j(\mathbf{k}) = \sum_{j=1}^{3P} \sum_{k=1}^N (n_j(\mathbf{k}) + 1/2)\hbar\omega_j(\mathbf{k})$$

Phonon

$$\hbar\omega_j(\mathbf{k})$$

Photon
 $h\nu, \hbar\omega$

$$E_j(\mathbf{k}) = (n_j(\mathbf{k}) + 1/2)\hbar\omega_j(\mathbf{k})$$

$$E_j(\mathbf{k}) = (n_j(\mathbf{k}) + 1/2)\hbar\omega_j(\mathbf{k})$$

$$E_j(\mathbf{k}) = (\mathbf{n}_j(\mathbf{k}) + 1/2)\hbar\omega_j(\mathbf{k})$$

Average energy of harmonic oscillators with angular frequency ω_j at temperature T

$$\overline{E}_i = \frac{\sum_{n_i} (n_i + \frac{1}{2})\hbar\omega_i e^{-(n_i + \frac{1}{2})\hbar\omega_i / k_B T}}{\sum_{n_i} e^{-(n_i + \frac{1}{2})\hbar\omega_i / k_B T}} = \frac{1}{2}\hbar\omega_i + \hbar\omega_i \frac{\sum n e^{-nx}}{\sum e^{-nx}}$$

where $x = \hbar\omega_i / k_B T$ and k_B is Boltzmann constant.

Cause

$$\frac{\sum n e^{-nx}}{\sum e^{-nx}} = -\frac{d}{dx} \ln \sum e^{-nx} = \frac{d}{dx} \ln(1 + e^{-x} + e^{-2x} + \dots) = \frac{d}{dx} \ln(1 - e^{-x}) = \frac{1}{e^x - 1}$$

We get

$$\overline{E}_i = \frac{1}{2}\hbar\omega_i + \hbar\omega_i \frac{1}{e^{\hbar\omega_i / k_B T} - 1} = \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega_i / k_B T} - 1}\right)\hbar\omega_i$$

$$\overline{n}_i = \frac{1}{e^{\hbar\omega_i / k_B T} - 1}$$

Average energy of harmonic oscillators with angular frequency ω_i at temperature T

$$\overline{E}_i = \frac{1}{2} \hbar \omega_i + \hbar \omega_i \frac{1}{e^{\hbar \omega_i / k_B T} - 1} = \left(\frac{1}{2} + \frac{1}{e^{\hbar \omega_i / k_B T} - 1} \right) \hbar \omega_i$$

T=0K

$$\overline{E}_i = \frac{1}{2} \hbar \omega_i \quad \text{Zero point energy}$$

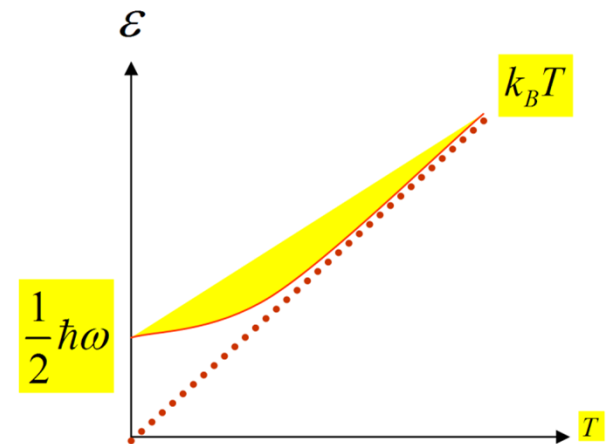
T >> 0K

$$\hbar \omega \ll k_B T$$

$$e^x = 1 + x + \frac{x^2}{2!} + \dots \quad \text{when } x \ll 1 \quad e^x = 1 + x$$

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

$$\overline{E}_i = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{1 + \frac{\hbar \omega}{k_B T} - 1} = \frac{1}{2} \hbar \omega + k_B T \approx k_B T$$



Average energy of harmonic oscillators with angular frequency ω_i at temperature T

$$\overline{E}_i = \frac{1}{2} \hbar \omega_i + \hbar \omega_i \frac{1}{e^{\hbar \omega_i / k_B T} - 1} = \left(\frac{1}{2} + \frac{1}{e^{\hbar \omega_i / k_B T} - 1} \right) \hbar \omega_i$$

Total lattice vibration energy of a crystal

$$E = \sum_i \overline{E}_i = \sum_i \left(\frac{1}{2} + \frac{1}{e^{\hbar \omega_i / k_B T} - 1} \right) \hbar \omega_i = \sum_i \frac{1}{2} \hbar \omega_i + \sum_i \frac{\hbar \omega_i}{e^{\hbar \omega_i / k_B T} - 1} = E_0 + E(T)$$

The problem is that the summation is very difficult to obtain cause the number of independent lattice waves or equivalent harmonic oscillators is very large (10^{23}).

We need a new concept called “Density of state” to change the summation into integration.

The density of states $g(\omega)$ is defined as the number of oscillators (or k) per unit frequency interval.

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

Total number of oscillators

$$\int_0^{\omega_m} g(\omega) d\omega = dNp$$

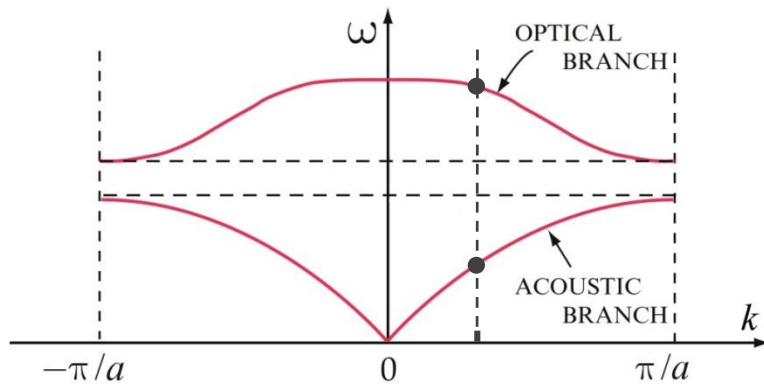
where d is dimension, N is unit cell number and p is atom number in a cell

$$E_0 = \sum_i \frac{1}{2} \hbar \omega_i = \int_0^{\omega_m} \frac{1}{2} \hbar \omega g(\omega) d\omega$$

$$E(T) = \sum_i \frac{\hbar \omega_i}{e^{\hbar \omega_i / k_B T} - 1} = \int_0^{\omega_m} \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} g(\omega) d\omega$$

$$\bar{E} = E_0 + E(T) = \sum_i \frac{1}{2} \hbar \omega_i + \sum_i \frac{\hbar \omega_i}{e^{\hbar \omega_i / k_B T} - 1} = \int_0^{\omega_m} \frac{1}{2} \hbar \omega g(\omega) d\omega + \int_0^{\omega_m} \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} g(\omega) d\omega$$

• Density of k distribution • Equivalence • Phonon • Lattice vibration energy • **Density of states**



For one branch

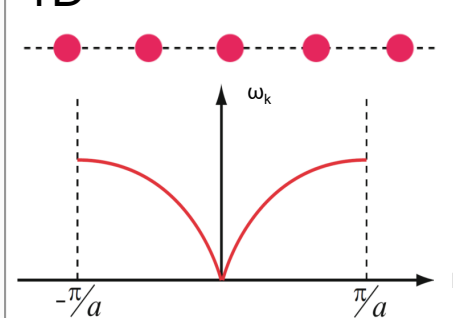
$$dn = g_j(\omega)d\omega = \rho_j(k)dk$$

$$\rho_j(k) = \begin{cases} \frac{L}{2\pi}, & 1\text{D} \\ \frac{S}{4\pi^2}, & 2\text{D} \\ \frac{V}{8\pi^3}, & 3\text{D} \end{cases}$$

$$g_j(\omega) = \rho_j(k) \frac{dk}{d\omega_j}$$

$$g(\omega) = \sum_{j=1}^{dp} g_j(\omega)$$

1D



$$\omega = 2\sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right|$$

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

$$g(\omega) = \rho_s(k) \frac{dk}{d\omega} = \rho_s(k) \cdot \frac{1}{a} \sqrt{\frac{m}{\beta}} \frac{1}{\cos \frac{ka}{2}}$$

$$\omega(k) = \omega(-k)$$

$$\rho_s(k) = 2 \cdot \rho(k) = 2 \frac{L}{2\pi} = \frac{Na}{\pi}$$

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

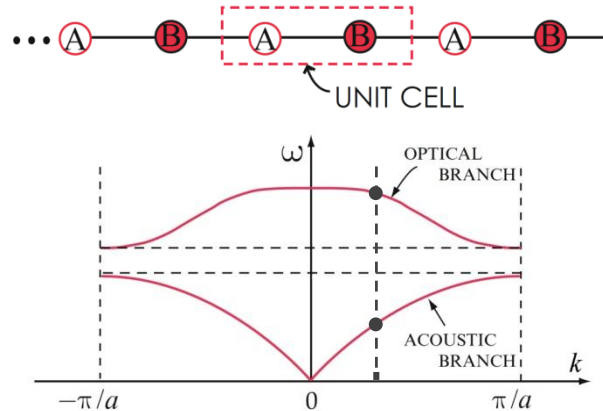
$$\omega_{\max} = 2\sqrt{\frac{\beta}{m}}$$

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

$$\bar{E} = E_0 + E(T) = \int_0^{\omega_m} \frac{1}{2} \hbar \omega \mathbf{g}(\omega) d\omega + \int_0^{\omega_m} \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} \mathbf{g}(\omega) d\omega$$

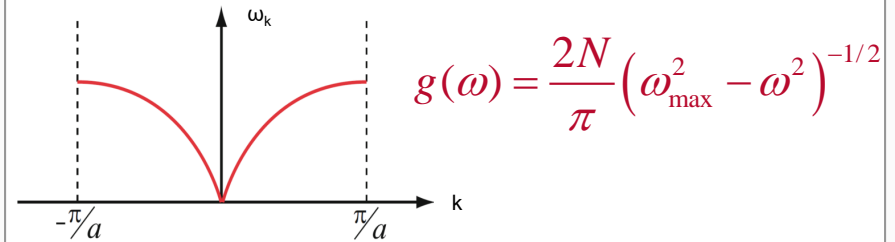
• Density of k distribution • Equivalence • Phonon • Lattice vibration energy • **Density of states**

1D



$$g(\omega) = \sum_{j=1}^2 g_j(\omega)$$

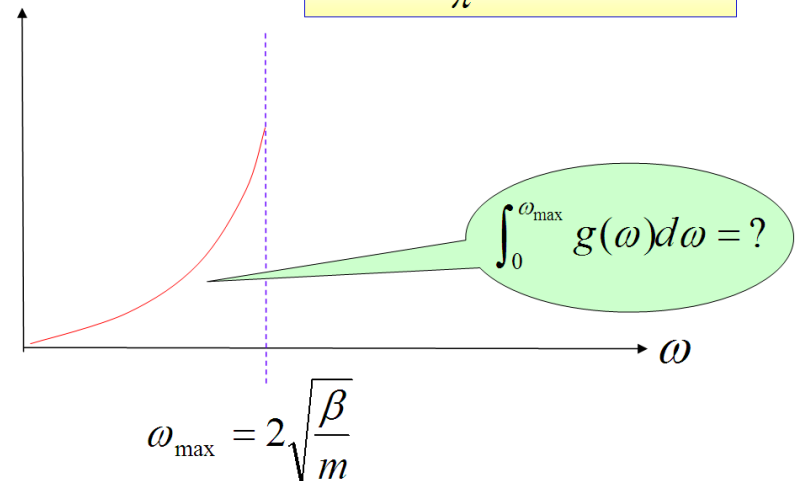
1D



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

 $g(\omega)$

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



$$\omega_{\max} = 2\sqrt{\frac{\beta}{m}}$$

3D

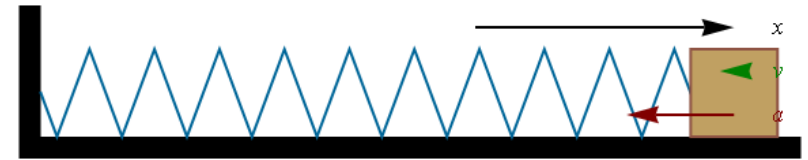
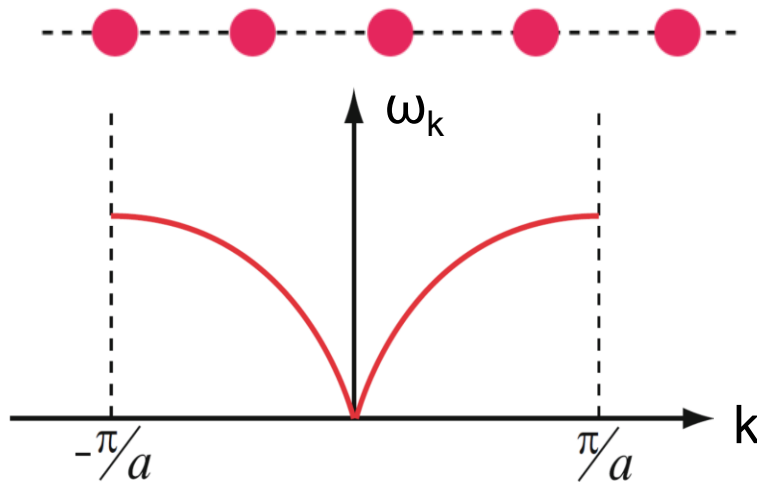
$$g(\omega) = \sum_j^{3p} g_j(\omega) \quad \int_0^{\omega_m} g_j(\omega) d\omega = N$$

$$\int_0^{\omega_m} g(\omega) d\omega = 3Np$$

$$\bar{E} = E_0 + E(T) = \sum_{j=1}^{3P} \left(\int_0^{\omega_m} \frac{1}{2} \hbar \omega_j \mathbf{g}_j(\omega) d\omega_j + \int_0^{\omega_m} \frac{\hbar \omega_j}{e^{\hbar \omega_j / k_B T} - 1} \mathbf{g}_j(\omega) d\omega_j \right)$$

Summary

lattice vibration ~ harmonic oscillator ~ phonon



$$E = (1/2 + n)\hbar\omega$$

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v$$

$$\overline{E}_i = \frac{1}{2}\hbar\omega_i + \hbar\omega_i \frac{1}{e^{\hbar\omega_i/k_B T} - 1} = \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega_i/k_B T} - 1} \right) \hbar\omega_i$$

$$\overline{E} = \sum_i \overline{E}_i = \sum_i \frac{1}{2}\hbar\omega_i + \sum_i \frac{\hbar\omega_i}{e^{\hbar\omega_i/k_B T} - 1} = E_0 + E(T)$$

$$\overline{E} = E_0 + E(T) = \int_0^{\omega_m} \frac{1}{2}\hbar\omega \mathbf{g}(\omega) d\omega + \int_0^{\omega_m} \frac{\hbar\omega}{e^{\hbar\omega_i/k_B T} - 1} \mathbf{g}(\omega) d\omega$$