

Structure of Matter

The Solid State

WS 2013/14

Lectures (Tuesday & Friday)

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Last time:

Reciprocal lattice and diffraction

Today:

Reciprocal lattice and diffraction

cont'd

Phonons

Diffraction conditions

The set of reciprocal vectors \vec{G}
determines the possible x-ray reflections

Scattering from k to k' is proportional to charge density $n(r)$

Scattering amplitude:

$$F = \int d^3r n(\vec{r}) e^{-i(\vec{k} - \vec{k}') \cdot \vec{r}} = S_{\Delta\vec{k}} = \sum_{\vec{G}} \int d^3r n_{\vec{G}} e^{-i(\vec{G} - \Delta\vec{k}) \cdot \vec{r}}$$

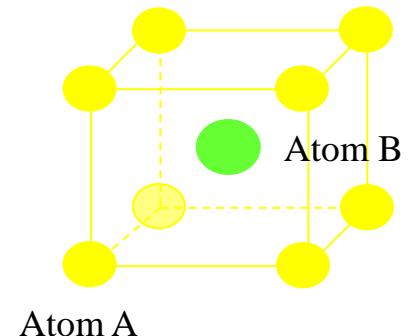
Periodicity $n(r) \Rightarrow \Delta\vec{k} = \vec{G}$

CsCl, exponential charge distributions

$$n(\vec{r}) = \sum_{\vec{T}} \left[\frac{A}{\pi \rho_A^3} e^{-2\frac{|\vec{r}-\vec{T}|}{\rho_A}} + \frac{B}{\pi \rho_B^3} e^{-2\frac{|\vec{r}-\vec{T}-\vec{r}_{AB}|}{\rho_A}} \right]$$

$$\vec{T} = a(m\vec{e}_x + n\vec{e}_y + p\vec{e}_z)$$

$$\vec{r}_{AB} = \frac{a}{2} (\vec{e}_x + \vec{e}_y + \vec{e}_z)$$



Atomic form factors: $f_j = \int d^3\vec{r} e^{-i\vec{G}\cdot\vec{r}} n_j(\vec{r})$

$$f_A(\vec{G}) = \frac{16A}{4 + |\vec{G}|^2 \rho_A^2}$$

$$f_B(\vec{G}) = \frac{16B}{4 + |\vec{G}|^2 \rho_B^2}$$

CsCl, diffraction conditions

$$\vec{r}_{AB} = \frac{a}{2}(\vec{e}_x + \vec{e}_y + \vec{e}_z)$$

Structure factor: $S_{\vec{G}} = \sum_j f_j \exp\{-i\vec{G} \cdot \vec{r}_j\}$

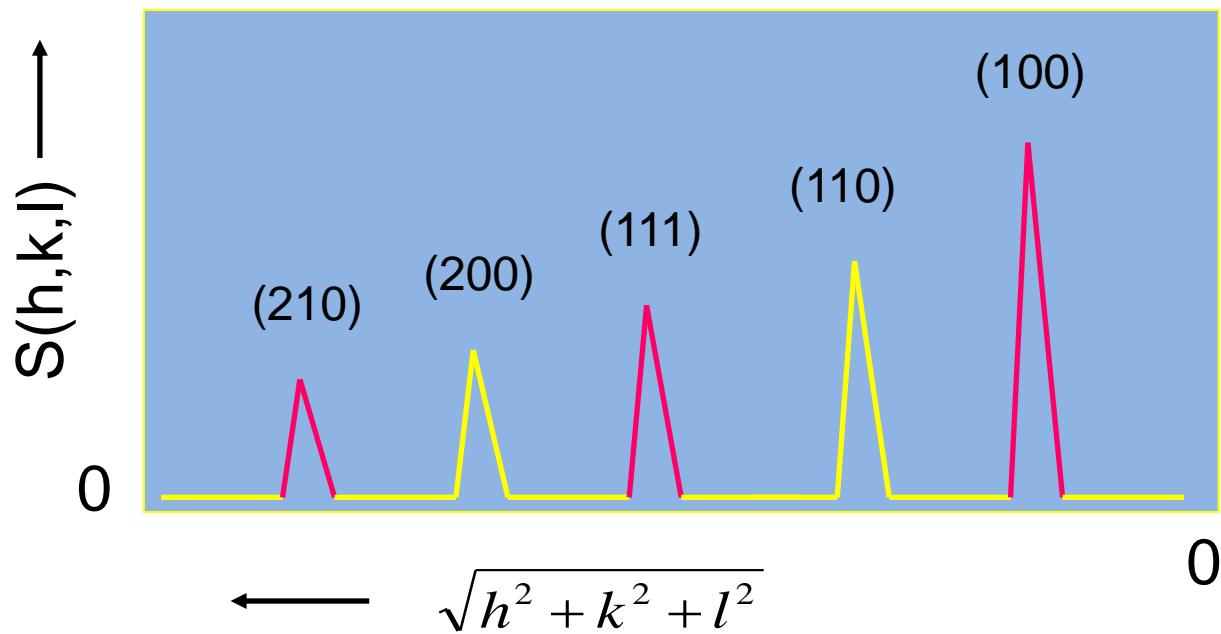
$$S_{\vec{G}} = f_A(\vec{G}) + f_B(\vec{G}) e^{-i\vec{G} \cdot \vec{r}_{AB}} = f_A(\vec{G}) + f_B(\vec{G}) e^{-i[G_x + G_y + G_z]a/2}$$

Simple cubic lattice, Bragg condition:

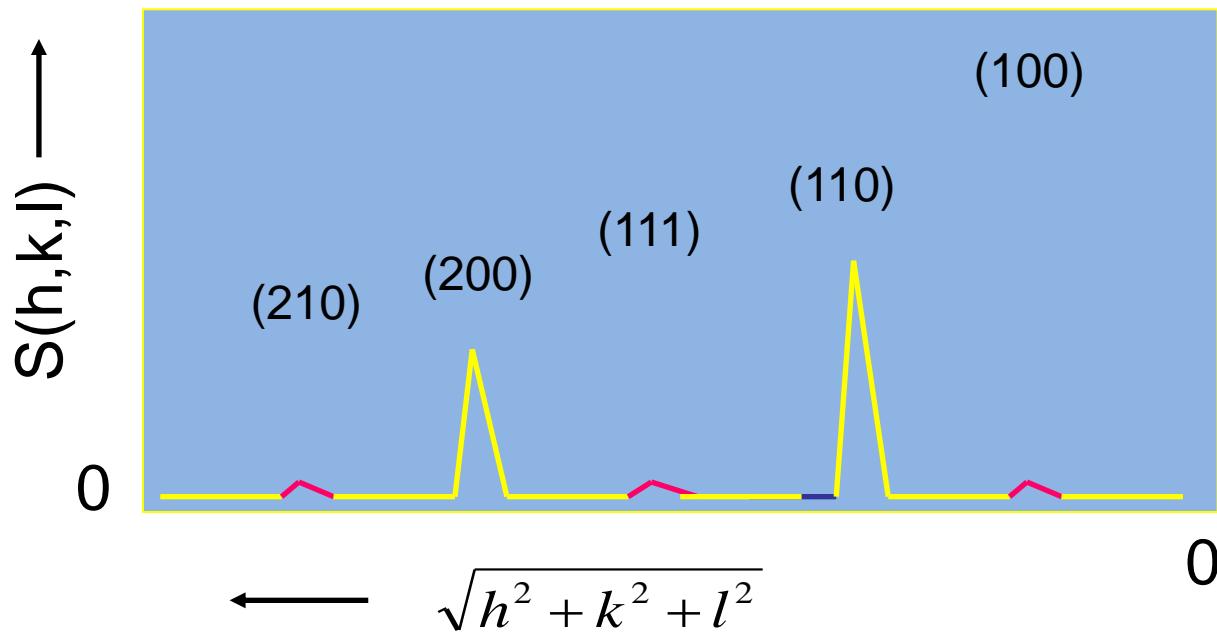
$$\vec{G} = \frac{2\pi}{a} \{h\hat{x} + k\hat{y} + l\hat{z}\}$$

$$\begin{aligned} S(h,k,l) &= f_A + f_B e^{-i\pi(h+k+l)} = \\ &= f_A + f_B \quad h+k+l \text{ even} \\ &= f_A - f_B \quad h+k+l \text{ odd} \end{aligned}$$

Case I: $f_A \gg f_B$



Case II: $f_A \approx f_B$



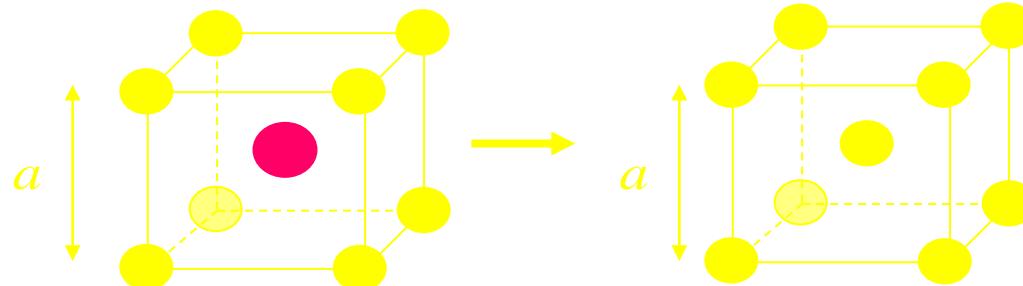
Pseudo-bcc

Diffraction for

When $f_A \approx f_B$

with $h + k + l$ even strong

with $h + k + l$ odd weak \rightarrow 'pseudo-bcc'



S.C.

B.C.C.

PHONONS

Elementary excitations in solids

Charge

Electronic excitations

EM field

Photon

Elastic

Phonon

Magnetic

Magnon (spin-wave)

Multi-particle

Exciton, polariton, polaron

Collective

Plasmon

...

...

Phonons

- Propagation of sound
- Optical properties (infrared)
- Lattice expansion
- Heat capacity
- Thermal conductivity

General

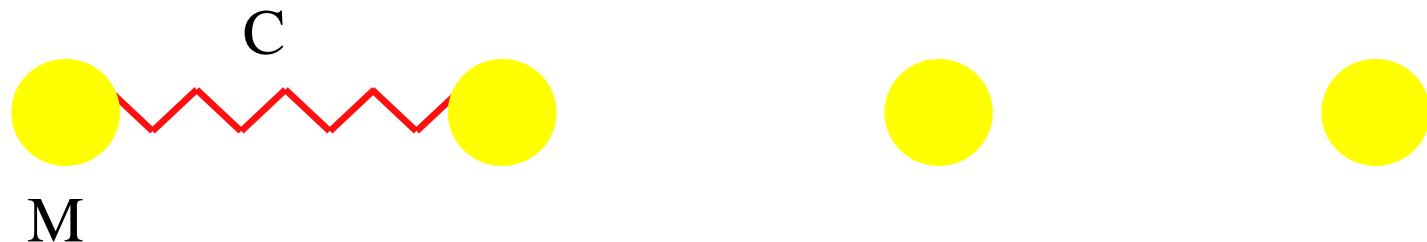
Total lattice energy $U_{\text{total}} = \sum_{<\text{ij}>} U_{\text{ij}} (\vec{R}_j - \vec{R}_i)$

Stability: $\left. \frac{\partial U_{\text{total}}}{\partial R_j} \right|_{R_j=R_j^0} = 0 \Rightarrow$ equilibrium coordinates

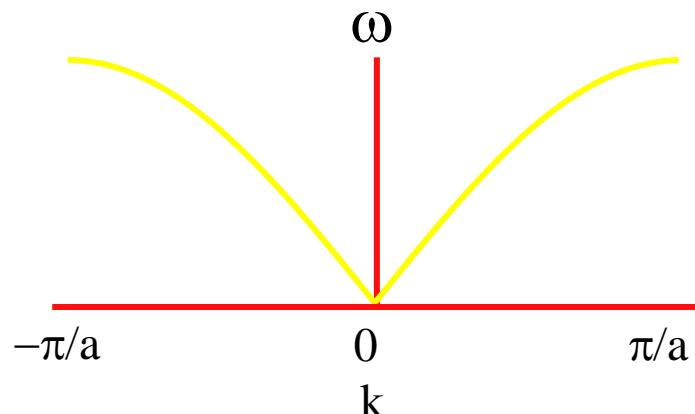
Harmonic approximation:

$$F_j = - \frac{\partial U_{\text{total}}}{\partial R_j}$$

1D, 1 at./cell

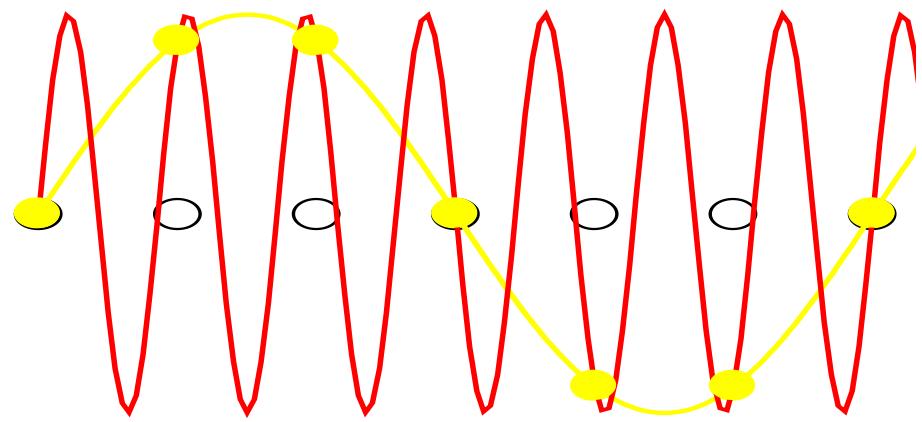


$$H = T + U = \sum_i \frac{p_i^2}{m_i} + \frac{1}{2} \sum_{\langle ij \rangle} C_j (u_i - u_j)^2$$



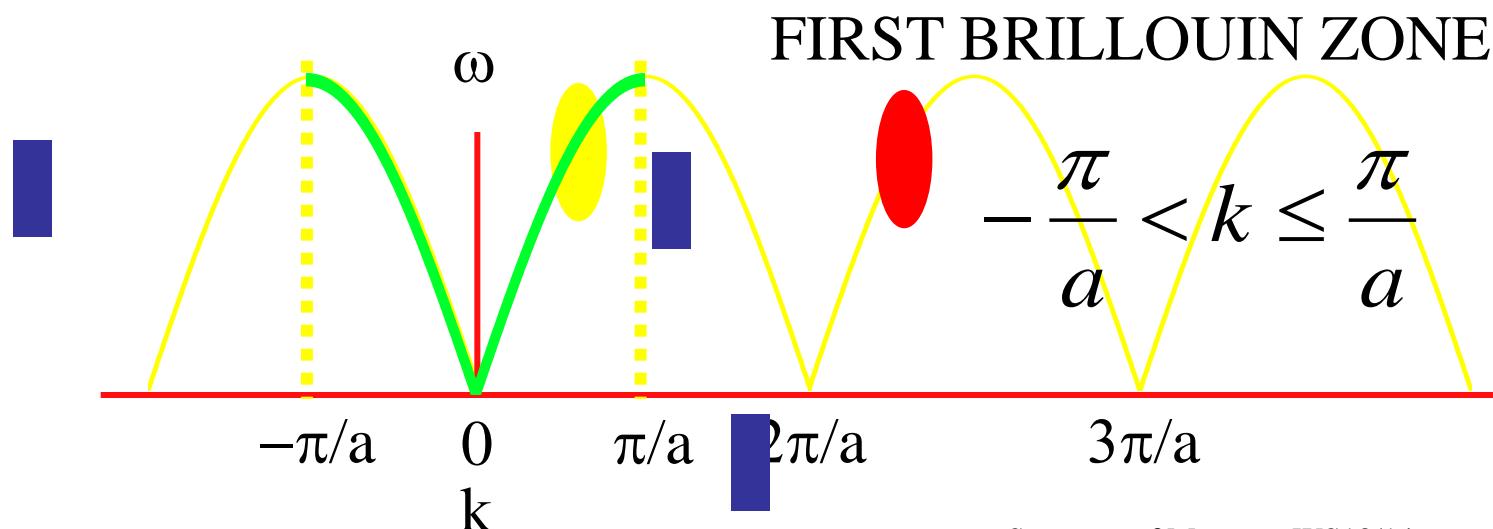
$$\omega(k) = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

Relevant values of k

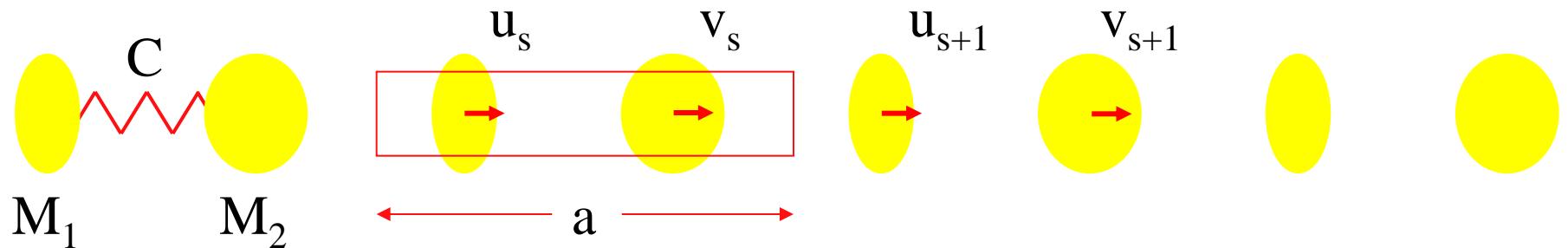


$$e^{i\left(\omega t - \frac{\pi}{3a}r\right)}$$

$$e^{i\left(\omega t - \frac{7\pi}{3a}r\right)}$$



1 dimensional -- 2 at./cell



EOM

$$M_1 \ddot{u}_s = -C(2u_s - v_s - v_{s-1})$$

$$M_2 \ddot{v}_s = -C(2v_s - u_s - u_{s+1})$$

Traveling wave

$$u_s(t) = u \cdot e^{ikas} \cdot e^{-i\omega t}$$

$$v_s(t) = v \cdot e^{ikas} \cdot e^{-i\omega t}$$

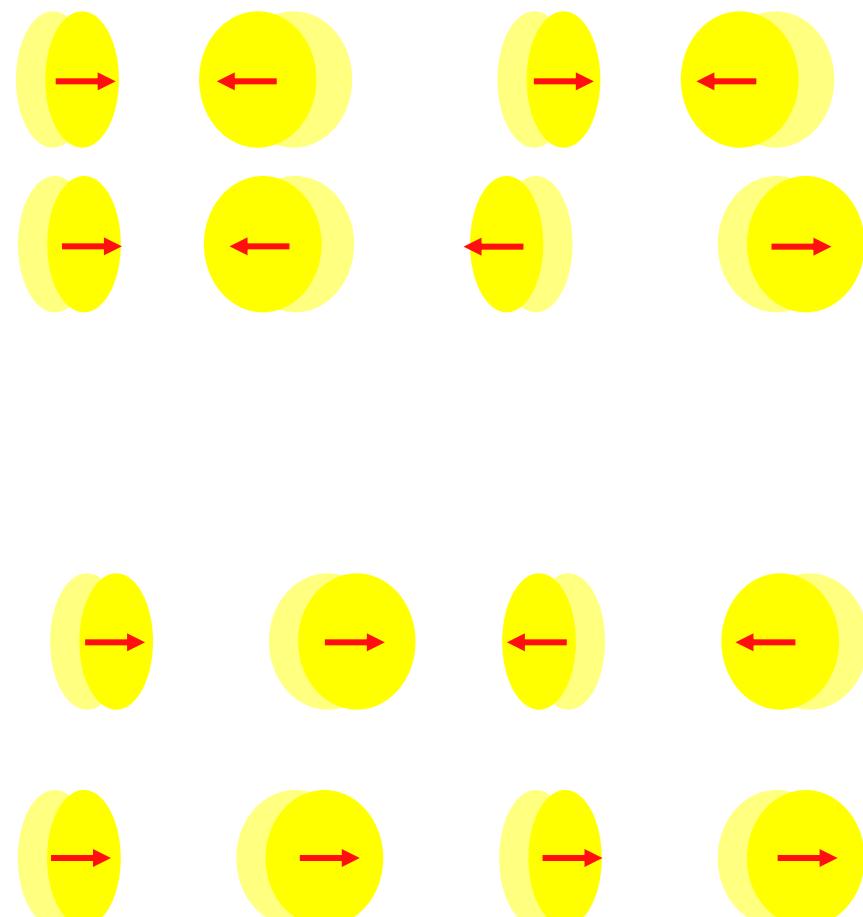
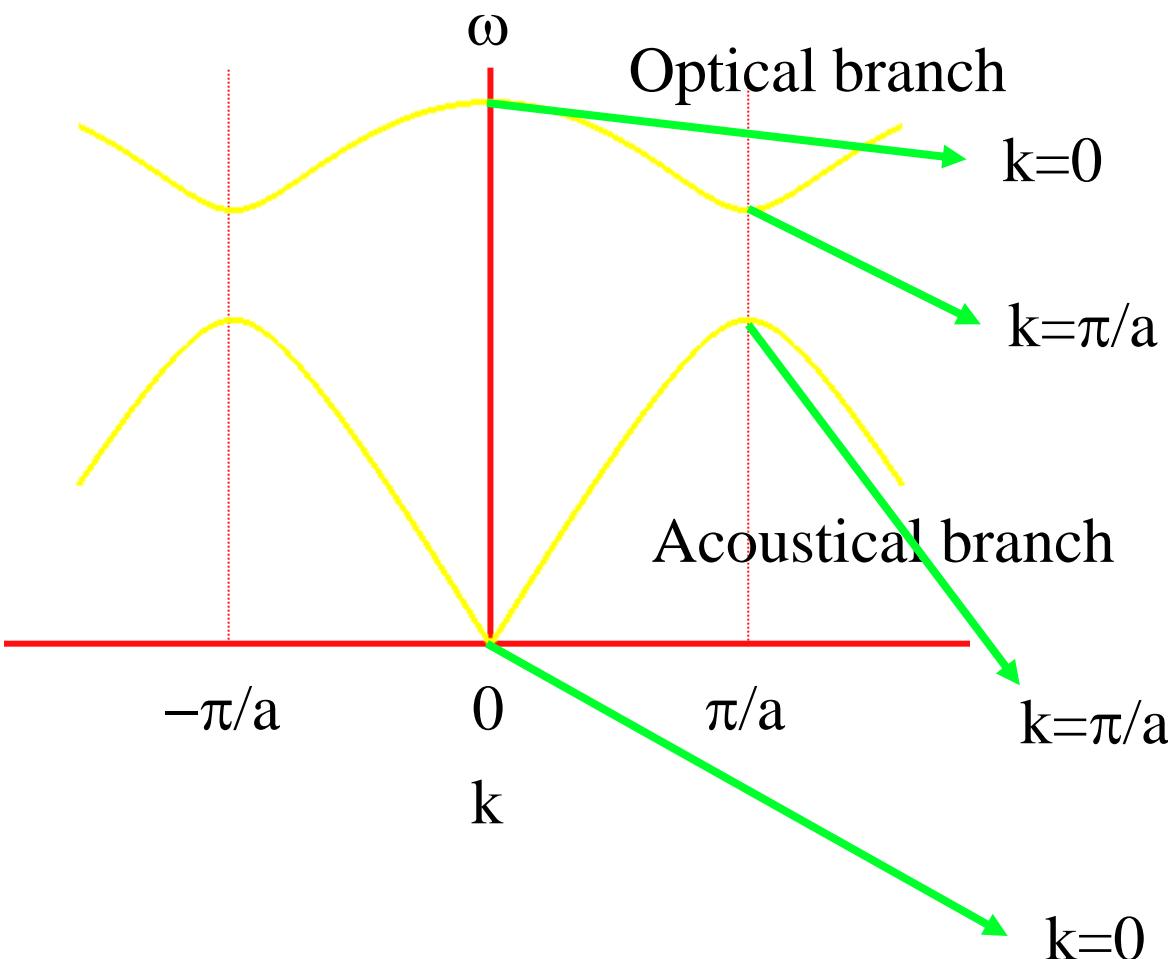
Dispersion

$$\omega^2(k) = \frac{C}{\mu} \left\{ 1 \pm \sqrt{1 - \frac{4\mu}{M} \sin^2(ka/2)} \right\}$$

$$\mu = \frac{1}{M_1} + \frac{1}{M_2}; \quad M = M_1 + M_2$$

Dispersion

$$\omega(k) = \sqrt{\frac{C}{\mu} \left\{ 1 \pm \sqrt{1 - \frac{4\mu}{M} \sin^2(ka/2)} \right\}}$$



Relevant values for k

$$\omega(k) = \sqrt{\frac{C}{\mu} \left\{ 1 \pm \sqrt{1 - \frac{4\mu}{M} \sin^2(ka/2)} \right\}}$$

Solutions for k and for $k+h \cdot 2\pi/a$

have the same frequency

$$\sin\left(\frac{ka}{2}\right) = \sin\left(\frac{ka}{2} + h \cdot 2\pi\right) \Rightarrow \omega(k + h \frac{2\pi}{a}) = \omega(k)$$

have the same wavefunctions

$$u_{k+h \cdot 2\pi/a}(s, t) = u \cdot e^{ikas} \cdot e^{i(h \cdot 2\pi/a)as} \cdot e^{-i\omega t} = u_k(s, t)$$

Are identical

Group velocity

$$v_g = \frac{\partial \omega(k)}{\partial k}$$

$$\omega(k) = \sqrt{\frac{C}{\mu} \left\{ 1 \pm \sqrt{1 - \frac{4\mu}{M} \sin^2(ka/2)} \right\}}$$

$$k \approx 0 \quad \omega(k) = \sqrt{\frac{2C}{M}} \cdot \frac{ka}{2} \quad v_g = \sqrt{\frac{2C}{M}} \frac{a}{2} \quad \text{Sound velocity} \quad \omega = v_g \cdot k$$

$$\omega(k) = \sqrt{\frac{2C}{\mu}} \quad v_g = 0$$

$k \approx \pm\pi/a$ $\omega(k) \approx \text{constant}$: Standing wave

Three dimensions

3-dimensional crystal:

s atoms per primitive cell:

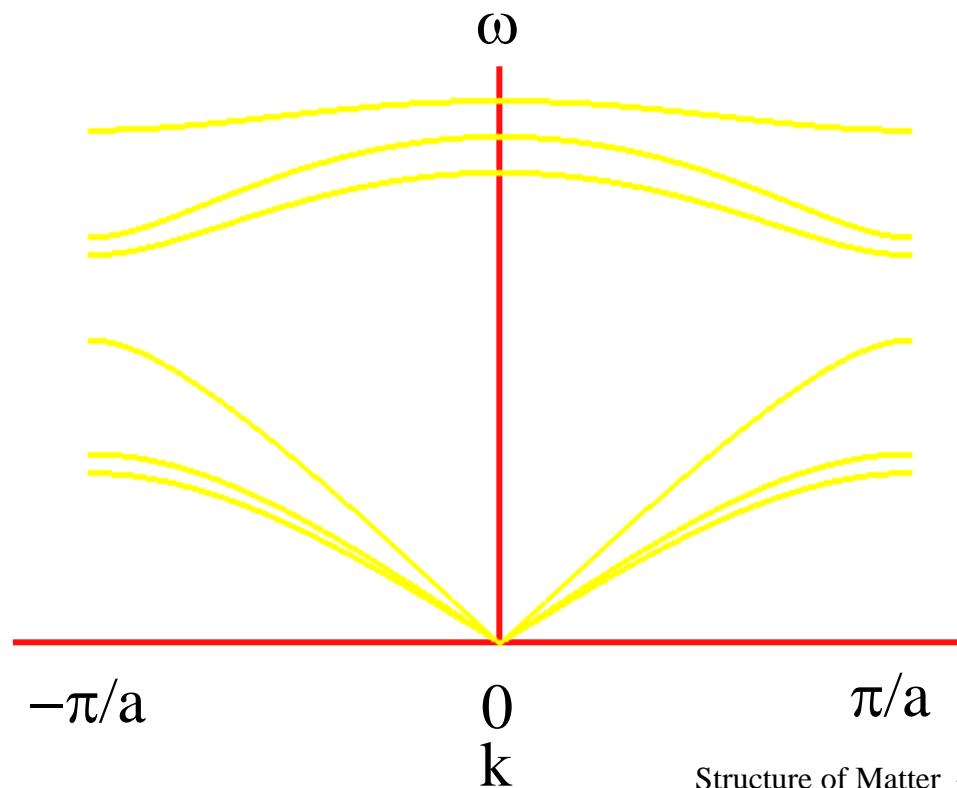
3 degrees of freedom per atom

3 acoustical branches

$3s$ -3 optical branches

Optical modes

Acoustical modes



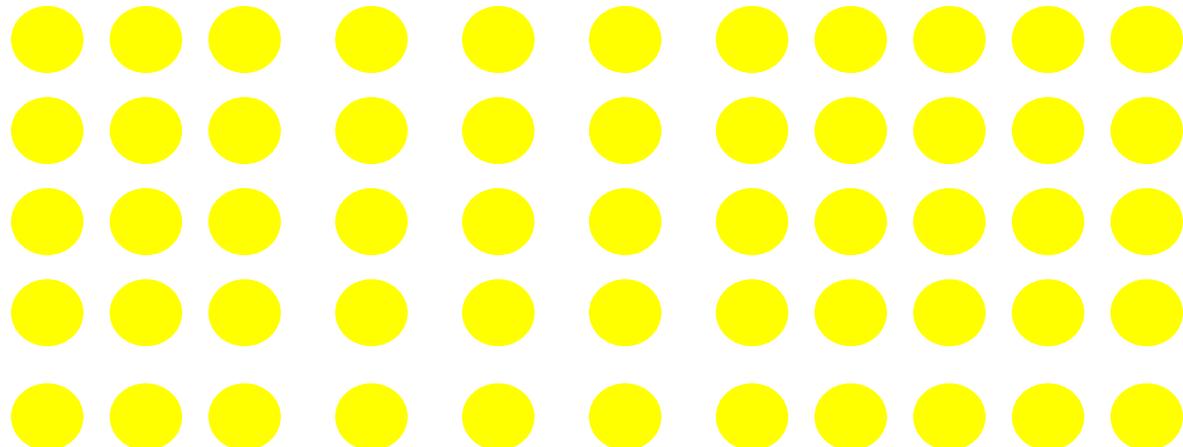
Longitudinal: $u \parallel k$

Transverse: $u \perp k$

Sound waves

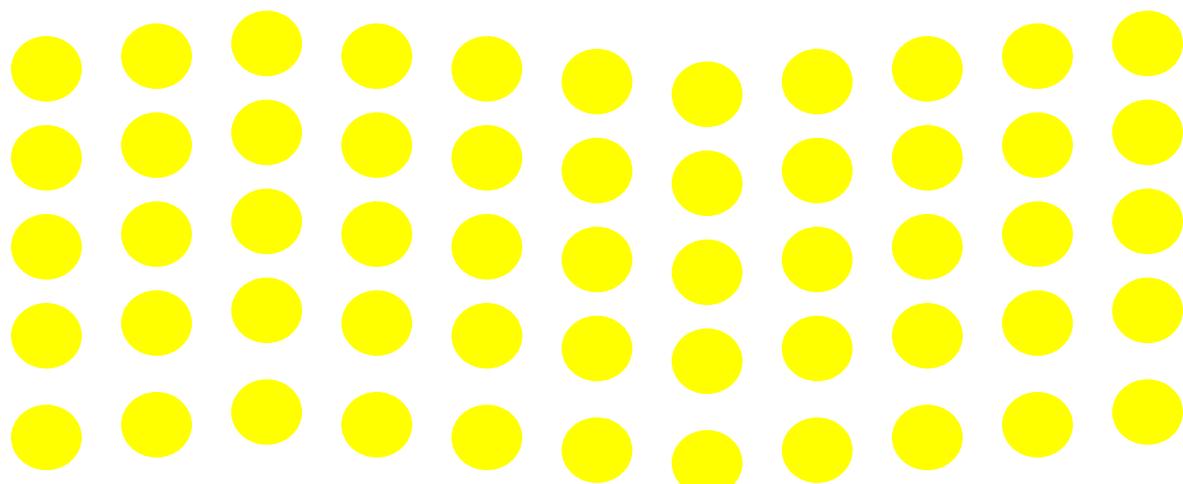
Longitudinal
Acoustical

$$u // k$$



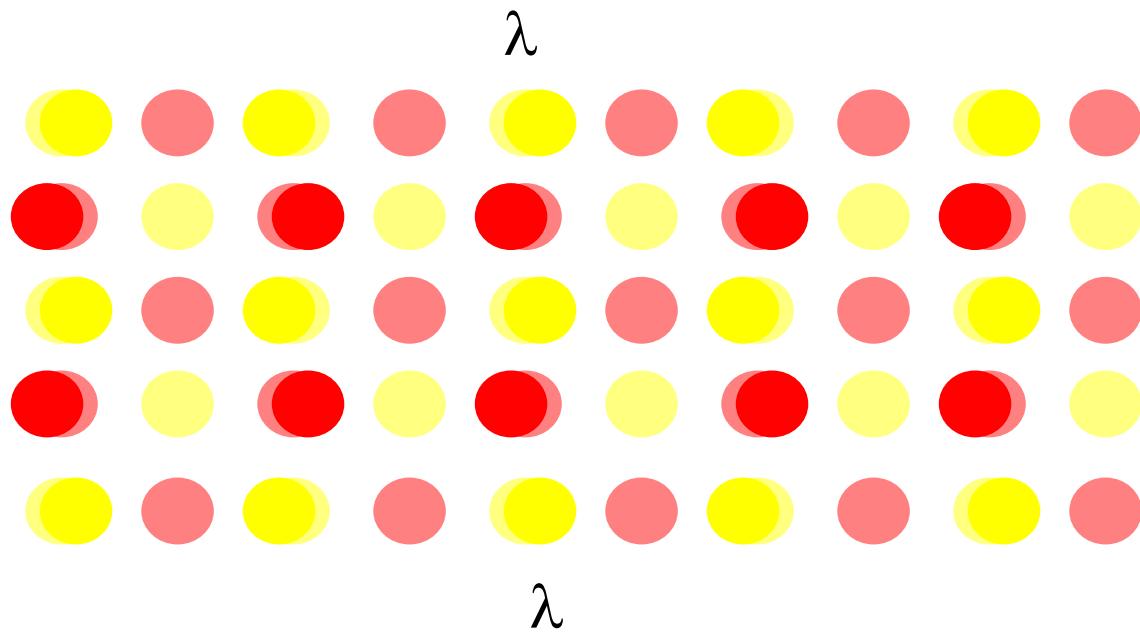
Transverse
acoustical

$$u \perp k$$

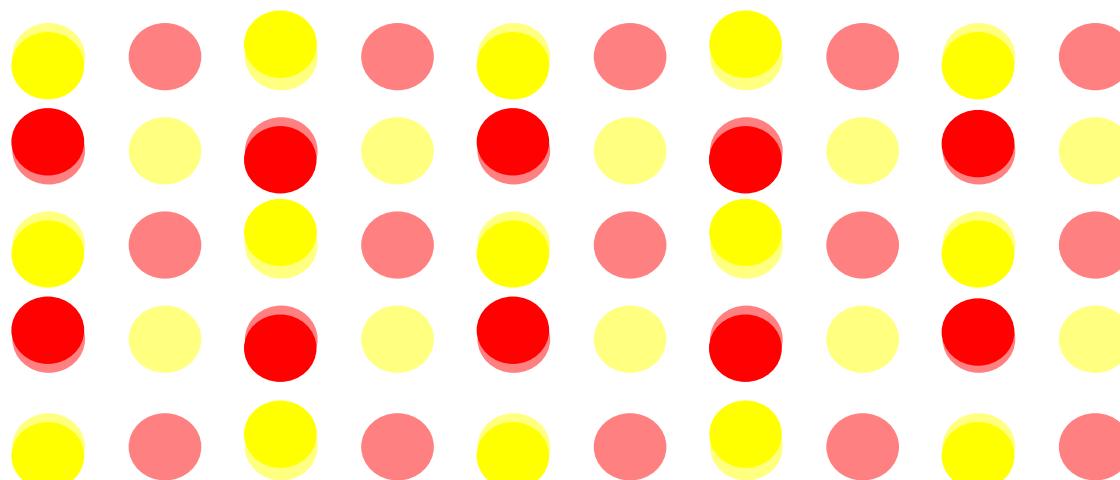


Optical waves

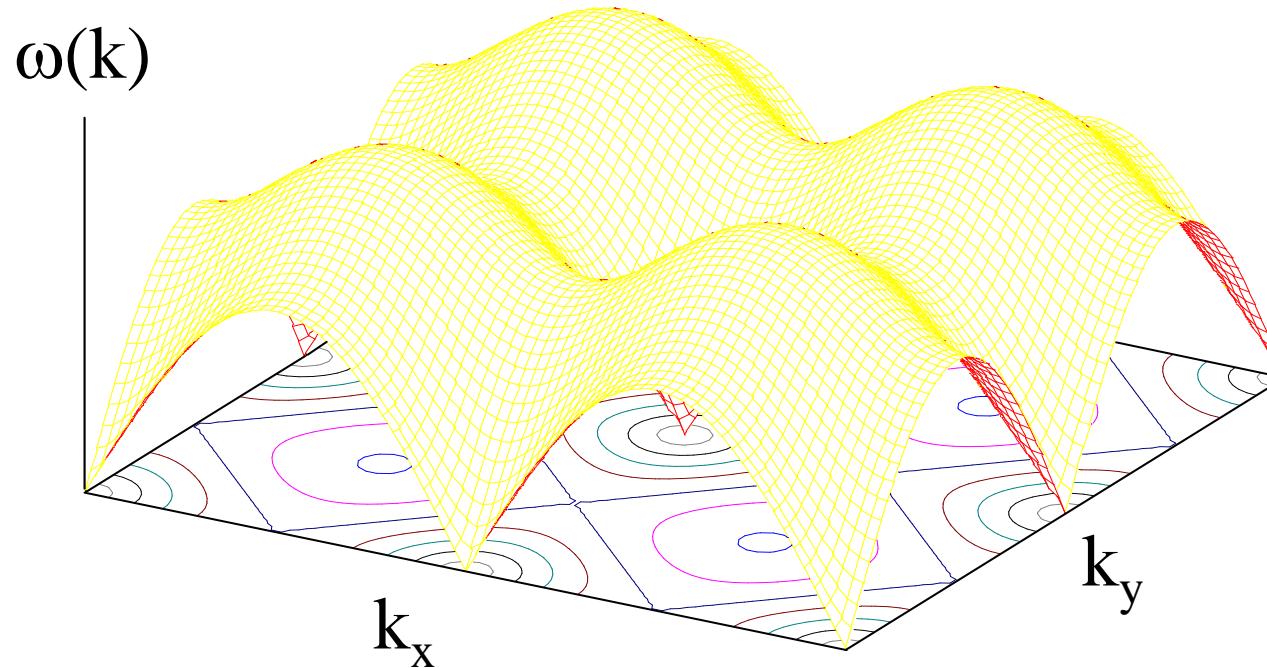
Longitudinal
optical phonons



Transversal
optical phonons



Dispersion in two dimensions



$$\omega_k = \sqrt{\frac{4C}{m}} \sqrt{\sin^2\left(\frac{k_x a}{2}\right) + \sin^2\left(\frac{k_y a}{2}\right)}$$

phonons

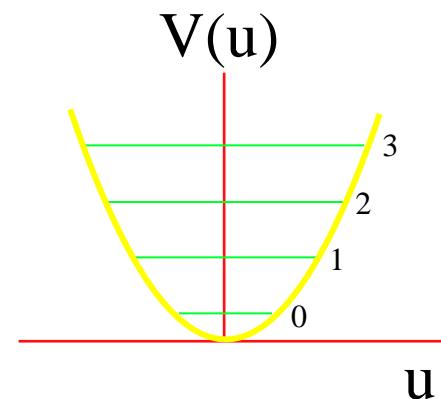
Classical: $u_s(t) = u_k(t) e^{i \omega_k t}$

EOM: $m\ddot{u}_k(t) = -C_k u_k(t)$ with $C_k = m\omega_k^2$

Quantum states of elastic waves:

$$\left\{ -\frac{\hbar}{2m} \frac{\partial^2}{\partial u_k^2} + \frac{1}{2} m \omega_k^2 u_k^2 \right\} \cdot \psi_k(u_k) = E_k \cdot \psi_k(u_k)$$

$$\psi_k(u_k, t) = e^{i(E_k/\hbar)t} \cdot \psi_k(u_k) \quad E_k = (n + \frac{1}{2}) \cdot \hbar \omega_k$$



See appendix C: quantization of elastic waves: phonons

Properties of phonons

Any number can occupy the same vibrational mode u_k

Phonons are *bosons*

Thermal occupation given by Planck's distribution

$$\langle n_k \rangle = \frac{1}{e^{(\hbar\omega_k/k_bT)} - 1}$$

Zero-point energy: $E_0 = \sum_k \frac{1}{2} \hbar\omega_k$

Energy of 1 phonon: $\hbar\omega_k$

“Momentum” of 1 phonon: $\hbar k$

Phonons: Quantum excitations of solids

Measuring phonons

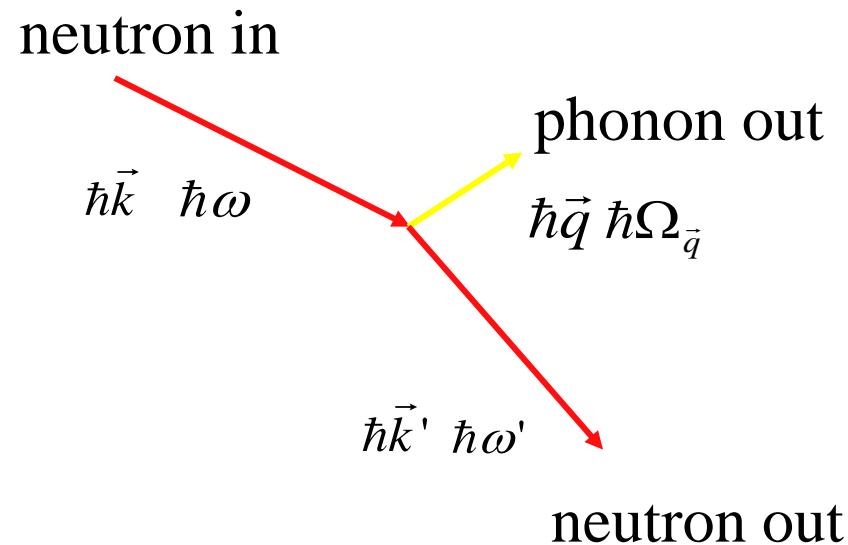
Inelastic neutron scattering
Inelastic light scattering (Raman/Brillouin)
(far) Infrared absorption
Electron energy loss spectroscopy
Inelastic X-ray scattering
Ultrasound propagation
Point and Tunnel spectroscopy

...

Phonon momentum

Total momentum of a crystal with phonon k is zero !

$$P = M \frac{\partial}{\partial t} \sum_s^N u_s = M \frac{\partial u}{\partial t} \cdot \sum_s e^{i k a s} = M \frac{\partial u}{\partial t} \cdot \frac{1 - e^{i k a N}}{1 - e^{i k a}} = 0$$



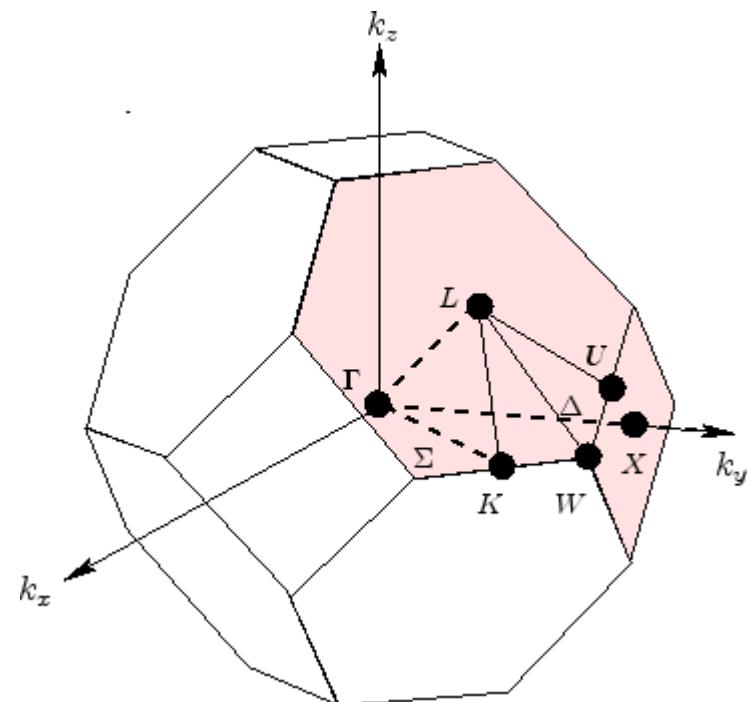
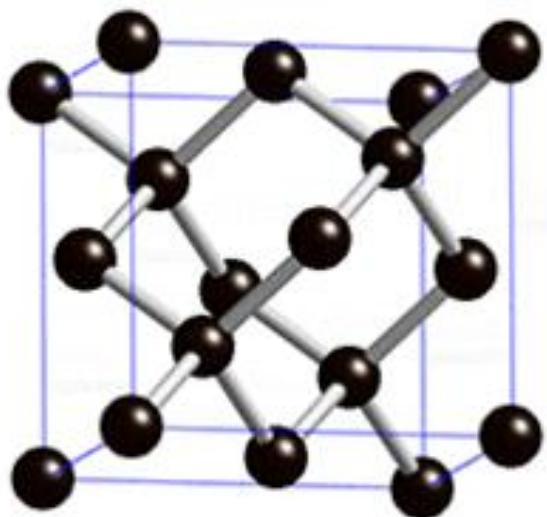
Energy conservation

$$\frac{\hbar^2 k^2}{2m_n} = \frac{\hbar^2 k'^2}{2m_n} \pm \hbar\Omega$$

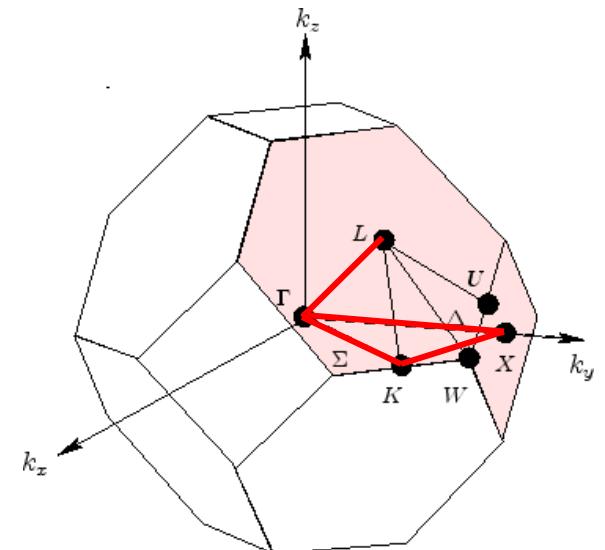
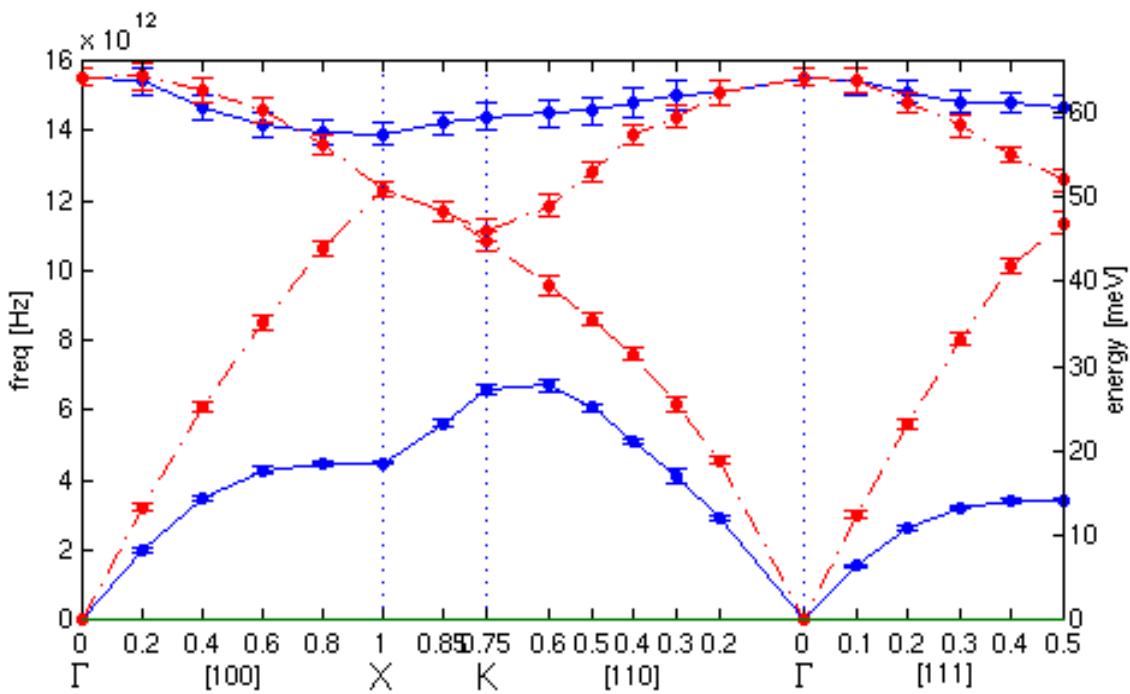
“Momentum” conservation

$$k = k' \pm q + G$$

Diamond lattice



Phonon dispersion in Si

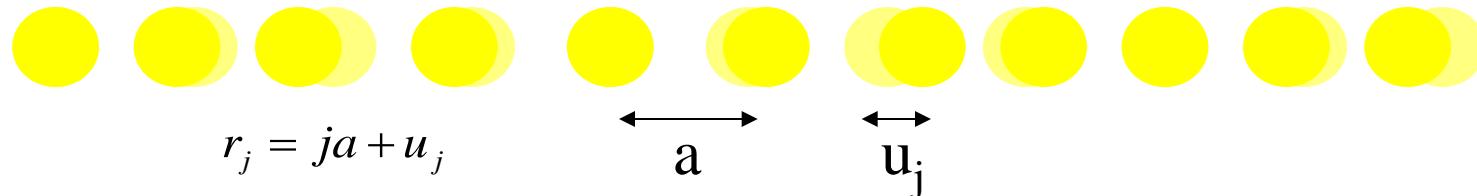


Thermal properties

Thermal expansion



Harmonic crystal: No thermal expansion!!



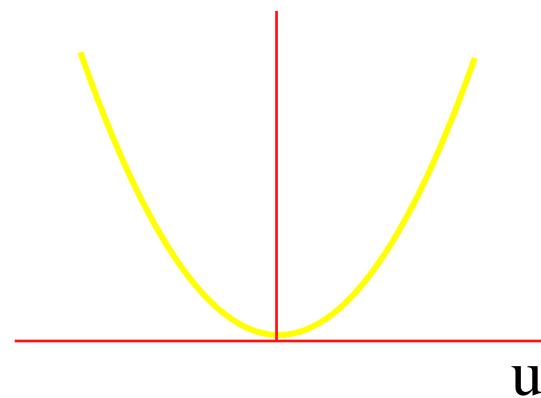
Harmonic

$$V(u_j) = \alpha \cdot u_j^2$$

$$a(T) = a + \langle u_j \rangle_T = a$$

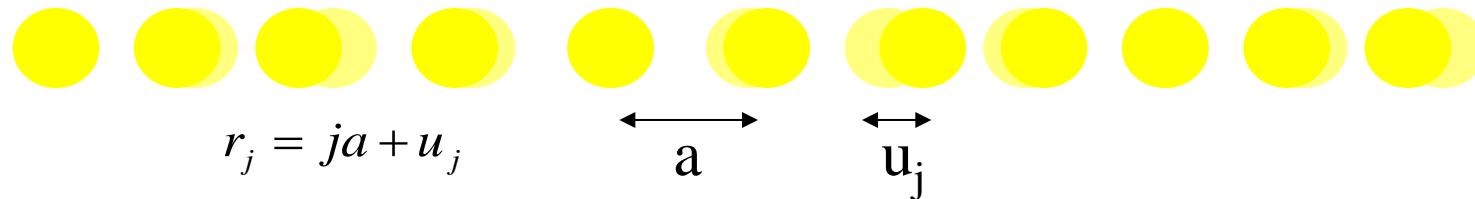
$$\langle u_j \rangle_T = \frac{\int du \cdot u e^{-V(u_j)/k_B T}}{\int du \cdot e^{-V(u_j)/k_B T}} = 0$$

$$V(u)$$



No lattice expansion !!

Anharmonicity: Thermal expansion (classical)

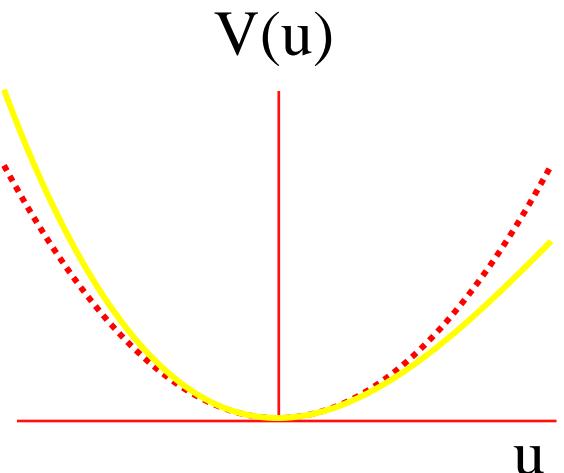


Weak anharmonicity

$$V(u_j) = \alpha \cdot u_j^2 - \gamma \cdot u_j^3$$

$$\langle u_j \rangle_T = \frac{\int du \cdot u e^{-V(u_j)/k_B T}}{\int du \cdot e^{-V(u_j)/k_B T}} \approx \frac{3/4 (k_B T)^{3/2} \sqrt{\pi} \gamma \alpha^{-5/2}}{\sqrt{k_B T} \sqrt{\pi} \alpha^{-1/2}}$$

$$a(T) = a_0 + \langle u_j \rangle_T = a_0 + \frac{3\gamma}{4\alpha^2} k_B T$$



Lattice expansion is caused by anharmonicity !