Phonons - Theoretical description

Lecture 17

CHM 637

Chemistry & Physics of Materials

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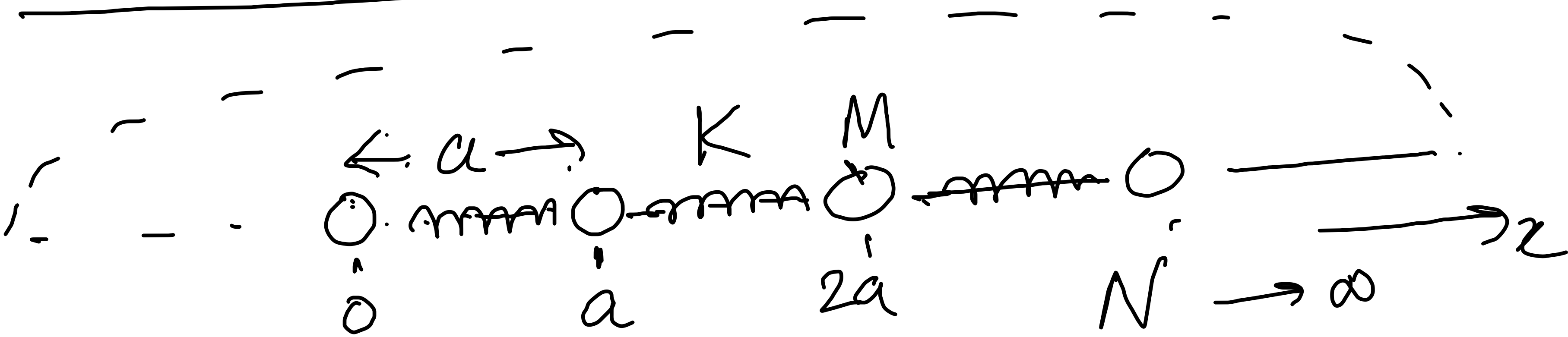
Lecture Plan

- 1-d lattice model - classical model and quantization
- Bose-Einstein statistics and thermal properties
- 1-d diatomic lattice - acoustic and optic modes
- General approach for 3-d crystals

Lattice waves in a 1-d lattice



P.B.C.

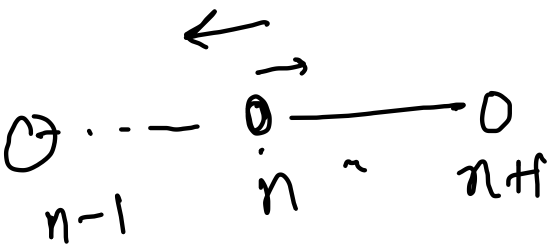
$$x_n(t) = (na) + u_n(t)$$

$$n = 1, 2, 3, \ldots, N$$

$$x_{n+N}(t) = x_n(t)$$

Classical eqns. of motion:

$$M\ddot{u}_n(t) = K\left(u_{n+1}(t) - u_n(t)\right) - K\left(u_n(t) - u_{n-1}(t)\right)$$



$n = 1, 2, 3, \ldots N$

$$N+1 \longrightarrow 1$$

$$0 \longrightarrow N$$

$$u_n(t) = U_j \exp\left(i q_j \underbrace{(na)}_{x_n^{(0)}} - i\omega_j t\right)$$

$$-M\omega_j^2 U_j = K U_j \left\{ e^{i q_j a} + e^{-i q_j a} - 2 \right\}$$

$$= 4 K U_j \sin^2\left(\frac{q_j a}{2}\right)$$

For non-trivial solutions (ie $U_j \neq 0$)

$$\omega_j^2 = \left(\frac{4K}{M}\right) \sin^2\left(\frac{q_j a}{2}\right)$$

$$\boxed{\omega_j = \sqrt{\frac{4K}{M}}\left|\sin\left(\frac{q_j a}{2}\right)\right|}$$

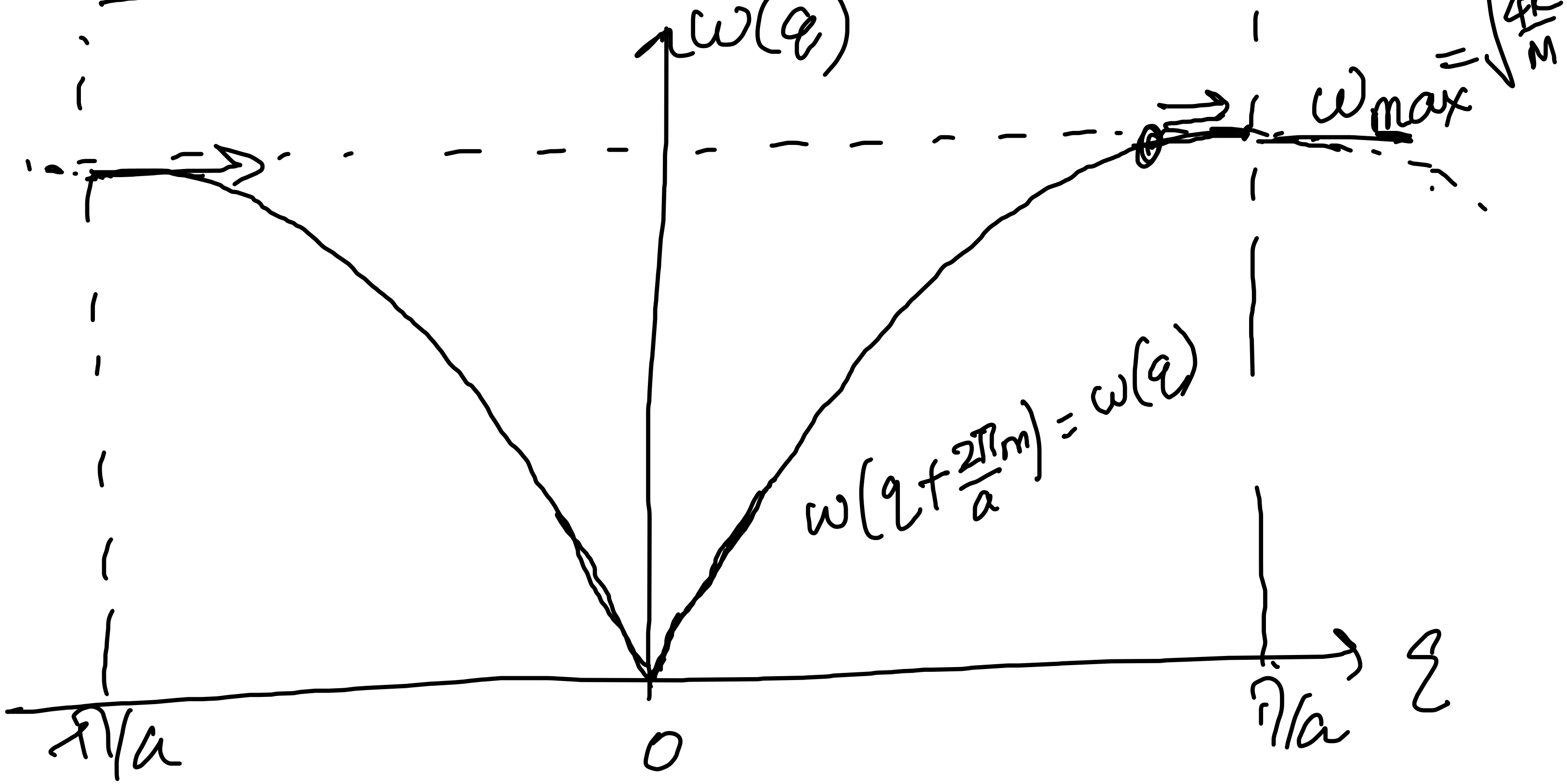
$$u_{n+N}(t) = u_n(t) \quad (\because \text{PBC})$$

$$\Rightarrow \quad q_j = \frac{2\pi j}{Na}, \quad j \in \mathbb{Z}$$

$j = 0, 1, 2, \cdots, N-1$

$$\text{F.B.Z.} \Leftarrow \boxed{-\pi/a \le q < \pi/a} \quad (N \to \infty)$$

$$\boxed{\omega(q) = \sqrt{\frac{4K}{M}}\left|\sin\left(\frac{qa}{2}\right)\right|}$$



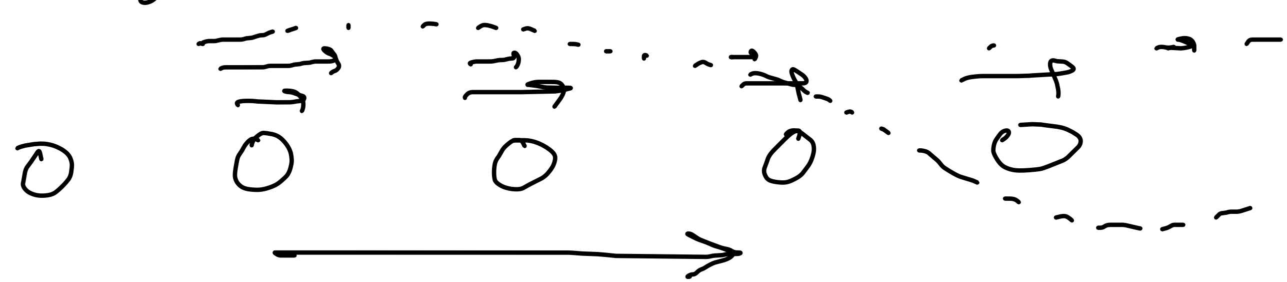
$$\omega(q \to 0) \simeq \omega_{max}\left(\frac{qa}{2}\right)$$

$$\equiv c_s q$$

$$c_s = \frac{\omega_{max} a}{2} \longrightarrow$$ speed of sound in the lattice

$$\omega = c_s q \implies \nu\lambda = c_s$$

@ $k=0$



$$C_g = \frac{d\omega}{dq} = \frac{C_s \cos\left(\frac{qa}{2}\right) \operatorname{sgn}(q)}{}$$

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

$$\omega_{max} = \sqrt{\frac{4K}{M}} \sim 10^{14} \text{ rad/s}$$

$$C_s = a\sqrt{\frac{K}{M}} \sim 10^{3} - 10^{4} \text{ m/s}$$

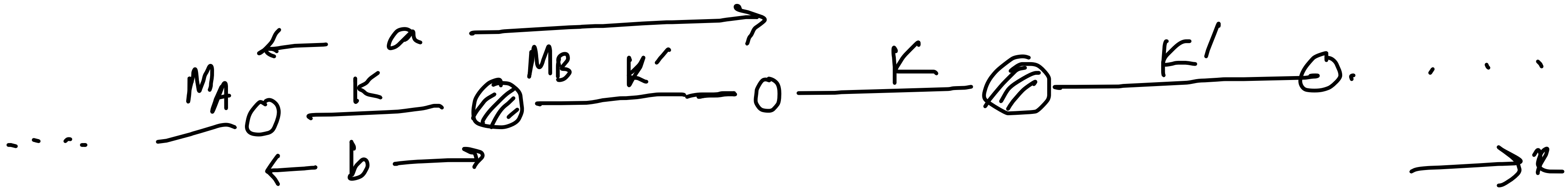
$C_g \to 0$ at zone boundaries $k = \pm \pi/a$

@ $k = \pi/a$ $\quad \lambda = 2a$ Bragg reflection

As many modes as atom in the unit cell. (reminiscent of bands)

→ Acoustic Mode

Diatomic lattice in 1-D



Let displacements of A → u

B → v

$$u_n(t) = U \exp[i(nqa - \omega t)]$$

$$v_n(t) = V \exp[i(nqa - \omega t)]$$

$$M_A \ddot{u}_n(t) = K(v_n(t) - u_n(t)) - K'(u_n(t) - v_{n-1}(t))$$

$$M_B \ddot{v}_n(t) = K'(u_{n+1}(t) - v_n(t)) - K(v_n(t) - u_n(t))$$

$$\Delta \begin{bmatrix} U \\ V \end{bmatrix} = \omega^2 \underline{\underline{\mathbb{M}}} \begin{bmatrix} U \\ V \end{bmatrix} \ell$$

$$\Delta = \begin{bmatrix} K+K' & -K-K'\eta^* \\ -K-K'\eta & K+K' \end{bmatrix}$$

Force constant matrix

mass matrix $\mathbb{M} = \begin{bmatrix} M_A & 0 \\ 0 & M_B \end{bmatrix}$ $\quad \eta = e^{iqa}$

$$-\pi/a \leq q < \pi/a$$

premultiplication by $\mathbb{M}^{-1/2}$ knowing that $\mathbb{M}^{1/2}\,\mathbb{M}^{-1/2} = \hat{\mathbb{1}}$

$$\begin{bmatrix} U' \\ V' \end{bmatrix} \equiv \mathbb{M}^{1/2} \begin{bmatrix} U \\ V \end{bmatrix}$$

$$\boxed{\mathbb{M}' \begin{bmatrix} U' \\ V' \end{bmatrix} = \omega^2 \begin{bmatrix} U' \\ V' \end{bmatrix}}$$

$$\mathbb{M}' = \mathbb{M}^{-1/2}\, \underline{\Delta}\, \mathbb{M}^{1/2}$$

Dynamical matrix

$$\mathbb{M}' = \begin{pmatrix} A + B & C - iD \\ C + iD & A - B \end{pmatrix}$$

$$A = \tfrac{1}{2}\left(K + K'\right)\left(\frac{1}{M_A} + \frac{1}{M_B}\right)$$

$$B = \tfrac{1}{2}\left(K + K'\right)\left(\frac{1}{M_A} - \frac{1}{M_B}\right)$$

$$C = -\frac{1}{\sqrt{M_A M_B}}\left(K + K'\cos(qa)\right)$$

$$D = -K'/\sqrt{M_A M_B} \times \sin(qa)$$

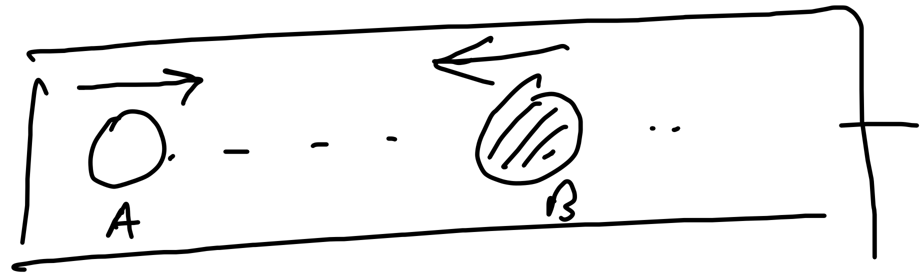
Eigenvalues: $\omega^2_{\pm} = A \pm \sqrt{B^2+C^2+D^2}$

The eigenvectors at $q=0$ correspond to

In general: $$\frac{V'}{U'} = \frac{C+iD}{\omega^2 - A + B}$$

at $q=0$: $$\left.\frac{V}{U}\right|_{+} = -\frac{M_A}{M_B} \;;\; \left.\frac{V}{U}\right|_{-} = 1$$

+)



Optic Mode.

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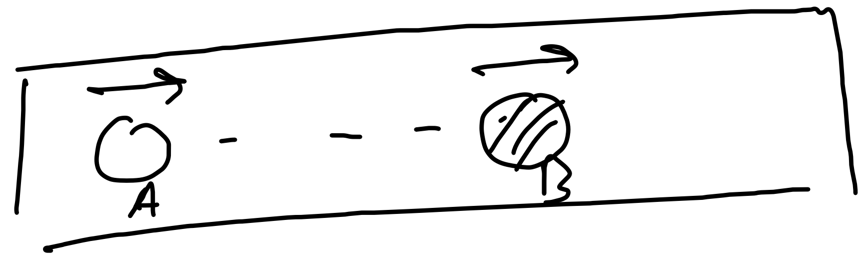
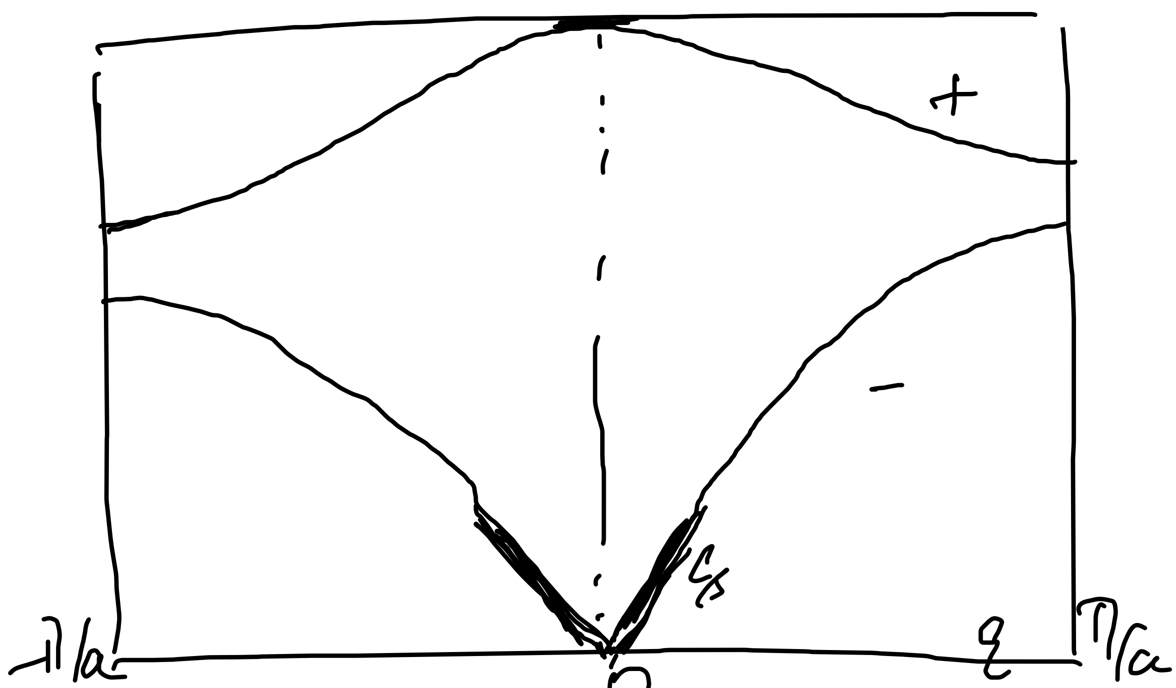
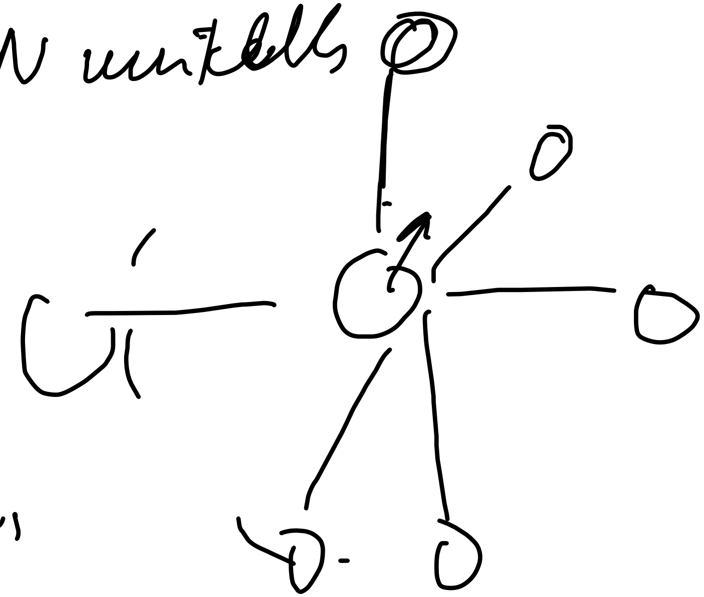


Acoustic mode



General Method for obtaining phonon dispersion

Consider a crystal of N unit cells each of s atoms in the basis



$\{\vec{R}_l\}$ $l = 1, N$

$\{\vec{w}_j\}_{j=1,s} \rightarrow$ position of the basis atoms in the cell

$$\boxed{M_j \ddot{\vec{u}}_{l,j} = -\frac{\partial \mathcal{E}}{\partial \vec{u}_{l,j}}}$$

$\mathcal{E} \rightarrow$ lattice energy

$$\hat{\mathcal{H}} = T_{ion} + V_{ion\text{-}ion} + H_e$$

$$H_e = T_e + V_{ion\text{-}e} + V_{ee}$$

$\hat{H}_e \Psi_n = E_n \Psi_n$ at fixed nuclear position $\{\vec{X}_{l\,j}\}$

$E_n \equiv E_n(\{\vec{X}_{l,j}\})$ $\qquad \vec{X}_{l,j}(t) = \vec{R}_l + \vec{W}_j(t)$

↳ potential energy surface

Born-Oppenheimer Approximation

$$\mathcal{H} = T_{ion} + \underbrace{V_{ion\text{-}ion} + E_0(\{\vec{X}_{l,j}\})}_{\mathcal{E}(\{\vec{X}_{l,j}\})}$$

equilb. lattice energy

$$\mathcal{E}\left(\{\vec{x}_{l,j}\}\right) = \mathcal{E}_0 + \sum_{l,l'}\sum_{j,j'}\sum_{\alpha,\beta}\Big(\Big)$$

$$\vec{x}_0$$

$$\left(\frac{\partial^2 \mathcal{E}}{\partial u^{\alpha}_{lj}\,\partial u^{\beta}_{l'j'}}\right)_0 u^{\alpha}_{lj}\, u^{\beta}_{l'j'} + O(u)^3$$

$$\frac{\partial \mathcal{E}}{\partial u_{lj}} = \sum_{l',j',\beta} \underbrace{\left(\frac{\partial^2 \mathcal{E}}{\partial u^{\alpha}_{lj}\,\partial u^{\beta}_{l'j'}}\right)_0}_{K^{\alpha\beta}_{lj,l'j'}} u^{\beta}_{l'j'}$$

$$M_j \ddot{u}^{\alpha}_{\ell j} = -\sum_{\ell', j', \beta} \left(K^{\alpha\beta}_{\ell j, \ell' j'} \right) u^{\beta}_{\ell' j'}$$

Force constant matrix.

$$\mathbb{M} \ddot{\vec{u}} = - \mathbb{K} \vec{u}$$

$3s \times 3s$

$$-\omega^2 \mathbb{M} \vec{U}(\vec{q}) = - \mathbb{K} \vec{U}(\vec{q})$$

F.T. amplitude vector

$3s \times 1$

$U^{\alpha}_j(\vec{q}) \equiv$ Fourier amplitude of the wave at $\vec{q}$ on the j^{th} atom's α^{th} coordinate

$j = 1, s$, $\alpha = 1, 3$

$$\boxed{\underline{\underline{M}}'(\vec{q})\,\vec{U}'(\vec{q}) = \omega^2(\vec{q})\,\vec{U}'(\vec{q})}$$

Dynamical matrix.

$$\vec{q} = q_1\vec{b}_1 + q_2\vec{b}_2 + q_3\vec{b}_3$$

$$= \underline{\underline{M}}^{-1/2}\,\mathbb{K}\,\underline{\underline{M}}^{1/2} \qquad -\frac{|\vec{b}_i|}{2} \le q_i < \frac{|\vec{b}_i|}{2} \qquad \vec{b}_i \rightarrow \text{primitive reciprocal lattice vectors}$$

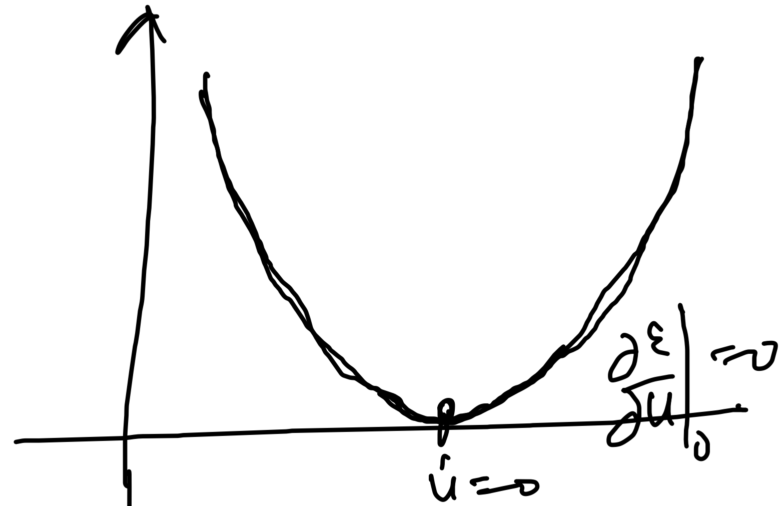
$\underline{\underline{M}}' \rightarrow 3s \times 3s \Rightarrow$ we have $3s$ eigenvalues & eigenvectors $\Rightarrow 3s$ modes per $\vec{q}$.

$$\frac{\partial^2 \varepsilon}{\partial u^2}\Big|_0 > 0$$

$\varepsilon(u)$

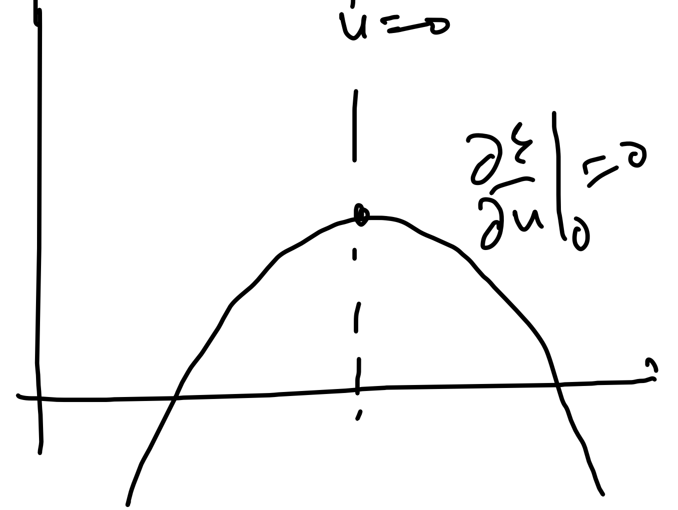
$\omega^2 > 0$

$\Rightarrow \omega$ is real



$$\frac{\partial^2 \varepsilon}{\partial u^2}\Big|_0 < 0 \Rightarrow \omega^2 < 0$$

$\Rightarrow \omega$ is purely imaginary



General features in 3d dispersion

→ If there are s atoms in the unit cell then there will be 3 acoustic modes & $3s-3$ optic modes

→ Polarization of each mode determines the direction of displacement of each atom

→ If polarization $\parallel \vec{q}$ → Longitudinal mode
$\qquad$ " $\perp \vec{q}$ → Transverse mode

Longitudinal Acoustic (LA)
Transverse " (TA)

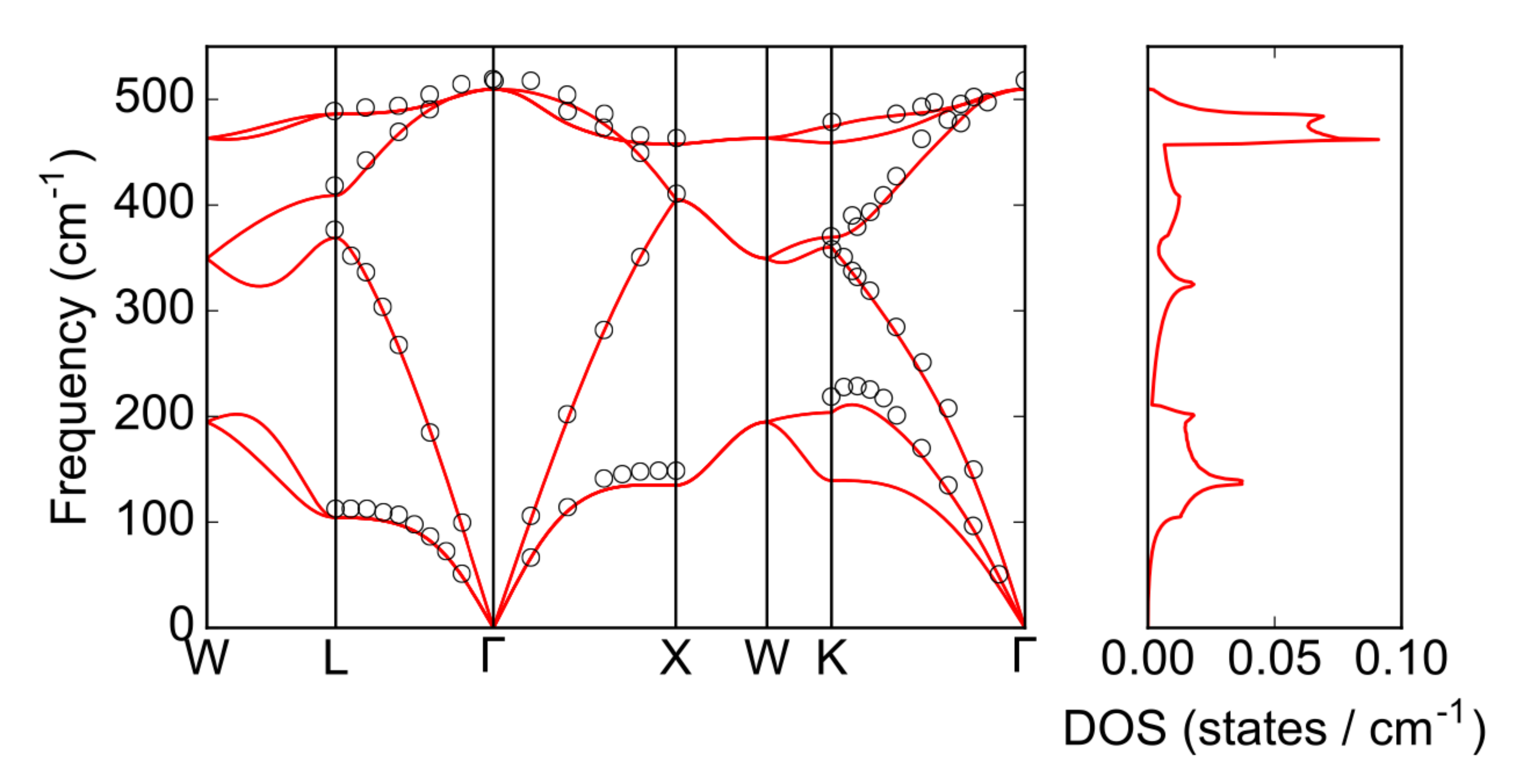
Longitudinal Optic (LO)
Transverse Optic (TO)

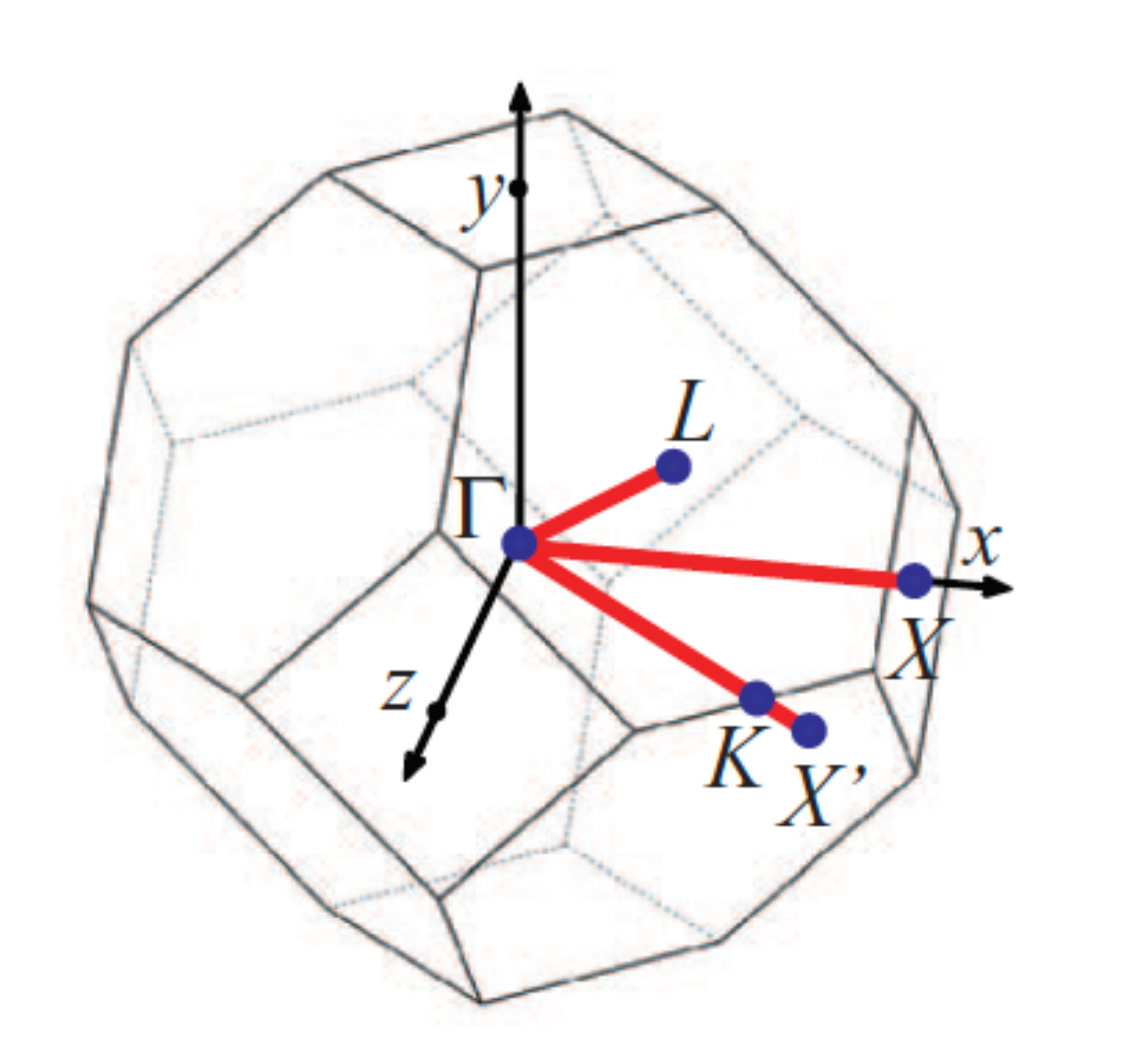
→ In general, L or T only along some high symmetry direction. Along other directions they are usually mixed.

→ LO, TO in general diff speeds in given
LA, TA directions.

Phonon Dispersion

E.g. Silicon

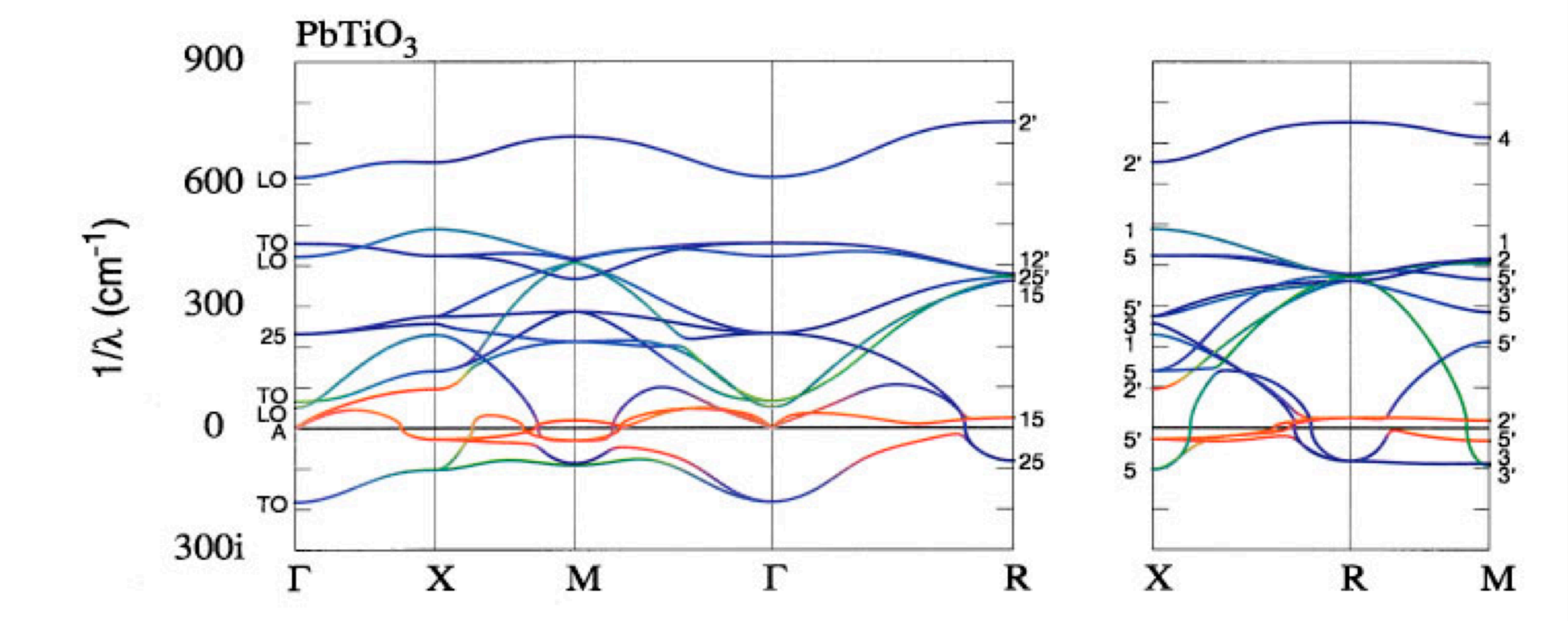




Source: arXiv:1911.05826v1, AIP Advances 1, 041701 (2011)

Phonon Dispersion

E.g. $PbTiO_3$ - unstable modes



Source: Phys. Rev. B **60**, 836 (1999)

Phonons and their thermal properties

Quantization of lattice waves

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$$

$\omega_n(\vec{q})$

Many atom system: $\hat{H} = \sum_n \left(\frac{\hat{p}_n^2 + \hat{q}_n^2 \omega_n^2}{2} \right)$

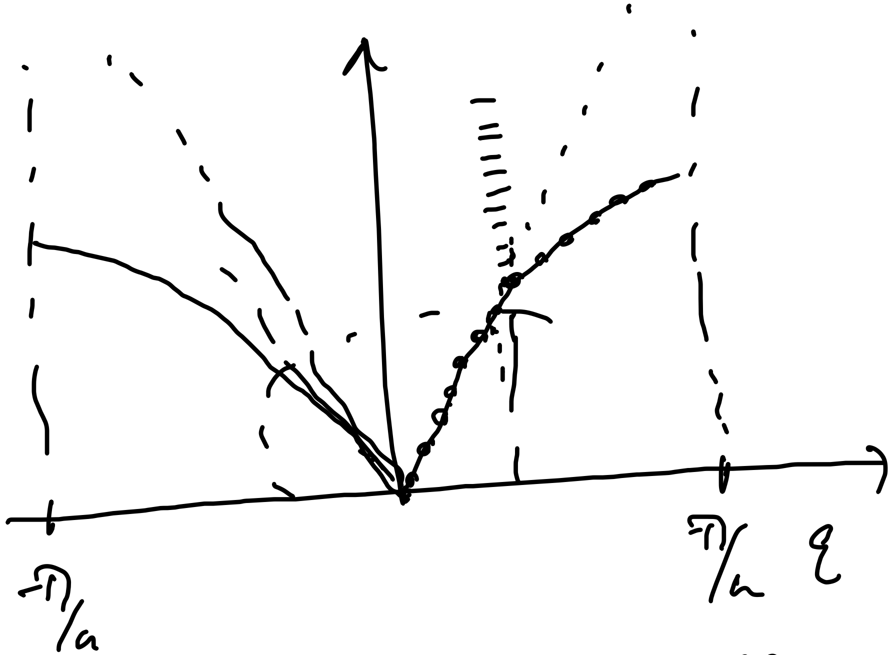
$$E_\nu(n, \vec{q}) = \left(\nu + \frac{1}{2}\right) \hbar \omega_n(\vec{q})$$

$\nu = 0, 1, 2, 3, \ldots$

phonons.

$\vec{p} = \hbar \vec{q}$

$\omega_n(\vec{q})$, $\hat{e}$



$\nu = 0$

$$E_2(n, \vec{q}) = \frac{1}{2}\hbar\omega_n(\vec{q})$$

Zero Point Energy

$\nu = 2$

$$\langle E(T) \rangle = \frac{\sum_{\nu=0}^{\infty} (\nu + \frac{1}{2})\hbar\omega \, e^{-\beta(\nu+\frac{1}{2})\hbar\omega}}{\sum_{\nu=0}^{\infty} e^{-\beta\hbar\omega(\nu+\frac{1}{2})}}$$

$$= \left(\langle n \rangle + \frac{1}{2} \right)\hbar\omega$$

$$\langle n(\omega,T)\rangle = \frac{1}{e^{\beta\hbar\omega}-1} \longrightarrow$$ Bose-Einstein distribution function

Classical $\langle E(T)\rangle = k_B T$. $\beta = 1/k_B T$

At high temperature where $\beta\hbar\omega \ll 1$

$$\langle n(\omega,T)\rangle \simeq \frac{k_B T}{\hbar\omega}$$

$$\langle E(T)\rangle = \left(\langle n(\omega,T)\rangle + \tfrac{1}{2}\right)\hbar\omega$$

$$\simeq k_B T/\hbar\omega \times \hbar\omega = k_B T$$

at low temperatures $(T \to 0)$

$$\langle n(\omega, T) \rangle \approx e^{-\beta \hbar \omega}$$

$$\langle E(T) \rangle \approx \left(\underline{\underline{e^{-\beta \hbar \omega}}} + 1/2 \right) \hbar \omega$$

$\to \frac{\hbar \omega}{2}$ = zero point energy

For a lattice of oscillators (monoatomic)

$$U(T) = \langle E(T) \rangle = V \int_{B.Z.} \frac{d^3q}{(2\pi)^3} \left\{ \left(\langle \eta(\omega_n, T) \rangle + \frac{1}{2} \right) \hbar \omega_n(\vec{q}) \right\}$$

$$= \int_0^\infty d\omega \, g_{ph}(\omega) \left(\langle \eta(\omega, T) \rangle + \frac{1}{2} \right) \hbar\omega$$

$$U(T) - \underset{\substack{\uparrow \\ \text{ZPE}}}{U_0} = \int_0^\infty d\omega \, g_{ph}(\omega) \left(\frac{1}{e^{\beta\hbar\omega} - 1} \right)$$

$g_{ph}(\omega) = 0$ beyond ω_{max}

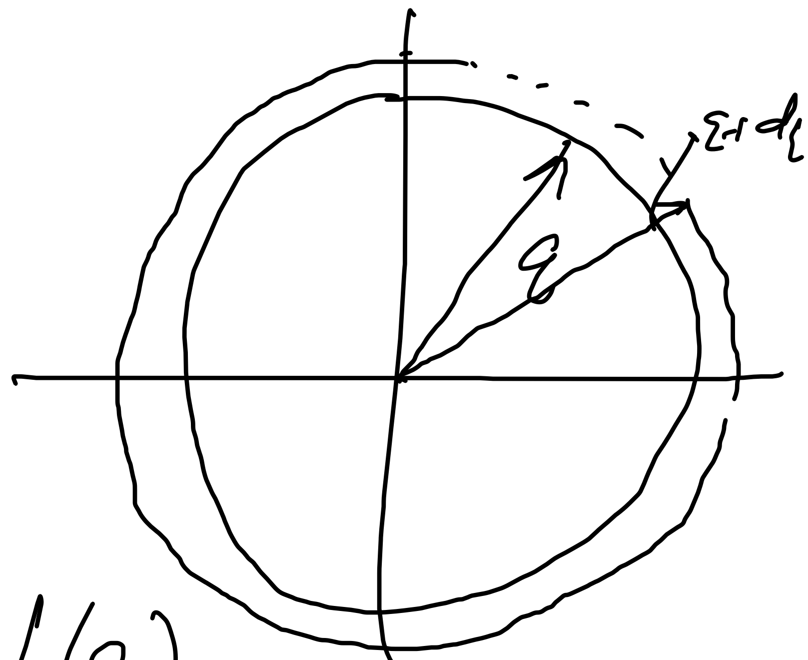
Let's assume that $\omega(\vec{q}) = c_s q$

vol. of a $\vec{q}$ pt. is $\frac{(2\pi)^3}{V}$

No. of q pts in a sphere of radius q

$$= \frac{\frac{4}{3}\pi q^3}{(2\pi)^3/V}$$

$$= \frac{V}{6\pi^2} q^3 = \mathcal{N}(q)$$



$$N(q+dq) = \frac{V}{6\pi^2}(q+dq)^3$$

$$dN = \frac{V}{6\pi^2}\left\{(q+dq)^3 - q^3\right\}$$

$$\simeq \frac{V}{6\pi^2} \times (3q^2 dq) = \frac{V}{2\pi^2} q^2 dq$$

$$= \frac{V}{2\pi^2} \frac{\omega^2}{c_s^2} \times \frac{d\omega}{c_s} = \frac{V}{2\pi^2}\frac{\omega^2}{c_s^3} d\omega$$

$$\boxed{g_m(\omega) = \frac{dN}{d\omega} = \frac{V}{2\pi^2}\frac{\omega^2}{c_s^3}}$$

$$U(T) - U_0 = \int_0^{\omega_{max} = \omega_D} d\omega \, g_{ph}(\omega) \left(\frac{1}{e^{\beta\hbar\omega} - 1} \right)$$

$$= \int_0^{\Theta_D/T} d\omega \frac{V}{2\pi^2} \frac{\omega^2}{c_s^3} \times \frac{1}{e^{\beta\hbar\omega} - 1}$$

Debye wave vector

$$k_D = \frac{\omega_D}{c_s}$$

$$= \frac{3V}{2\pi^2 \beta^4 \hbar^3 c_s^3} \boxed{\int_0^{\Theta_D/T} dx \frac{x^3}{e^x - 1}}$$

$$\Theta_D = \frac{\hbar c_s k_D}{k_B} = \frac{\hbar \omega_D}{k_B}$$

ω_D = Max. freq. upto which phonons occupied

@ $T \gg \Theta_D$: $\displaystyle\int_0^{\Theta_D/T} dx \, \frac{x^3}{e^x - 1} \simeq \int_0^{\Theta_D/T} dx \; x^2$

$$= 1/3 \left(\frac{\Theta_D}{T}\right)^3$$

$$U(T) - U_0 = V D T^4 \times \left(\frac{\Theta_D}{T}\right)^3 \sim T$$

$$= 3 N k_B T$$

$\Rightarrow$ molar specific $c_V = \left(\frac{\partial U}{\partial T}\right)_V = 3 n R$

$\downarrow$

Dulong-Petit law.

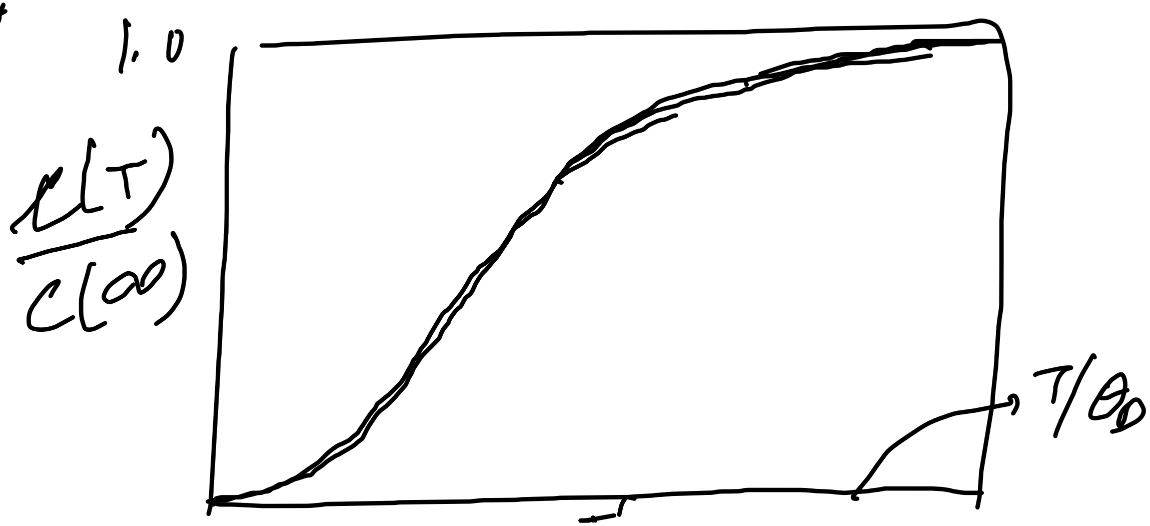
@ $T \ll \Theta_D$:

$$\int_0^{\Theta_D/T \to \infty} dx \, \frac{x^3}{e^x - 1} \approx \frac{\pi^4}{15}$$

$$\therefore \quad U(T) - U_0 \simeq \frac{A}{4} V T^4$$

$$\Rightarrow \quad c_V = \frac{1}{V}\left(\frac{\partial U}{\partial T}\right)_V = \underline{\underline{A T^3}}$$

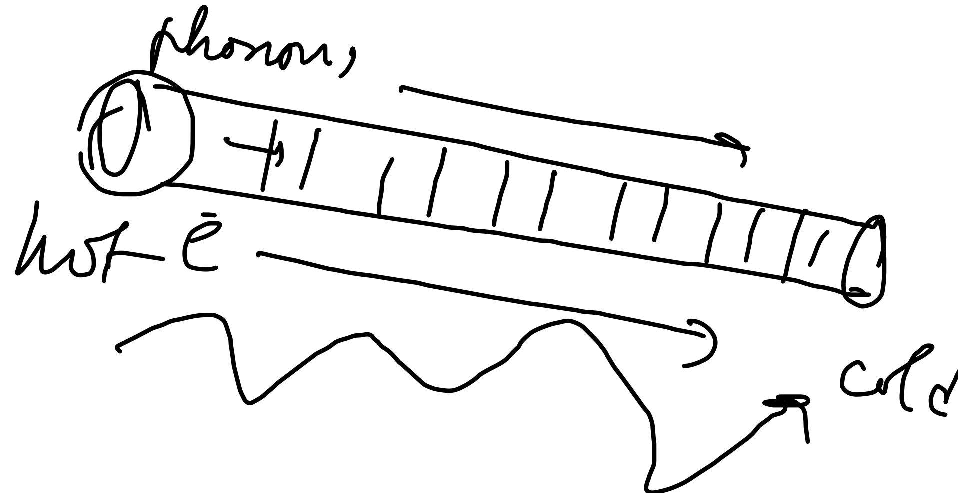
vol. specific heat



Thermal conductivity by the lattice

phonon gas

$\tau \rightarrow$ relaxation or collision time



$$\vec{J}_Q = -\underbrace{K}_{\text{Thermal conductivity } W/mK} \vec{\nabla} T$$

$$K = \underline{K_L} + K_{e/h}$$

Assuming only phonon mediated mechanism for conducting heat we can show that

$$\vec{J}_{\varphi} = -\frac{1}{3} c_s^2 \tau \left(\frac{du}{dT}\right) \nabla T$$

average / isotropic speed of sound in the material

$$= -\frac{1}{3} c_s l_{ph} \left(\frac{du}{dT}\right) \nabla T$$

mean free path of phonon collision,

$$\therefore \boxed{K_L = \frac{1}{3} c_s l_{ph}(T) c_v(T)}$$

Temp. dependence of K_L comes from c_v & l_{ph}.

Lattice Thermal Conductivity

TABLE 5.4 Thermal Conductivities

Material	κ (W/m·K)	Material	κ (W/m·K)
Ag	429	AlN	82
Al	237	Ge	64
Au	317	Si	124
Cu	401	GaAs	56
Fe	80	Fused silica glass	2.0
Mg	156	Pyrex	1.1
Mo	138	α-Alumina	36
Ni	91	Silica	1.4
Pb	35	BeO	210
Pt	72	MgO	36
W	174	β-SiC (at 400 K)	121
Steel	45–65	TiO_2	
Quasicrystal (Al–Cu–Fe)	1.8	$\parallel c$ axis at 273 K	13
NaCl	6.4	$\perp c$ axis at 273 K	9
Diamond	1000	α-SiO_2	
Graphite		$\parallel c$ axis	12
$\perp c$ axis	2000	$\perp c$ axis	6.8
$\parallel c$ axis	5.7		

Source: Data largely from, D. R. Lide, ed., *CRC Handbook of Chemistry and Physics*, 78th ed., CRC Press, Boca Raton, Fla. 1997.

$$\kappa = \kappa_L + \kappa_e$$

$$\kappa_L = \frac{1}{3} c_s l_{ph}(T) C(T)$$

Source: Gersten and Smith