Lattice Waves

Thus far, static lattice model.

In reality, atoms vibrate even at $T = 0$ because of zero-point vibration.

Monatomic Crystals

Basis = 1 atom.   Lattice: $\mathbf{R} = \sum_i n_i \mathbf{a}_i$ $i = 1, 2, 3$

$\mathbf{r}(\mathbf{R}) = \mathbf{R} + \mathbf{u}(\mathbf{R}; t)$ Actual atomic position = lattice position + vibration

$\langle \mathbf{r} \rangle_{ave} = \mathbf{R}$ $\langle \mathbf{u} \rangle = 0$

$\dot{\mathbf{r}}$ = ionic velocity ($\leq 10^5$ cm/sec, typically) $\ll$ electronic velocities ($\sim 10^8$ cm/sec)

Adiabatic approximation: system always in the electronic ground state; i.e., the electons follow the slow ionic motion. Good at moderate temperatures.

Potential energy $= U(\{\mathbf{r}(\mathbf{R})\})$; no need to specify the electronic quantum numbers.

$$U = U(\{\mathbf{r}(\mathbf{R})\}) = U(\{\mathbf{R}\}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \nabla_{\mathbf{R}} U(\{\mathbf{R}\}) + \frac{1}{2} \left(\sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \nabla_{\mathbf{R}} \right)^2 U(\{\mathbf{R}\}) + \dots$$

1$^{\text{st}}$ term = constant; set to 0.

2$^{\text{nd}}$ term = 0 because U is a minimum at $\mathbf{r} = \mathbf{R}$ (equilibrium position).

Harmonic approximation (keeping 2$^{\text{nd}}$ order terms only):

$$U = \frac{1}{2} \left(\sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \nabla_{\mathbf{R}} \right)^2 U(\{\mathbf{R}\})$$

Terms $O(u^3), O(u^4) \Rightarrow$ **anharmonic effects** or **phonon-phonon interactions** (later).

$$U = \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'\mu\nu} u_\mu(\mathbf{R}) u_\nu(\mathbf{R}') \ \frac{\partial^2 U}{\partial R_\mu \partial R_\nu'} \equiv \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'\mu\nu} u_\mu(\mathbf{R}) \, u_\nu(\mathbf{R}') \, D_{\mu\nu}(\mathbf{R}, \mathbf{R}')$$

$$
\begin{aligned}
D_{\mu\nu}(\mathbf{R}, \mathbf{R}') &= D_{\mu\nu}(\mathbf{R} - \mathbf{R}') && \text{translational symmetry (} U \text{ and } D \text{ are periodic)} \\
&= D_{\mu\nu}(\mathbf{R}' - \mathbf{R}) && \text{inversion symmetry} \\
&= D_{\nu\mu}(\mathbf{R} - \mathbf{R}') && \text{because } \frac{\partial^2 U}{\partial R_\mu \partial R_\nu'} = \frac{\partial^2 U}{\partial R_\nu' \partial R_\mu} \ \text{\& inversion symmetry}
\end{aligned}
$$

D = 3x3 symmetric tensor (for one atom per unit cell)

$$\boxed{U = \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'\mu\nu} u_\mu(\mathbf{R}) \, D_{\mu\nu}(\mathbf{R} - \mathbf{R}') u_\nu(\mathbf{R}') \equiv \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \mathbf{D}(\mathbf{R} - \mathbf{R}') \cdot \mathbf{u}(\mathbf{R}')}$$

Equations of motion: $M\ddot{u}_\mu(\mathbf{R}) = F_\mu(\mathbf{R}) = -\dfrac{\partial U}{\partial u_\mu(\mathbf{R})} = -\sum_{\mathbf{R}'\nu} D_{\mu\nu}(\mathbf{R} - \mathbf{R}') u_\nu(\mathbf{R}')$

$$M\ddot{\mathbf{u}}(\mathbf{R}) = \mathbf{F}(\mathbf{R}) = -\sum_{\mathbf{R'}} \mathbf{D}(\mathbf{R} - \mathbf{R'}) \cdot \mathbf{u}(\mathbf{R'})$$

If $\mathbf{u}(\mathbf{R})$ = same for all $\mathbf{R}$ (uniform translation), $\mathbf{F}(\mathbf{R}) = 0$.

$$\sum_{\mathbf{R}} \mathbf{D}(\mathbf{R} - \mathbf{R'}) = 0. \qquad \text{Shifting origin} \Rightarrow \boxed{\sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) = 0}$$

N atoms. 3*N* coupled equations of motion. Normal-mode coordinate transformation to decouple the motions. First step – apply Bloch theorem (lattice Fourier transform).

Bloch theorem for electrons: $\psi \propto e^{i\mathbf{k}\cdot\mathbf{r}} w_{\mathbf{k}}(\mathbf{r})$

For lattice vibrations, $\mathbf{r} \to \mathbf{R}$, $w_{\mathbf{k}}(\mathbf{R}) = w_{\mathbf{k}}(\mathbf{R'})$ = constant. So, $u \propto e^{i\mathbf{k}\cdot\mathbf{R}}$.

Solution: $\mathbf{u}(\mathbf{R}) \propto \mathbf{e}\, e^{i(\mathbf{k}\cdot\mathbf{R} - \omega t)}$; $\mathbf{k}$ in 1$^{\text{st}}$ BZ; $\mathbf{e}$ = unit **polarization vector**.

$$-M\omega^2\, \mathbf{e}\, e^{i(\mathbf{k}\cdot\mathbf{R} - \omega t)} = -\sum_{\mathbf{R'}} \mathbf{D}(\mathbf{R} - \mathbf{R'}) \cdot \mathbf{e}\, e^{i(\mathbf{k}\cdot\mathbf{R'} - \omega t)} \qquad -M\omega^2\, \mathbf{e} = -\left(\sum_{R'} \mathbf{D}(\mathbf{R} - \mathbf{R'})\, e^{-i\mathbf{k}\cdot(\mathbf{R} - \mathbf{R'})} \right) \cdot \mathbf{e}$$

Definition: **dynamic matrix**: $\boxed{\mathbf{D}(\mathbf{k}) = \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) e^{-i\mathbf{k}\cdot\mathbf{R}}}$ 3x3 symmetric tensor

$$\boxed{\mathbf{D}(\mathbf{k}) \cdot \mathbf{e} = M\omega^2\, \mathbf{e}} \qquad\qquad \boxed{\sum_{\nu} D_{\mu\nu}(\mathbf{k}) e_{\nu} = M\omega^2 e_{\mu}}$$

Eigenvalue problem: $\mathbf{e}(\mathbf{k})$ = eigenvector, $M\omega^2(\mathbf{k})$ = eigenvalue; 3 modes (one atom cell).

$$\mathbf{D}(\mathbf{k}) = \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) e^{-i\mathbf{k}\cdot\mathbf{R}} = \frac{1}{2} \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) \left[e^{i\mathbf{k}\cdot\mathbf{R}} + e^{-i\mathbf{k}\cdot\mathbf{R}} - 2 \right] \text{ because } \mathbf{D}(\mathbf{R}) = \mathbf{D}(-\mathbf{R}) \text{ & } \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) = 0.$$

$$\mathbf{D}(\mathbf{k}) = -2 \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) \sin^2\left(\frac{1}{2} \mathbf{k} \cdot \mathbf{R} \right) = \text{real}$$

D is real and symmetric; it has three real eigenvalues, $M\omega_s^2(\mathbf{k})$, for each $\mathbf{k}$, where *s* = 1, 2, and 3 (**branch index**).

The eigenvalues $M\omega_s^2(\mathbf{k})$ are positive, because *U* is a minimum. So, $\omega_s(\mathbf{k})$ = real. Keep positive root only. With *s* included, $\mathbf{D}(\mathbf{k}) \cdot \mathbf{e}_s(\mathbf{k}) = M\omega_s^2(\mathbf{k}) \mathbf{e}_s(\mathbf{k})$.

D is real and symmetric; so $\mathbf{e}_s(\mathbf{k}) \cdot \mathbf{e}_{s'}(\mathbf{k}) = \delta_{s,s'}$ (orthonormal set).

For each $\mathbf{k}$, there are 3 normal modes: $\omega_s(\mathbf{k})$ & $\mathbf{e}_s(\mathbf{k})$

N distinct $\mathbf{k}$ in 1$^{\text{st}}$ BZ $\Rightarrow$ 3*N* normal modes for the solid = number of degrees of freedom of system

$\omega_s(\mathbf{k})$ = **phonon dispersion relation**
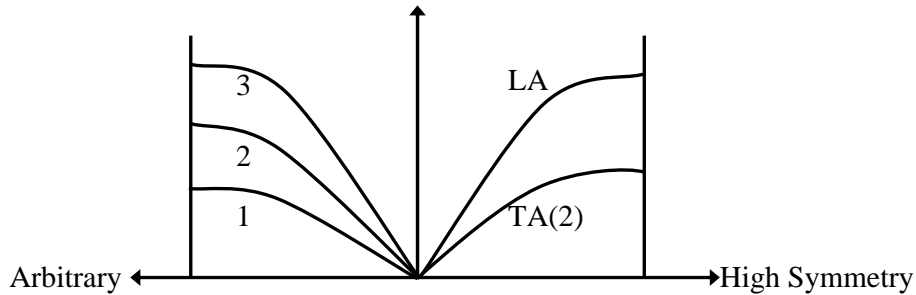
For $k \to 0$ (long wavelength limit),

$$\mathbf{D}(\mathbf{k}) = -2 \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) \sin^2\left(\frac{1}{2}\mathbf{k}\cdot\mathbf{R}\right) \rightarrow -\frac{k^2}{2}\sum_{\mathbf{R}}\mathbf{D}(\mathbf{R})\left(\hat{\mathbf{k}}\cdot\mathbf{R}\right)^2 \propto k^2$$

With $\mathbf{D}(\mathbf{k})\cdot\mathbf{e}_s(\mathbf{k}) = M\omega_s^2(\mathbf{k})\mathbf{e}_s(\mathbf{k})$, $\omega_s^2(\mathbf{k}) \propto k^2$.

$\omega \propto k \Rightarrow$ linear dispersion near zone center.

Long wavelength lattice vibrations correspond to **sound waves**.

Sound waves: λ ~ order of cm, k ~ 10^{-7} Å^{-1} << BZ size

All three branches are **acoustic branches**, i.e., $\omega \propto k$.

For $\mathbf{k}$ along a high symmetry direction, we typically have:

$\mathbf{e}_{1,2} \perp \mathbf{k}$: **transverse acoustic modes** $\omega_{TA}(\mathbf{k})$

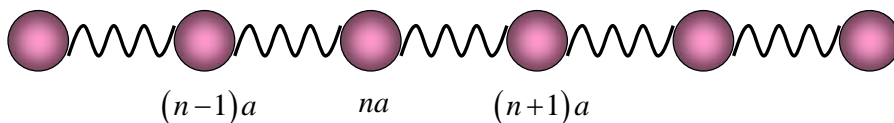$\mathbf{e}_3 \| \mathbf{k}$: **longitudinal acoustic mode** $\omega_{LA}(\mathbf{k})$

Typically, $\omega_{LA} > \omega_{TA}$ (harder to compress than to bend a spring).

For $\mathbf{k}$ along an arbitrary direction, the modes are generally mixed. One might have quasi-LA & quasi-TA modes.

3D $\rightarrow$1D, 3x3 tensor **D** becomes 1x1. Just one branch (LA).

2D: 2 branches, one LA and one TA along high symmetry directions.

1D Model (one atom per unit cell)

$(n-1)a$ na $(n+1)a$

= atom or atomic plane; connected by springs of force constant *K*

Harmonic approximation: $U = \dfrac{1}{2} K \sum_n \left(u(na) - u\big((n+1)a\big) \right)^2$

$M\ddot{u}(na) = -\dfrac{\partial U}{\partial u(na)} = -K\Big[2u(na) - u\big((n+1)\big)a) - u\big((n-1)a\big) \Big]$

Discrete plane wave solutions (Bloch form): $u(na) \propto e^{i(kR - \omega t)} = e^{i(kna - \omega t)}$, where $R = na$.

$-M\omega^2 = -K\left[2 - e^{-ika} - e^{ika} \right]$ Take positive root only (frequency is always +).

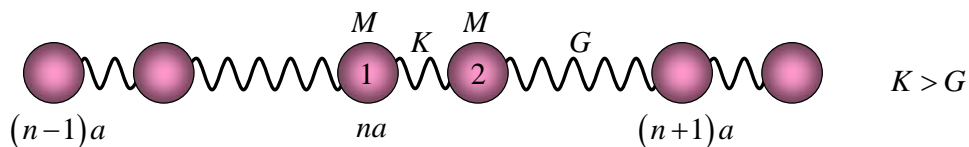**Dispersion relation**: $\omega(k) = 2\sqrt{\dfrac{K}{M}}\; \left| \sin\left(\dfrac{1}{2}ka \right) \right|$
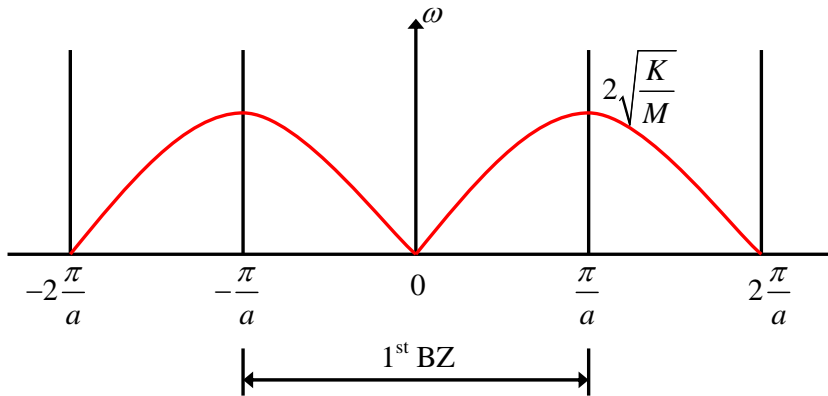
A single branch: *N* atoms, *N* modes, *N* solutions, *N* degrees of freedom.

For $ka \to 0$, $\omega \to \sqrt{\dfrac{K}{M}}\, a\, |k|$

Phase velocity $= \dfrac{\omega}{k}$ = group velocity $= \dfrac{d\omega}{dk} = a\sqrt{\dfrac{K}{M}}$ = sound velocity.

1D Model with 2 Atoms per Unit Cell

$U = \dfrac{K}{2} \sum_n \left[u_2(na) - u_1(na) \right]^2 + \dfrac{G}{2} \sum_n \left[u_1\big((n+1)a\big) - u_2(na) \right]^2$

$= \dfrac{K}{2} \sum_n \left[u_2(na) - u_1(na) \right]^2 + \dfrac{G}{2} \sum_n \left[u_1(na) - u_2\big((n-1)a\big) \right]^2$

$M\ddot{u}_1(na) = -\dfrac{\partial U}{\partial u_1(na)} = K\left[u_2(na) - u_1(na) \right] + G\left[u_2\big((n-1)a\big) - u_1(na) \right]$

$M\ddot{u}_2(na) = -\dfrac{\partial U}{\partial u_2(na)} = K\left[u_1(na) - u_2(na) \right] + G\left[u_1\big((n+1)a\big) - u_2(na) \right]$

Bloch theorem: $\quad u_1(na) = e_1\, e^{ikna - i\omega t} \qquad\qquad u_2(na) = e_2\, e^{ikna - i\omega t}$

$$\left[M\omega^2 - (K+G)\right]e_1 + \left(K + G\, e^{-ika}\right)e_2 = 0 \qquad \left(K + G\, e^{ika}\right)e_1 + \left[M\omega^2 - (K+G)\right]e_2 = 0$$

2 equations with 2 unknowns. Nontrivial solution $\Rightarrow$ determinant = 0

$$\omega^2 = \frac{K+G}{M} \pm \frac{1}{M}\sqrt{K^2 + G^2 + 2KG\cos ka} \qquad\qquad \omega^2 \geq 0 \qquad \text{Choose } \omega \geq 0.$$

$$\frac{e_2}{e_1} = \mp\, \frac{K + G\, e^{ika}}{\left|K + G\, e^{ika}\right|} \qquad \text{relative amplitudes.}$$
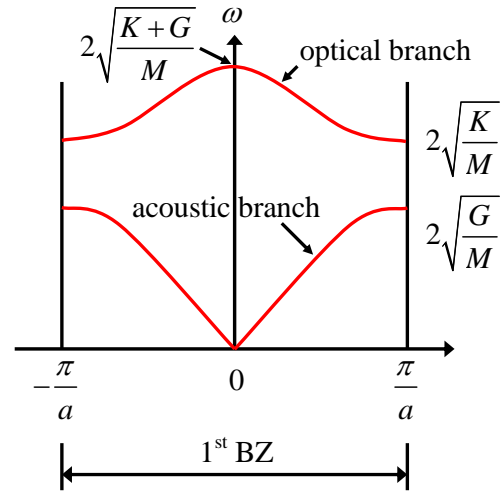
2 solutions (2 different frequencies) for each k.

Total $2N$ normal modes corresponding to $2N$ degrees of freedom.

Acoustic branch (lower branch):

$ka \to 0$, $\omega \to \sqrt{\dfrac{KG}{2M(K+G)}}\,(ka) \propto k$, sound waves.

$\dfrac{e_2}{e_1} \to 1$, the two atoms move together.

At the zone center, all atoms move togther $\Rightarrow$ uniform motion, no restoring force, frequency = 0.

Optical branch:

$ka \to 0$, $\omega \to \sqrt{\dfrac{2(K+G)}{M}}$, $\dfrac{e_2}{e_1} \to -1$, the two atoms move against each other. If the two atoms have opposite charges (ionic crystals), the oscillating dipole can couple to EM waves. The mode is "optically active" and so the name is "optical branch." EM waves (infrared) with energies matching the lattice vibrations have very smal momentum ($k \to 0$).
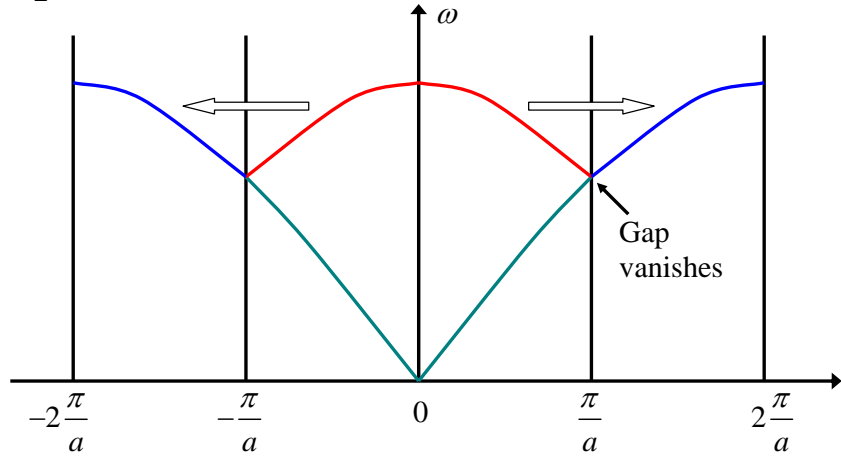
Zone center $k = 0$:

acoustic mode:

optical mode:
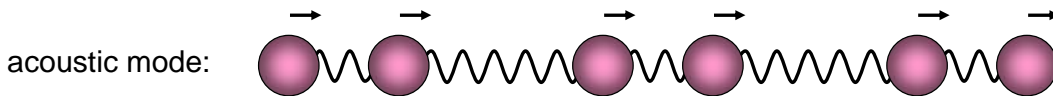
Zone boundary $k = \dfrac{\pi}{a}$, motions in neighboring unit cells are out of phase.

acoustic mode:
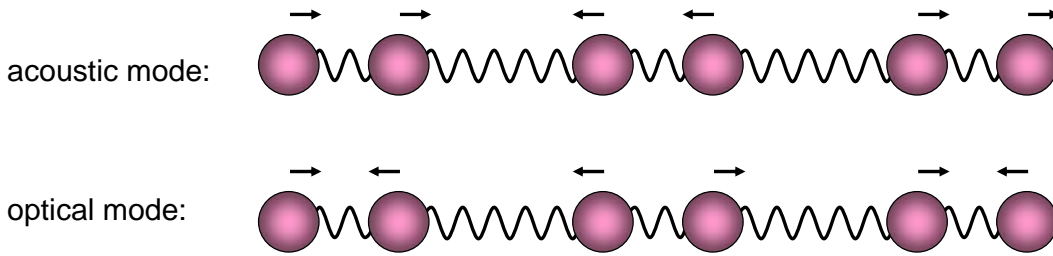
optical mode:

Limiting case: $K = G$; all atoms (same mass) are equally spaced $\Rightarrow$ one atom per unit cell with spacing $\frac{a}{2}$. Brillouin zone **folding** (**unfolding**)

ω

Gap vanishes

$-2\dfrac{\pi}{a}$ $-\dfrac{\pi}{a}$ 0 $\dfrac{\pi}{a}$ $2\dfrac{\pi}{a}$

Mode counting:

|	Basis	Branches
1D	1 atom	1 acoustic
	2 atoms	1 acoustic + 1 optical
	n atoms	1 acoustic + $(n-1)$ optical
3D	1 atom	3 acoustic
	2 atoms	3 acoustic + 3 optical
	n atoms	3 acoustic + $3(n-1)$ optical

Typical 3D crystal with 3 atoms per unit cell:

L = longitudinal; T = transverse;
A = acoustic; O = optical

Typically:

At zone center for each set, $\omega_{LO} > \omega_{TO}$ for ionic crystals; $\omega_{LO} = \omega_{TO}$ for covalent crystals

$\omega_{LA} > \omega_{TA}$ near zone center (higher longitudinal speed of sound)

ω

LO

TO (2)   LO

TO (2)

LA

TA (2)

k high symmetry ←   → k arbitrary
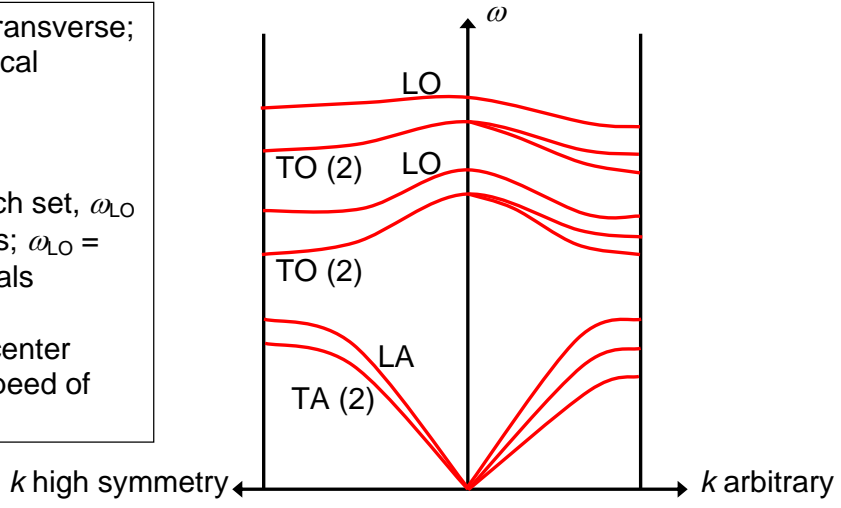
Quantization of Lattice Waves – Phonons

Each normal mode $(\mathbf{k}, s)$ corresponds to a simple harmonic oscillator (SHO) with frequency $\omega_s(\mathbf{k})$ and polarization $\mathbf{e}_s(\mathbf{k})$.

Normal mode coordinate $q_s(\mathbf{k})$ that satisfies $\ddot{q}_s(\mathbf{k}) + \omega_s^2(\mathbf{k}) q_s(\mathbf{k}) = 0$

3D Monatomic Crystal

Normal mode coordinate transformation (lattice Fourier transformation followed by diagnolizing the 3x3 dynamic matrix):

$$q_s(\mathbf{k}) = \left[\frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}} \mathbf{u}(\mathbf{R}) \right] \cdot \mathbf{e}_s(\mathbf{k}) \qquad p_s(\mathbf{k}) = \left[\frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}} \mathbf{P}(\mathbf{R}) \right] \cdot \mathbf{e}_s(\mathbf{k})$$

Inverse transform:

$$\mathbf{u}(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}s} q_s(\mathbf{k}) \mathbf{e}_s(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}} \qquad \mathbf{P}(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}s} p_s(\mathbf{k}) \mathbf{e}_s(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}}$$

Proof (that $q_s(\mathbf{k})$ is the correct choice):

$$\ddot{q}_s(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}} \ddot{\mathbf{u}}(\mathbf{R}) \cdot \mathbf{e}_s(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}} \mathbf{e}_s(\mathbf{k}) \cdot \left[-\frac{1}{M} \sum_{\mathbf{R}'} \mathbf{D}(\mathbf{R}-\mathbf{R}') \cdot \mathbf{u}(\mathbf{R}') \right]$$

$$= -\frac{1}{\sqrt{N}} \sum_{\mathbf{R}'} \frac{\mathbf{e}_s(\mathbf{k})}{M} \cdot \left[\sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')} \mathbf{D}(\mathbf{R}-\mathbf{R}') \right] \cdot \mathbf{u}(\mathbf{R}') e^{-i\mathbf{k}\cdot\mathbf{R}'}$$

$$= -\frac{1}{\sqrt{N}} \sum_{\mathbf{R}'} \frac{\mathbf{e}_s(\mathbf{k})}{M} \cdot \mathbf{D}(\mathbf{k}) \cdot \mathbf{u}(\mathbf{R}') e^{-i\mathbf{k}\cdot\mathbf{R}'} = -\frac{1}{\sqrt{N}} \sum_{\mathbf{R}'} \frac{1}{M} \mathbf{u}(\mathbf{R}') \cdot \mathbf{D}(\mathbf{k}) \cdot \mathbf{e}_s(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{R}'}$$

$$= -\frac{1}{\sqrt{N}} \sum_{\mathbf{R}'} \frac{1}{\cancel{M}} \mathbf{u}(\mathbf{R}') \cdot \cancel{M} \omega_s^2(\mathbf{k}) \mathbf{e}_s(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{R}'} = -\omega_s^2(\mathbf{k}) q_s(\mathbf{k}) \qquad \text{Q.E.D.}$$

Can be generalized to include a nontrivial basis (math is a bit more complicated).

$$H = \sum_{\mathbf{R}} \frac{1}{2M} P^2(\mathbf{R}) + \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \mathbf{D}(\mathbf{R}-\mathbf{R}') \cdot \mathbf{u}(\mathbf{R}')$$

After normal mode transformation, the motions are decoupled:

$$H = \sum_{\mathbf{k}s} \left[\frac{p_s^*(\mathbf{k}) p_s(\mathbf{k})}{2M} + \frac{1}{2} M \omega_s^2(\mathbf{k}) q_s^*(\mathbf{k}) q_s(\mathbf{k}) \right] = \sum_{\mathbf{k}s} h_s(\mathbf{k})$$

where we have chosen $\mathbf{e}_s(\mathbf{k}) = \mathbf{e}_s(-\mathbf{k})$, allowed by inversion symmetry.

Quantization: $\left[\mathbf{u}(\mathbf{R}), \mathbf{P}(\mathbf{R}') \right] = i\hbar \, \delta_{\mathbf{R},\mathbf{R}'}$

One can show:

$$\left[q_s\left(\mathbf{k}\right), p_{s'}\left(\mathbf{k}'\right)\right] = i\hbar\,\delta_{\mathbf{k},-\mathbf{k}'}\,\delta_{s,s'} \qquad\qquad \left[q_s\left(\mathbf{k}\right), p_{s'}{}^{+}\left(\mathbf{k}'\right)\right] = i\hbar\,\delta_{\mathbf{k},\mathbf{k}'}\,\delta_{s,s'}$$

$$p_s{}^{+}\left(\mathbf{k}\right) = p_s\left(-\mathbf{k}\right) \qquad \left[q_s\left(\mathbf{k}\right), q_{s'}\left(\mathbf{k}'\right)\right] = 0 \qquad \left[p_s\left(\mathbf{k}\right), p_{s'}\left(\mathbf{k}'\right)\right] = 0 \quad \text{etc.}$$

$$h_s\left(\mathbf{k}\right) = \frac{1}{2M}\, p_s{}^{+}\left(\mathbf{k}\right) p_s\left(\mathbf{k}\right) + \frac{1}{2} M\omega_s^2\left(\mathbf{k}\right) q_s^{+}\left(\mathbf{k}\right) q_s\left(\mathbf{k}\right)$$

Lowering operator: $a_{\mathbf{k}s} = \sqrt{M\omega_s\left(\mathbf{k}\right)/2\hbar}\; q_s\left(\mathbf{k}\right) + i\sqrt{1/2\,\hbar\,M\,\omega_s\left(\mathbf{k}\right)}\; p_s\left(\mathbf{k}\right)$

Raising operator: $a_{\mathbf{k}s}^{+} = \sqrt{M\omega_s\left(\mathbf{k}\right)/2\hbar}\; q_s^{+}\left(\mathbf{k}\right) - i\sqrt{1/2\,\hbar\,M\,\omega_s\left(\mathbf{k}\right)}\; p_s^{+}\left(\mathbf{k}\right)$

$$\left[a_{\mathbf{k}s}, a_{\mathbf{k}'s'}\right] = \left[a_{\mathbf{k}s}^{+}, a_{\mathbf{k}'s'}^{+}\right] = 0 \qquad\qquad \left[a_{\mathbf{k}s}, a_{\mathbf{k}'s'}^{+}\right] = \delta_{\mathbf{k},\mathbf{k}'}\delta_{s,s'}$$

$$\boxed{H = \sum h_s\left(\mathbf{k}\right) = \sum_{\mathbf{k}s}\left(a_{\mathbf{k}s}^{+} a_{\mathbf{k}s} + \frac{1}{2}\right)\hbar\,\omega_s\left(\mathbf{k}\right)}$$

3N independent SHOs

For mode $\left(\mathbf{k}, s\right)$, eigenstates $\left| n_{\mathbf{k}s}\right\rangle$

$n_{\mathbf{k}s}$ = 0, 1, 2, …. = mode occupation number = number of phonons

Phonons are bosons (occupation number is unlimited).

Total energy = $\displaystyle\sum_{\mathbf{k}s}\left(n_{\mathbf{k}s} + \frac{1}{2}\right)\hbar\omega_s\left(\mathbf{k}\right) = \left\langle \{n_{\mathbf{k}s}\}\left| H\right|\{n_{\mathbf{k}s}\}\right\rangle$

Phonon energy = $\hbar\,\omega_s\left(\mathbf{k}\right)$ $\qquad \dfrac{1}{2}\hbar\,\omega_s\left(\mathbf{k}\right)$ = zero point energy

$$\boxed{a_{\mathbf{k}s}\left| n_{\mathbf{k}s}\right\rangle = \sqrt{n_{\mathbf{k}s}}\;\left| n_{\mathbf{k}s} - 1\right\rangle}$$ phonon destruction operator

$$\boxed{a_{\mathbf{k}s}^{+}\left| n_{\mathbf{k}s}\right\rangle = \sqrt{n_{\mathbf{k}s} + 1}\;\left| n_{\mathbf{k}s} + 1\right\rangle}$$ phonon creation operator

$$\boxed{q_s\left(\mathbf{k}\right) = \sqrt{\hbar/2M\omega_s\left(\mathbf{k}\right)}\;\left(a_{\mathbf{k}s} + a_{-\mathbf{k}s}^{+}\right)}$$ Note the $a_{\mathbf{k}s} + a_{-\mathbf{k}s}^{+}$ combination (important later for anharmonic effects, electron-phonon coupling, etc.).

$$\boxed{p_s\left(\mathbf{k}\right) = -i\sqrt{M\hbar\omega_s\left(\mathbf{k}\right)/2}\;\left(a_{\mathbf{k}s} - a_{-\mathbf{k}s}^{+}\right)}$$

$$\mathbf{u}\left(\mathbf{R}\right) = \frac{1}{\sqrt{N}}\sum_{\mathbf{k}s}\sqrt{\frac{\hbar}{2M\omega_s(\mathbf{k})}}\;\left(a_{\mathbf{k}s} + a_{-\mathbf{k}s}^{+}\right)\mathbf{e}_s(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}}$$

$$\mathbf{P}(\mathbf{R}) = \frac{-i}{\sqrt{N}}\sum_{\mathbf{k}s}\sqrt{\frac{M\hbar\omega_s(\mathbf{k})}{2}}\left(a_{\mathbf{k}s} - a_{-\mathbf{k}s}^{+}\right)\mathbf{e}_s(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}}$$

$$a_{ks} = \mathbf{e}_{ks} \cdot \left[\sqrt{\frac{M\omega_s(\mathbf{k})}{2\hbar}} \left(\frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-1\mathbf{k}\cdot\mathbf{R}} \mathbf{u}(\mathbf{R}) \right) + i\sqrt{\frac{1}{2\hbar M\omega_s(\mathbf{k})}} \left(\frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-1\mathbf{k}\cdot\mathbf{R}} \mathbf{P}(\mathbf{R}) \right) \right]$$

$a_{ks}^{+} = ...$ (exercise for you)

Classical	Quantum
Normal modes	Phonon modes
SHO: $\ddot{q} + \omega^2 q = 0$	SHO: $h = \left(a^{+}a + \dfrac{1}{2} \right)\hbar\omega$
Energy arbitrary	Energy quantized $\left(n + \dfrac{1}{2} \right)\hbar\omega$
Amplitude arbitrary	Amplitude not arbitrary; zero-point vibration

Crystals with a Multi-atom Basis

The formulas are similar, with an additional index for the various atoms in the basis. The number of modes at each **k** increases to $3n$. Each polarization vector has $3n$ components, and it is generally complex (the motions of the atoms in the basis are related by certain phases).

Example: 6x6 dynamic matrix of Ge (2 atoms per unit cell); see F. Herman, Lattice Vibrational Spectrum of Ge, J. Phys. Chem. Solids 8, 405 (1959); 6-th neighbors

These will be denoted below by $\mathbf{G}_{ab}(\mathbf{q})$, where a or $b = 1, 2, 3$ for $s = 0$, and a or $b = 4, 5, 6$ for $s = 1$. The rows and columns of $\mathbf{G}(\mathbf{q})$ are ordered in the same fashion as in Smith's paper [cf. reference 11, equation (3.13)].

$\mathbf{G}_{11}(\mathbf{q}) = \mathbf{G}_{44}(\mathbf{q}) = 4\alpha + 4\lambda(1 - \cos \pi q_y \cos \pi q_z) + 4\mu(2 - \cos \pi q_z \cos \pi q_x - \cos \pi q_x \cos \pi q_y)$
$\qquad + 8\mu' + 4\lambda' + 2\lambda''(1 - \cos 2\pi q_x) + 2\mu''(2 - \cos 2\pi q_y - \cos 2\pi q_z)$
$\qquad + 8\mu''' + 4\lambda''' + 8\lambda''''(1 - \cos 2\pi q_x \cos \pi q_y \cos \pi q_z)$
$\qquad + 8\mu''''(2 - \cos 2\pi q_y \cos \pi q_z \cos \pi q_x - \cos 2\pi q_z \cos \pi q_x \cos \pi q_y)$.

$\mathbf{G}_{22}(\mathbf{q}) = \mathbf{G}_{55}(\mathbf{q})$ and $\mathbf{G}_{33}(\mathbf{q}) = \mathbf{G}_{66}(\mathbf{q})$ can be obtained from the above by cyclic permutation.

$G_{12}(\mathbf{q}) = \mathbf{G*}_{21}(\mathbf{q}) = G_{54}(\mathbf{q}) = G*_{45}(\mathbf{q}) = 4v \sin \pi q_x \sin \pi q_y - i4\delta \sin \pi q_z(\cos \pi q_x - \cos \pi q_y)$
$\qquad + 8v'''' \sin \pi q_x \sin \pi q_y \cos 2\pi q_z + 8\delta_{+}'''' \cos \pi q_z(\sin \pi q_x \sin 2\pi q_y - \sin \pi q_y \sin 2\pi q_x)$
$\qquad - i8\delta_{-}'''' \sin \pi q_z(\cos \pi q_x \cos 2\pi q_y - \cos \pi q_y \cos 2\pi q_x)$.

$G_{23}(\mathbf{q}) = G*_{32}(\mathbf{q}) = G_{65}(\mathbf{q}) = G*_{56}(\mathbf{q})$ and $G_{31}(\mathbf{q}) = G*_{13}(\mathbf{q}) = G_{46}(\mathbf{q}) = G*_{64}(\mathbf{q})$ by cyclic permutation:
$\qquad G_{12}(\mathbf{q}) \to G_{23}(\mathbf{q}) \to G_{31}(\mathbf{q})$.

$G_{14}(\mathbf{q}) = \mathbf{G*}_{41}(\mathbf{q}) = -\alpha[1 + \exp -\pi i(q_x + q_y) + \exp -\pi i(q_y + q_z) + \exp -\pi i(q_z + q_x)]$
$\qquad - \lambda'[\{1 + \exp -\pi i(q_y + q_z)\}\exp -2\pi i q_x + (\exp -\pi i q_y + \exp -\pi i q_z) \exp \pi i q_x]$
$\qquad - \mu'[\{1 + \exp -\pi i(q_z + q_x)\} \exp -2\pi i q_y + (\exp -\pi i q_z + \exp -\pi i q_x) \exp \pi i q_y]$
$\qquad - \mu'[\{1 + \exp -\pi i(q_x + q_y)\} \exp -2\pi i q_z + (\exp -\pi i q_x + \exp -\pi i q_y) \exp \pi i q_z]$
$\qquad - \lambda'''[\{\exp -\pi i(2q_y - q_z) + \exp -\pi i(2q_z - q_y)\} \exp -\pi i q_x + \exp \pi i(q_y + q_z) + \exp -2\pi i(q_y + q_z)]$
$\qquad - \mu'''[\{\exp -\pi i(2q_z - q_x) + \exp -\pi i(2q_x - q_z)\} \exp -\pi i q_y + \exp \pi i(q_z + q_x) + \exp -2\pi i(q_z + q_x)]$
$\qquad - \mu'''[\{\exp -\pi i(2q_x - q_y) + \exp -\pi i(2q_y - q_x)\} \exp -\pi i q_z + \exp \pi i(q_x + q_y) + \exp -2\pi i(q_x + q_y)]$

$\mathbf{G}_{25}(\mathbf{q}) \equiv \mathbf{G*}_{52}(\mathbf{q})$ and $\mathbf{G}_{36}(\mathbf{q}) = \mathbf{G*}_{63}(\mathbf{q})$ by cyclic permutation: $\mathbf{G}_{14}(\mathbf{q}) \to \mathbf{G}_{25}(\mathbf{q}) \to \mathbf{G}_{36}(\mathbf{q})$

$G_{15}(\mathbf{q}) = \mathbf{G*}_{51}(\mathbf{q}) = G_{24}(\mathbf{q}) = G*_{42}(\mathbf{q}) = -\beta[1 + \exp -\pi i(q_x + q_y) - \exp -\pi i(q_y + q_z) - \exp -\pi i(q_z + q_x)]$
$\qquad - \delta'[\{-1 + \exp -\pi i(q_y + q_z)\} \exp -2\pi i q_x + (-\exp -\pi i q_y + \exp -\pi i q_z) \exp \pi i q_x]$
$\qquad - \delta'[\{-1 + \exp -\pi i(q_z + q_x)\} \exp -2\pi i q_y + (+\exp -\pi i q_z - \exp -\pi i q_x) \exp \pi i q_y]$
$\qquad - v'[\{+1 + \exp -\pi i(q_x + q_y)\} \exp -2\pi i q_z + (-\exp -\pi i q_x - \exp -\pi i q_y) \exp \pi i q_z]$
$\qquad - \delta'''[\exp \pi i(q_y + q_z) - \exp -2\pi i(q_y + q_z) + \{+\exp -\pi i(2q_y - q_z) - \exp -\pi i(2q_z - q_y)\} \exp -\pi i q_x]$
$\qquad - \delta'''[\exp \pi i(q_z + q_x) - \exp -2\pi i(q_z + q_x) + \{-\exp -\pi i(2q_z - q_x) + \exp -\pi i(2q_x - q_z)\} \exp -\pi i q_y]$
$\qquad - v'''[\exp \pi i(q_x + q_y) + \exp -2\pi i(q_x + q_y) + \{-\exp -\pi i(2q_x - q_y) - \exp -\pi i(2q_y - q_x)\} \exp -\pi i q_z]$.

$G_{26}(\mathbf{q}) = \mathbf{G*}_{62}(\mathbf{q}) = G_{35}(\mathbf{q}) = G*_{53}(\mathbf{q})$ and $G_{34}(\mathbf{q}) = G*_{43}(\mathbf{q}) = G_{16}(\mathbf{q}) = G*_{61}(\mathbf{q})$
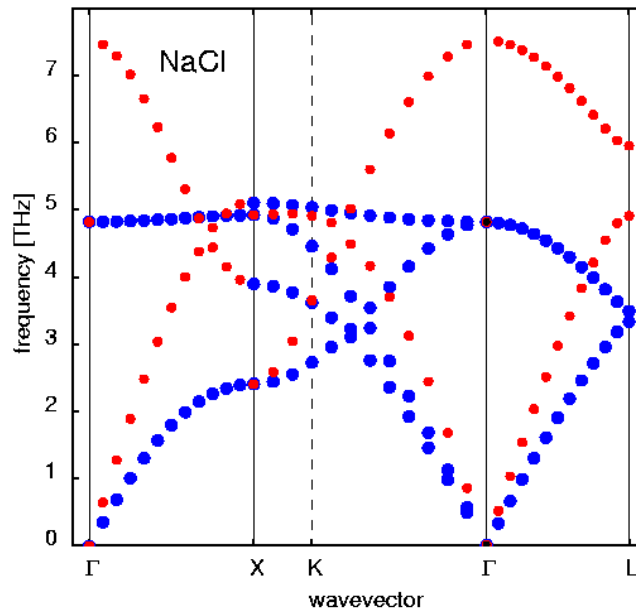$\qquad$ by cyclic permutation: $G_{15}(\mathbf{q}) \to G_{26}(\mathbf{q}) \to G_{34}(\mathbf{q})$.

Phonon Dispersion Relations of Ge (two atoms per unit cell):
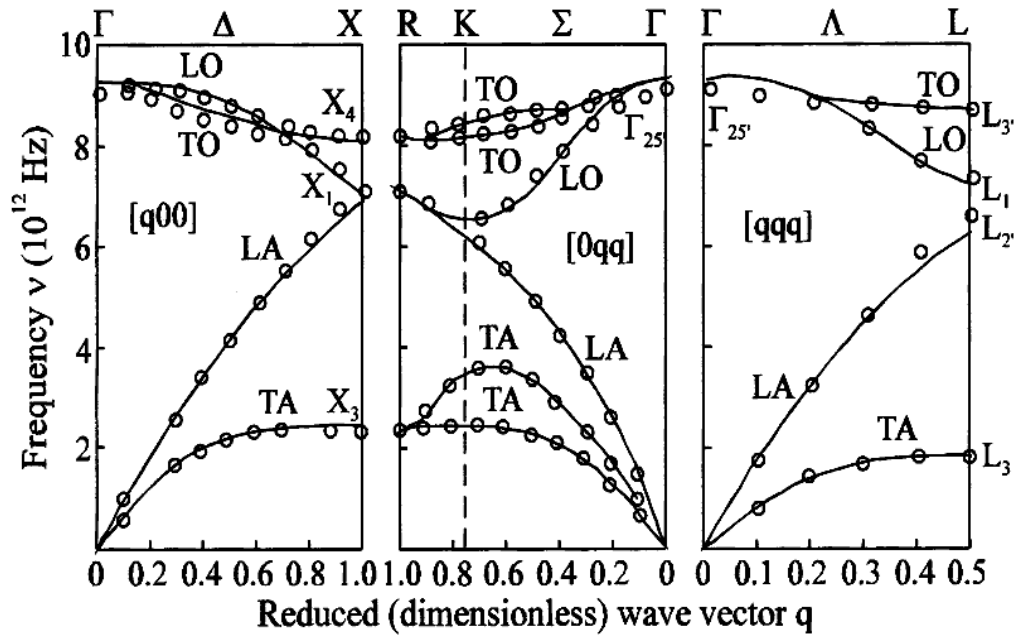
Note the TO and LO branches are degenerate at zone center.

http://www.ioffe.rssi.ru/SVA/NSM/Semicond/SiGe/mechanic.html

Phonon Dispersion Relations of NaCl (two atoms per unit cell):

Note the large splitting between TO and LO at zone center (LO-TO splitting related to ionicity)

http://people.web.psi.ch/delley/nacl.html

Phonon Dispersion Relations of Pu (fcc, one atom per unit cell) determined by inelastic x-ray scattering. Note the anomalies.
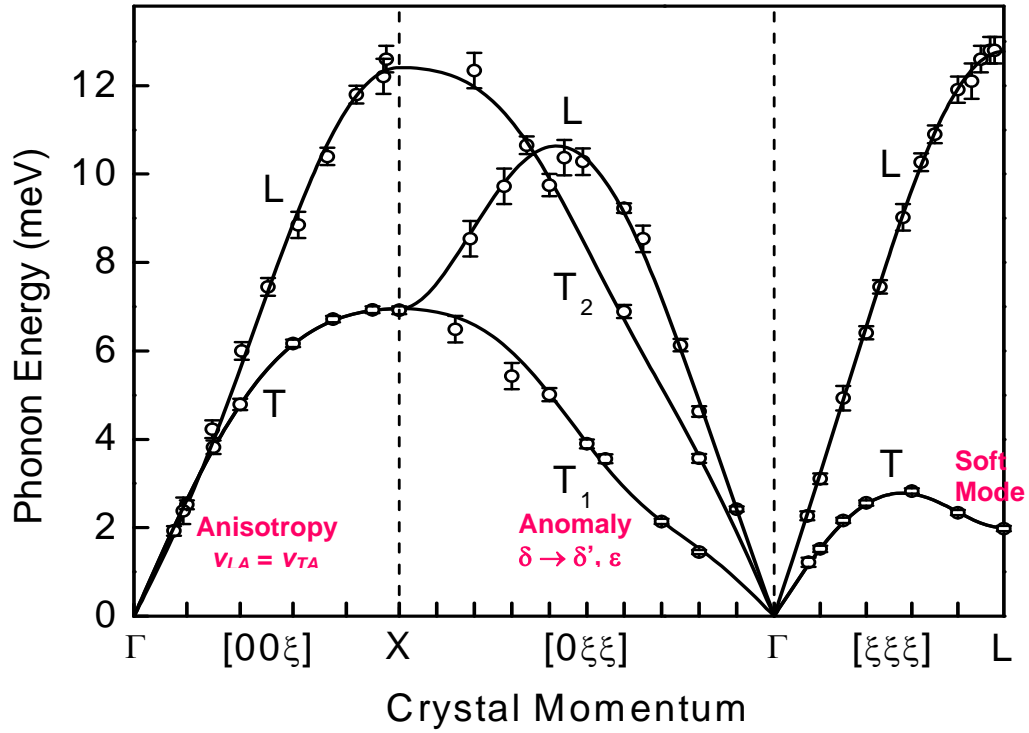
Phonon dispersion relations of graphite/graphene, M. Mohr et al., Phys. Rev. B 76, 035439 (2007). 2 atoms per unit cell in a graphene sheet.
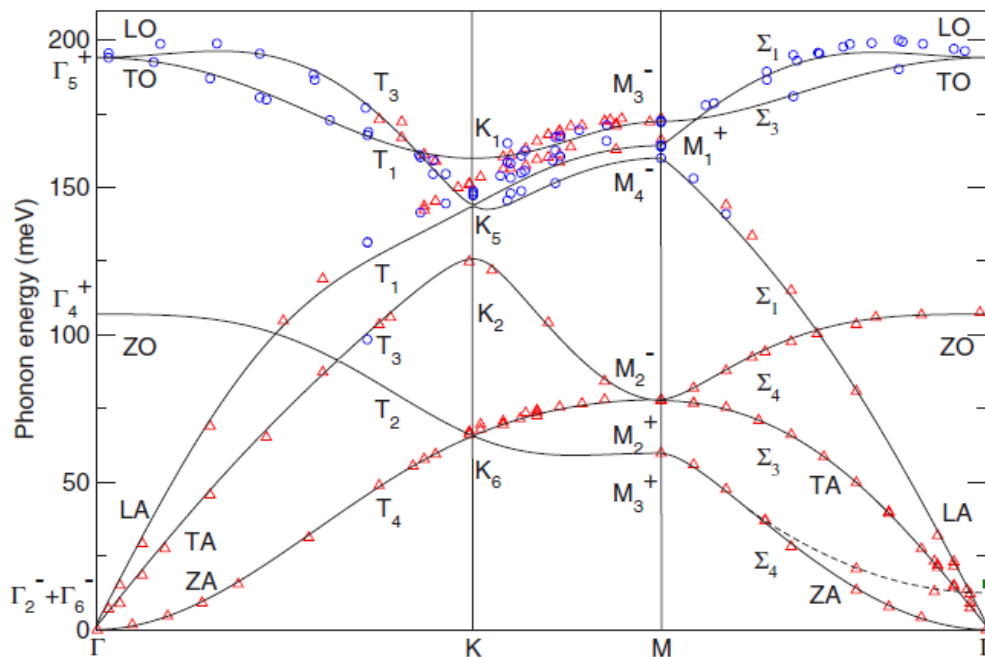
Phonon dispersion relations of chromium (a spin density wave system)
Phys. Rev. B 4, 969 (1971). **Kohn anomalies** indicated by vertical arrows.
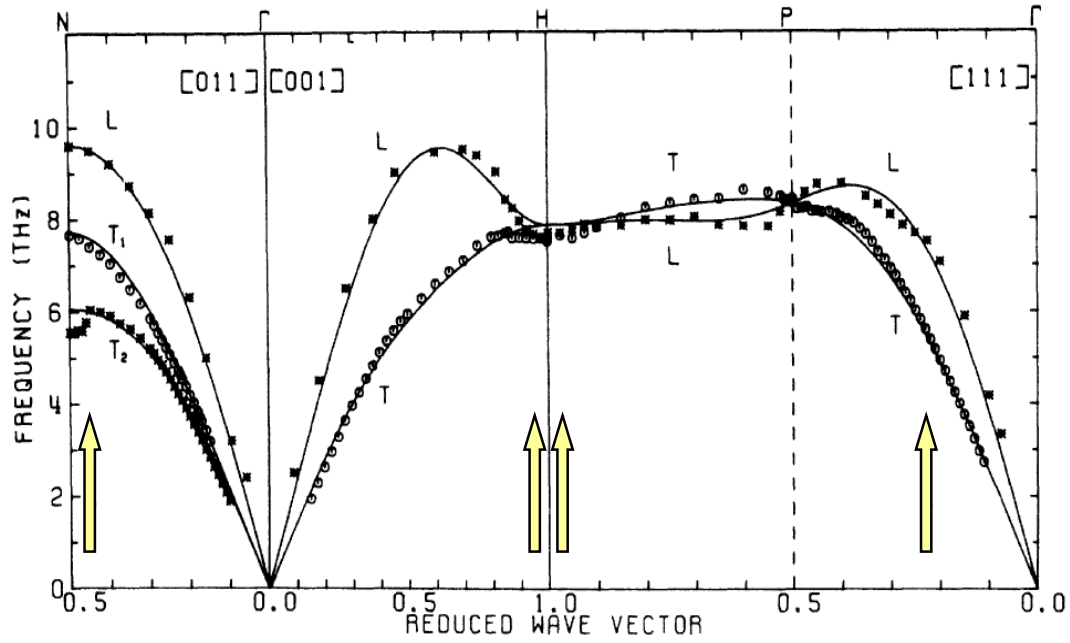
Phonon dispersion relation of TTF-TCNQ (quasi-1d) along the chain direction. PRL, 36, 801 (1976). Note the very pronounced Kohn anomaly (Periels instability, $2k_F$ anomaly). Flat bands are derived from molecular excitations.