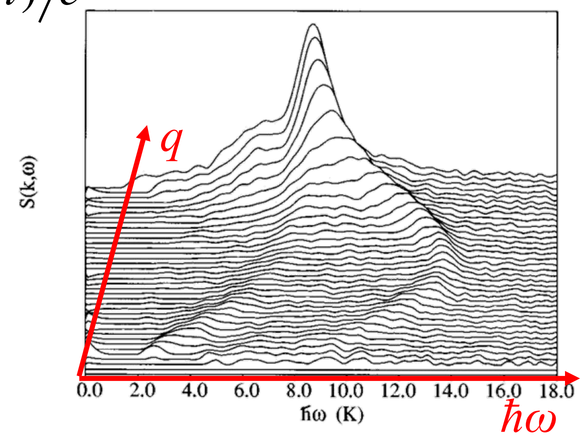
Lesson 5: Phonons in solids and in liquids, connections

- ✓ Recall of phonons in crystals
- ✓ Recall of phonons in homogeneous systems
- ✓ Elastic constants, and connection between liquids and crystals

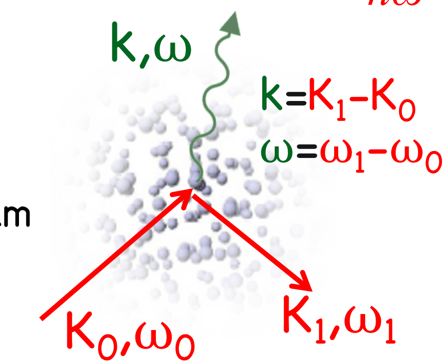
Dynamical extension of the structure of liquids

- ✓ The dynamics structure factor is proportional to the inelastic coherent scattering cross-section

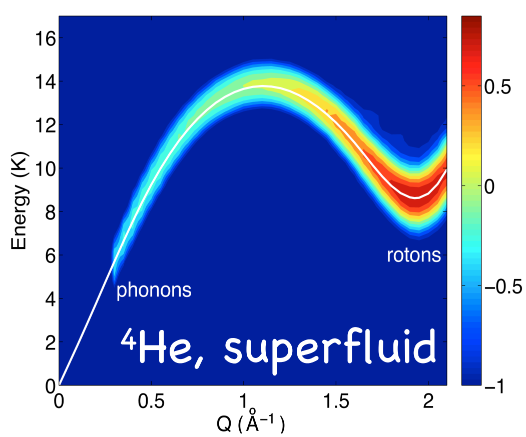
$$S(k,\omega) = \int dt F(k,t) e^{-i\omega t} = \int dt \int d\mathbf{r} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} G(r,t) = \frac{1}{N}\int dt \langle \bar{\rho}(-k,0)\bar{\rho}(k,t)\rangle e^{-i\omega t}$$

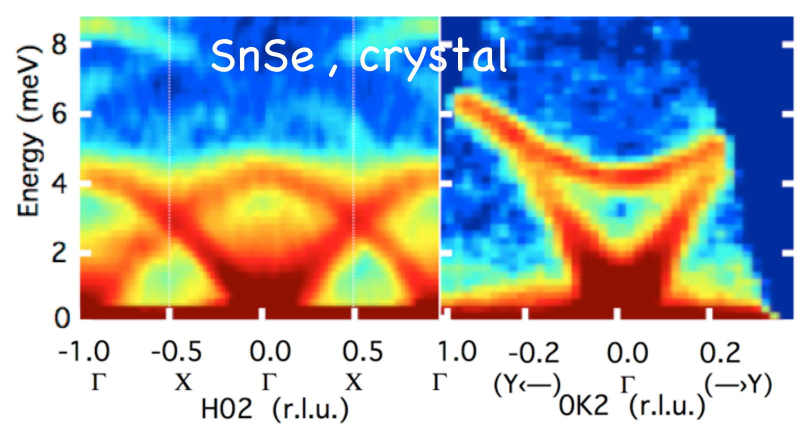


- ✓ $S(k,\omega)$ displays peaks (resonances) at those frequencies where the collective variables $\rho_k(t)$ vibrates coherently. Therefore it identifies the dispersion relation $\omega(k)$ of the collective vibration (= phonons, in crystals)
- ✓ The incoming particle (radiation) changes both momentum and energy in an inelastic scattering process
- ✓ The out-coming radiation is measured at any given momentum and energy, but displays preferences (= high cross section = resonances) only for given specific momenta and energy change related by $\omega(k)$
- ✓ On these cross-sectional maxima, the process is more likely to occur, therefore they correspond to absorption of momentum/energy by the system in the form of a "quasi-particle" that is the phonon (or collective excitation). The energy and momentum of the phonon is then obtained assuming the global and energy/momentum conservation. The dispersion relation $\omega(k)$ defines the quasi-particles itself (e.g. its "effective mass" if the dispersion is quadratic)

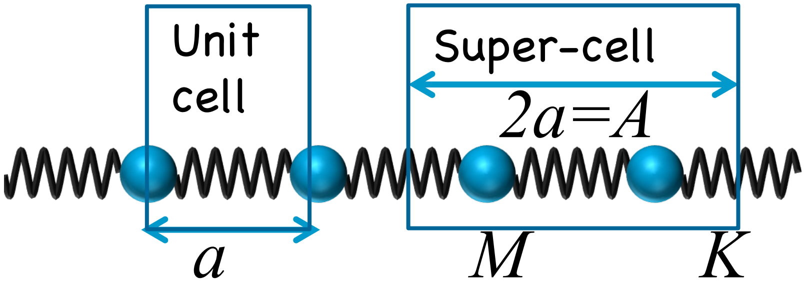


- ✓ The elastic scattering is a special case for which the energy variation is null (no propagation)
- ✓ The inelastic scattering is the method to measure the dispersion curves of collective excitations in fluids and solids

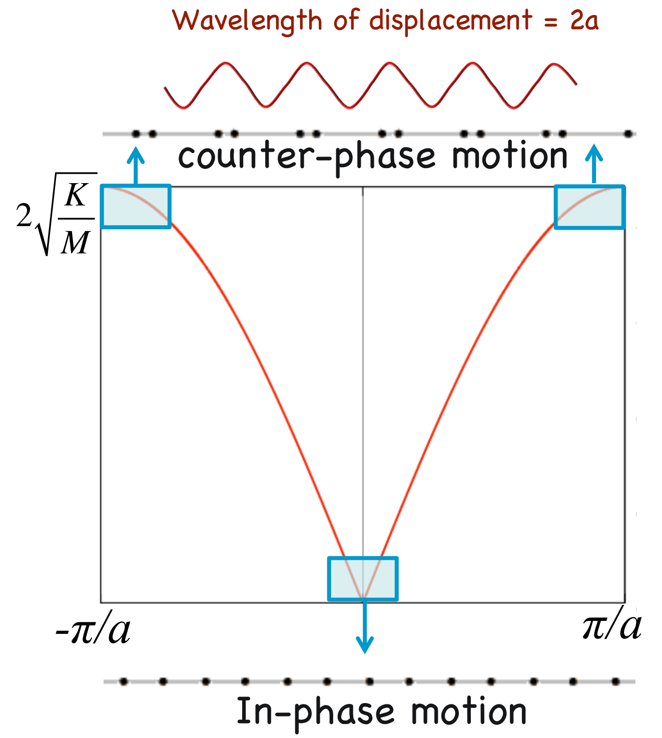




Phonons – 1D chain



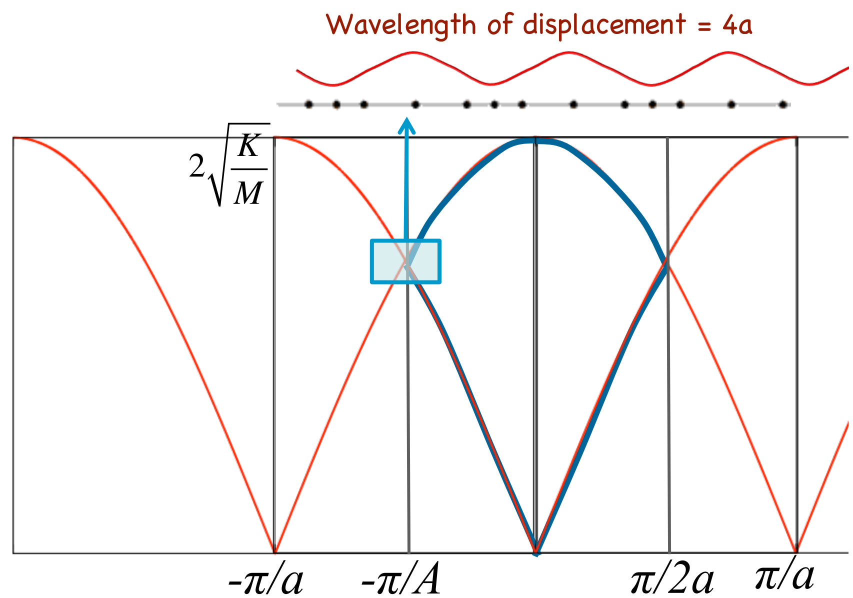
$$\omega(q) = 2\sqrt{\frac{K}{M}}\left|\sin\left(q\frac{a}{2}\right)\right|$$



✓ what if the **same** crystal is described by a doubled super-cell with a two atom basis?

- The Brillouin Zone is halved
- The dispersion branches become two

$$\omega(q) = \sqrt{2\frac{K}{M}}\sqrt{1 \pm \cos\left(q\frac{A}{2}\right)} = \begin{cases} 2\sqrt{\frac{K}{M}}\left|\cos\left(q\frac{A}{4}\right)\right| = 2\sqrt{\frac{K}{M}}\left|\cos\left(q\frac{a}{2}\right)\right| \\ 2\sqrt{\frac{K}{M}}\left|\sin\left(q\frac{A}{4}\right)\right| = 2\sqrt{\frac{K}{M}}\left|\sin\left(q\frac{a}{2}\right)\right| \end{cases}$$

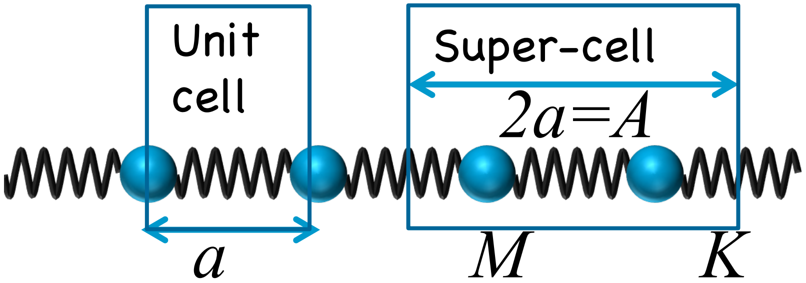


- The two branches are originating from the unit cell single branch by folding within the reduced BZ!

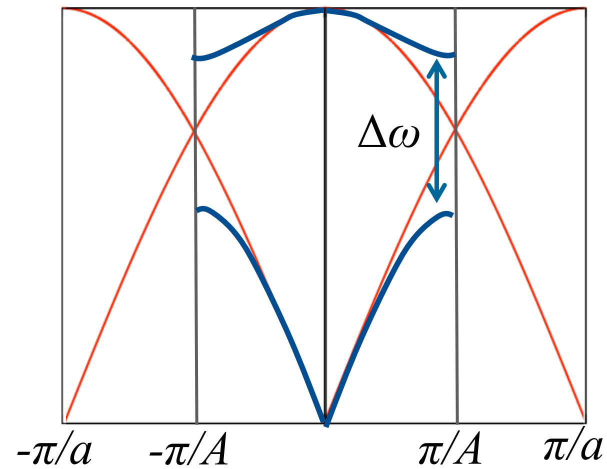
⇒ Same physics, no real additional modes!

Phonons – 1D chain

Optical branch: Counter-phase motion

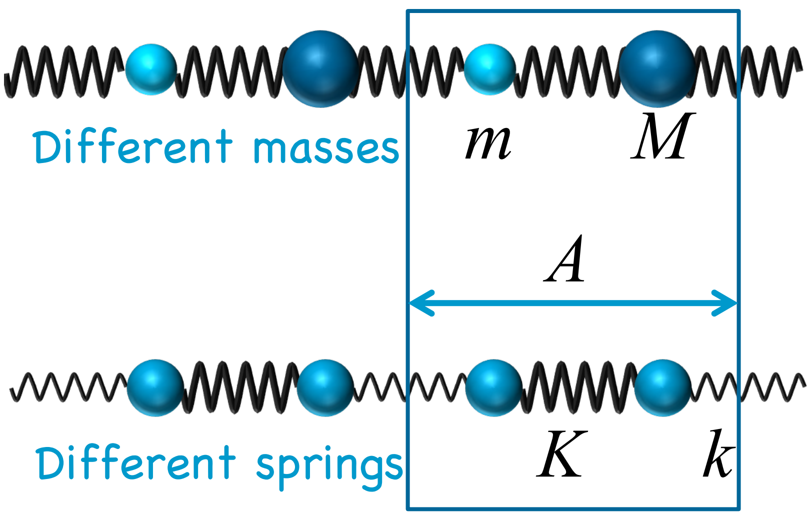


$$\omega(q) = \sqrt{2\frac{K}{M}}\sqrt{1 \pm \cos\left(q\frac{A}{2}\right)}$$



Acoustic branch: In-phase motion

- ✓ What if one really has a **crystal with a basis**?
  - ❖ REMARK: this can occur in different ways!



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

$$\omega(0) = \sqrt{2\frac{K(m+M)}{Mm}} = \sqrt{2\frac{K}{\mu}} \qquad \Delta\omega = \sqrt{2K}\left(\frac{1}{\sqrt{m}} - \frac{1}{\sqrt{M}}\right)$$

$$\omega(q) = \sqrt{\frac{K+k}{M}}\sqrt{1 \pm \sqrt{\left(1 - \frac{4kK}{(k+K)^2}\sin^2\left(q\frac{A}{2}\right)\right)}}$$

$$\omega(0) = 2\sqrt{\frac{k+K}{2M}} = \qquad \Delta\omega = \sqrt{\frac{2}{M}}\left(\sqrt{K} - \sqrt{k}\right)$$

- ✓ The branches split, two physically distinct modes appear (acoustic, optical)
- ✓ What if... one has same M, same K, but two different equilibrium distances?

$\Delta\omega$=0, BUT the crystal have a 2-atom basis, therefore the half BZ must be used Homework!

Phonons - General

✓ In general, phonons in crystal arise from the solution of the secular equation

$$\ddot{u}_i(\mathbf{R}_I) = \mathbf{D}_{ij,IJ} u_j(\mathbf{R}_J)$$

$u_i(R_I)$ being the mass weighted displacement of atoms from the R_I lattice sites

D is the dynamical matrix, obtained from Hessian of energy with respect to atomic displacement evaluated in the equilibrium configuration

Assuming a wavelike displacement $u_i(\mathbf{R}_I) = \varepsilon_i \exp(i(\mathbf{q}\cdot\mathbf{R} - \omega t))$

One gets the secular equation in the standard form $\omega^2 \varepsilon_i = \mathbf{D}_{ij}(\mathbf{q})\varepsilon_j$

This equation has 3 solutions for each q value.

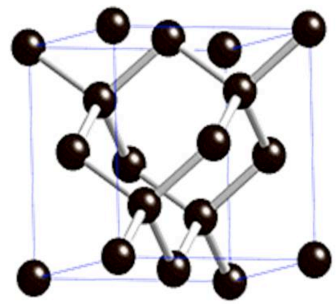
The crystal symmetry ensures that the solutions of this equations are Bloch functions, and that the three eigenvalues $\omega_I(q)$ (phonon branches) can be evaluated within the Brillouin zone

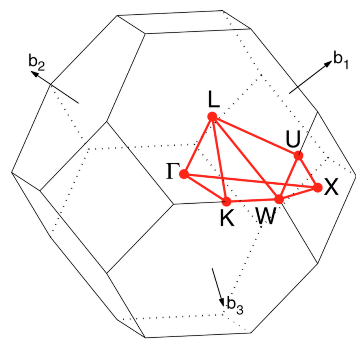
If more than one atom are present within the crystsal unit cell, then solutions are 3xn, with n the number of atoms. Therefore there are 3n phonon branches

Phonons – 3D crystals

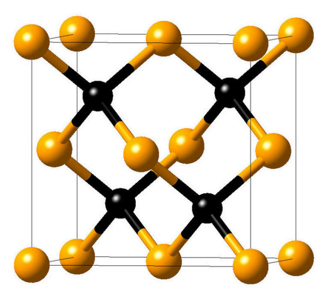
- ✓ Silicon and Silicon Carbide have both the Zink Blende struct: FCC with a two atom basis
- ✓ The BZ is the same, same symmetry points
- ✓ both have 3 optical and 3 acoustic branches with different polarization:
  - ❖ One longitudinal (i.e. along the propagation direction)
  - ❖ Two transverse (i.e. orthogonal to the propagation direction)
  - ❖ Longitudinal branches are generally higher in energy than transverse ones (always for the acoustic modes)
  - ❖ Transverse branches tend to be degenerate
- ✓ Some symmetry point degeneracies between branches are lifted by Si and C differences (mass or bond polarization)

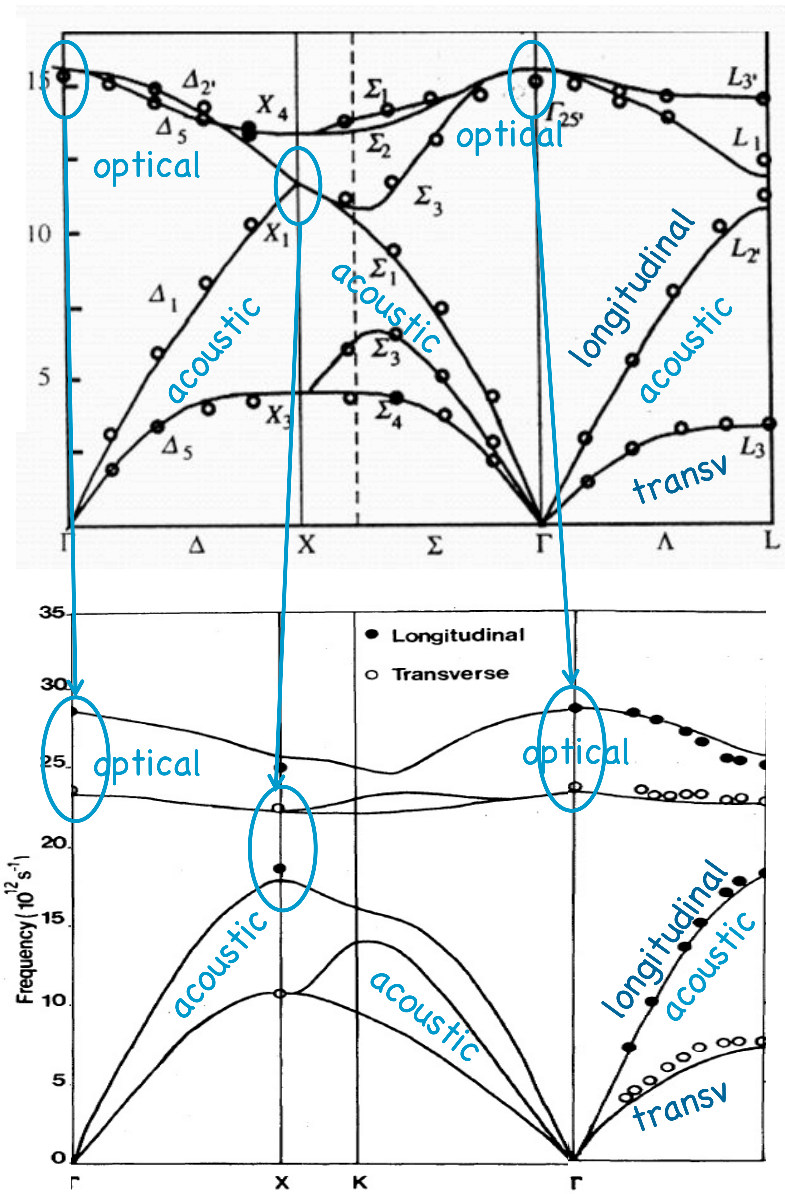
Si





SiC

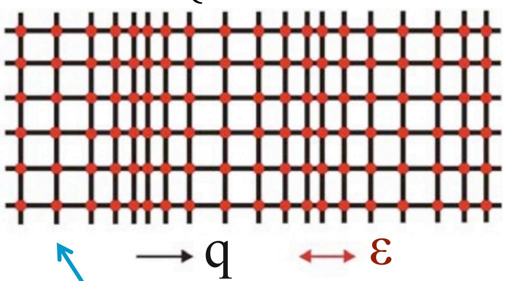


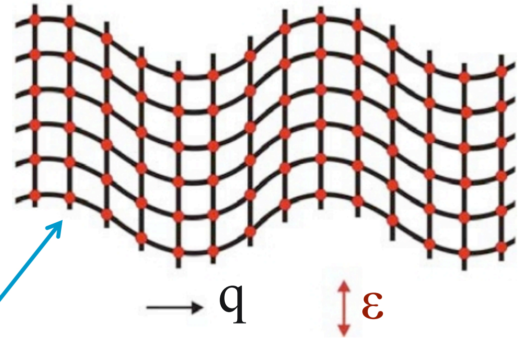


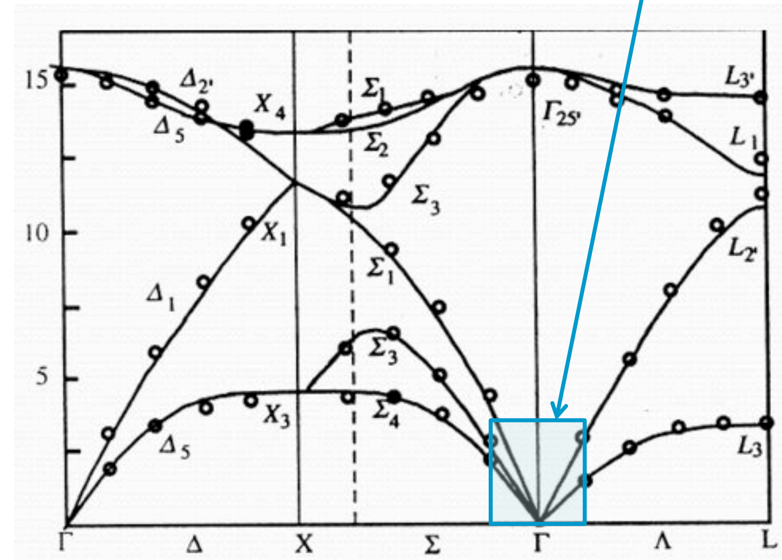
Phonons - the long wavelength limit

✓ Already at $q<(1/5)(\pi/a)$ (i.e. $\lambda>10a$) the dispersion curves of acoustic phonons are linear

$$\omega(q)=\begin{cases} c_l q \\ c_t q \end{cases}$$







✓ Longitudinal and transverse modes have different sound velocities, the transverse one being smaller; the two transverse modes tend to be degenerate

✓ Systems with finite compressibility (included fluids and gases) sustain compression waves; in the homogeneous approximation one has (Goodstain chapt 3)

1. Newton eqn of a voxel+ continuity eqn

$$\frac{\partial P}{\partial x}+\rho\frac{\partial v}{\partial t}=0$$

$$\frac{\partial \rho}{\partial t}+\frac{\partial}{\partial x}(\rho v)=0$$

2. Definition of density (pressure) perturbation and linearization of eqns

$$P=P_0+P' \qquad \frac{\partial P'}{\partial x}+\rho_0\frac{\partial v'}{\partial t}=0$$

$$\rho=\rho_0+\rho' \qquad \frac{\partial \rho'}{\partial t}+\rho_0\frac{\partial v'}{\partial x}=0$$

$$v=v'$$

3. Eqn of state (closure) and appearance of compressibility K

$$\rho=\rho(P_0)+\frac{\partial\rho}{\partial P}P'$$

$$c^2=\frac{\partial P}{\partial \rho}=\frac{1}{K\rho}$$

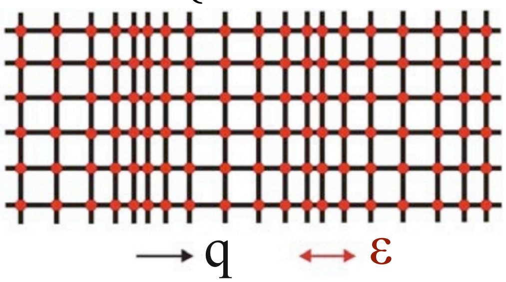
4. Wave equation!

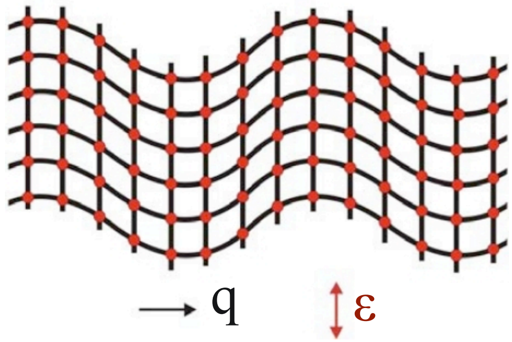
$$\frac{\partial^2\rho'}{\partial x^2}-\frac{1}{c^2}\frac{\partial^2\rho'}{\partial t^2}=0$$

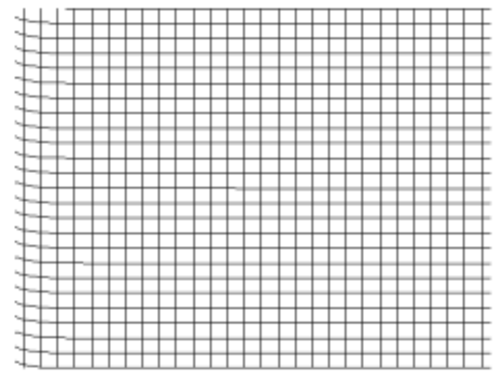
Phonons – the long wavelength limit

✓ Long waves in crystals: Linear dispersion, longitudinal and transverse with different vel

$$\omega(q) = \begin{cases} c_l q \\ c_t q \end{cases} \quad \text{with} \quad c_l > c_t$$

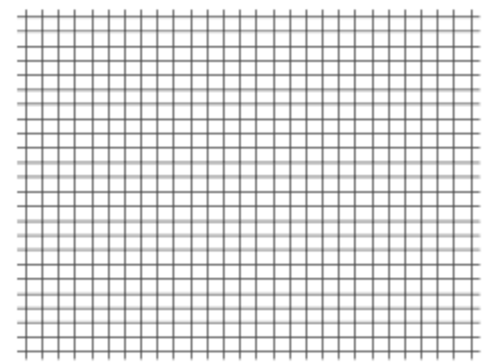






✓ Compression waves in homogeneous sytems: Linear dispersion, longitudinal, velocity dependent on compressibility

$$c^2 = \frac{\partial P}{\partial \rho} = \frac{1}{K\rho}$$



✓ Which is the relationship between the two?

✓ How do we make the connection?

✓ Why are the transversal waves absent in liquids and gases?

Phonons – the long wavelength limit – Theory of elasticity

✓ Hooke's law for continuous media: deformations (strains) are proportional to stress

$$\mathbf{T} = \mathbf{C} \cdot \mathbf{e}$$

$$\mathbf{T} = T_{ij} \qquad \mathbf{f} = \mathbf{T}\hat{\mathbf{n}}$$

Stress tensor, returning the force per unit surface (the diagonal part is pressure)

$$\mathbf{e} = e_{ij} = \frac{\partial u_i}{\partial x_j}$$

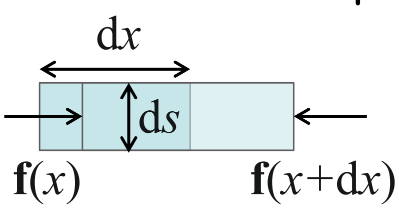
Strain tensor, the deformation per unit length (deform coefficient)

$$\mathbf{C} = C_{ijkl}$$

Elastic constants tensor, rank 4

Displacement vector

✓ The Newton equation for the voxel is



$$\rho \mathrm{d}x\mathrm{d}s \frac{\partial^2 \mathbf{u}}{\partial t^2} = \mathrm{d}s[\mathbf{f}(x+dx) - \mathbf{f}(x)] = \mathrm{d}x\mathrm{d}s\mathbf{C} \cdot \nabla \mathbf{e} \quad \rightarrow \quad \rho \frac{\partial^2 u_i}{\partial t^2} = C_{ikjl} \frac{\partial^2 u_j}{\partial x_k \partial x_l}$$

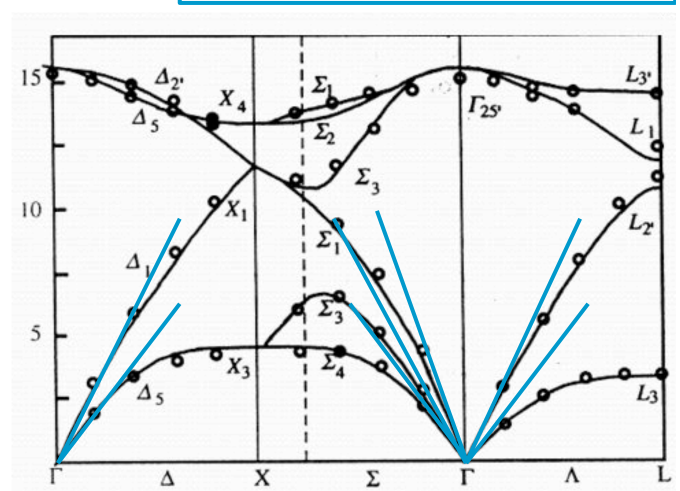
Elastic waves in solids !!

✓ Relationship to the dynamical matrix: $D_{ij} = \frac{q_k q_l}{\rho} C_{ikjl}$

$\mathbf{D}$ is quadratic in q ⇒ ω is linear in q !

✓ Solutions are non dispersive propagating waves with squared velocities which are linear combinations of the C_{ijkl}/ρ and can be found solving the eigenvalue problem

✓ Because the derivation assumes the elasticity law for continuous media, it is valid only when the atomistic effects are not relevant, i.e. in the long wavelength limit



Phonons – the long wavelength limit – Theory of elasticity

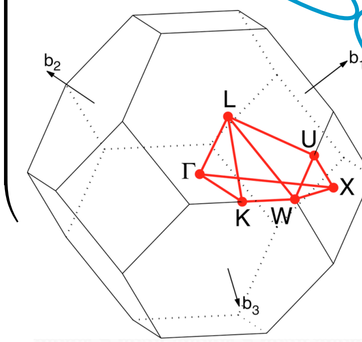
$$\frac{\partial^2 u_i}{\partial t^2} = \frac{C_{ijkl}}{\rho}\frac{\partial^2 u_j}{\partial x_k \partial x_l}$$

- ✓ At translational and rotational equilibrium, relationship between constants can be found and their number is reduced. A simplified 6 index notation is often used

$$xx \to 1 \quad yy \to 2 \quad zz \to 3 \quad xy \to 4 \quad yz \leftarrow 5 \quad zx \to 6 \quad \mathbf{T} = T_i \quad \mathbf{e} = e_i \quad \mathbf{C} = C_{ij}$$

- ✓ In addition, if the crystal is cubic, only 3 elastic constants are independent
- ✓ The values of these three constant are related to longitudinal and transverse waves velocities in specific directions:

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & & & \\ & C_{11} & C_{12} & & & \\ & & C_{11} & & & \\ & & & C_{44} & & \\ & & & & C_{44} & \\ & & & & & C_{44} \end{pmatrix}$$

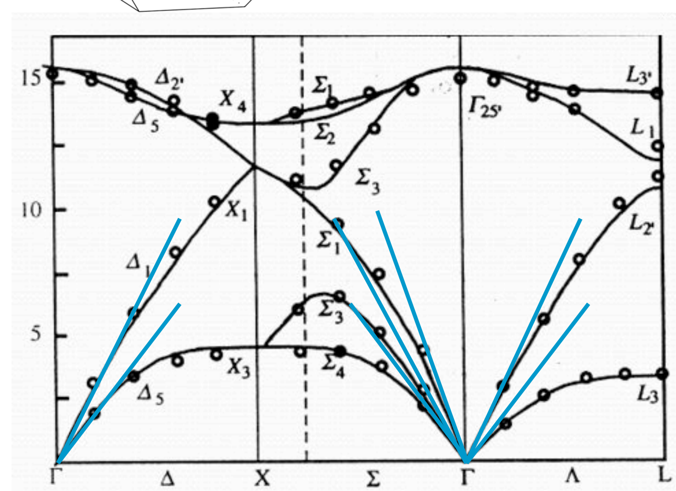


$$\langle 100 \rangle \quad \Gamma - X = \Delta: \qquad v_L = \sqrt{\frac{C_{11}}{\rho}} \qquad v_T = \sqrt{\frac{C_{44}}{\rho}}$$

$$\langle 111 \rangle \quad \Gamma - L = \Lambda: \qquad v_L = \sqrt{\frac{1}{3}\frac{C_{11}+2C_{12}+4C_{44}}{\rho}} \qquad v_T = \sqrt{\frac{1}{3}\frac{C_{11}-C_{12}+C_{44}}{\rho}}$$

$$\langle 110 \rangle \quad \Gamma - X = \Sigma: \qquad v_L = \sqrt{\frac{1}{2}\frac{C_{11}+C_{12}+2C_{44}}{\rho}} \qquad v_{T(-1,1,0)} = \sqrt{\frac{1}{2}\frac{C_{11}-C_{12}}{\rho}} \qquad v_{T(001)} = \sqrt{\frac{C_{44}}{\rho}}$$

- ✓ In <100> and <111> dir the two transverse modes are degenerate, in <110> they are not
- ✓ v_L is always larger than v_T
- ✓ The modes velocities are not all independent!



Phonons, summary

Goodstein, chapt 3 p ~152

✓ In fluids: no transverse modes. Longitudinal mode related to compressibility

$$v_L^2 = \frac{1}{\rho K}$$

✓ In ideal gases: the compressibility is γkT:

Adiabaticity index

$$v_L^2 = \frac{1}{\rho \frac{1}{n\gamma kT}} = \gamma \frac{kT}{m} \approx \gamma \langle v^2 \rangle$$

✓ In liquids: Ornstein Zernike says $S(k \to 0) = \rho k T K_T$ then $v_L^2 = \gamma \frac{kT}{mS(0)}$

March-Tosi, chapt 1 p. 7

✓ In crystals: (i) longitudinal velocity depends on the propagation direction

(ii) transverse modes appear, related to the shear elastic constants, absent in liquids:

liquids do not sustain elastic shear!!

(iii) The compressibility corresponds to the inverse of the bulk modulus B, but the anisotropy and response to shear stress imply the existence of other elastic moduli, inter-related and related to elastic constants

$$B = \frac{C_{11} + 2C_{12}}{3}$$

$$G_V = \frac{1}{5}(3C_{44} + C_{11} - C_{12})$$

$$C' = \frac{1}{2}(C_{11} - C_{12}) \quad C'' = \frac{1}{2}(C_{12} - C_{44})$$

$$Y = \frac{9BG_V}{3B + G_V}$$

$$\nu = -1 + \frac{Y}{2G_V}$$

$$v_L^2 = \frac{C_L}{\rho}$$

$$v_T^2 = \frac{C_T}{\rho}$$

M. Jamal, et al, Computational Materials Science 95 (2014) 592-599
K. Jakata and A. G. Every PHYSICAL REVIEW B 77, 174301 2008

✓ In crystal near melting:

$$v_L^2 \sim \frac{kT}{mS(0)} + \sum_{G\neq 0} f\left(S(G), S'(G), S''(G)\right) \qquad v_T^2 \sim \sum_{G\neq 0} f\left(S(G), S'(G), S''(G)\right)$$

MP Tosi, et al, Phil Mag B 1994, 69, p 833
Phil Mag B 1995, 72, 577

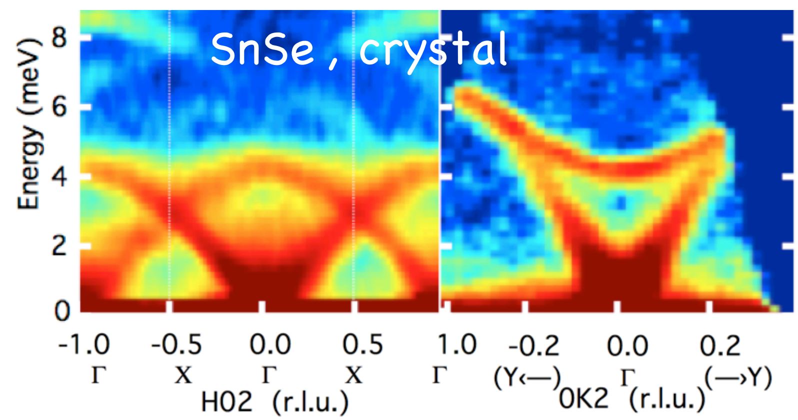
Liquid value

Vanishing upon melting, when crystal str disappear:
Transverse mode disappear, longitudinal mode are softer

Phonons, summary

✓ In all cases, the dispersion curves ω(q) can be measured from the peaks of S(q, ω), i.e. by inelastic scattering

✓ In crystals, the periodicity of the lattice can be seen



✓ In liquids, coherency is easily lost and the Measurement might not be easy. However in special cases it can be seen almost as in solids, when the system is strongly correlated,