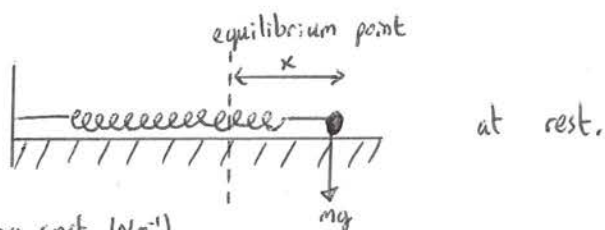


Phonons

phonon = collective excitation in a periodic, elastic arrangement of atoms or molecules

- represents an excited state in the QM quantization of modes of vibration of the system.

• Consider a mass-spring system



Now apply "F=ma" (→):

$$F = -\gamma x$$

↑
restoring force (N)

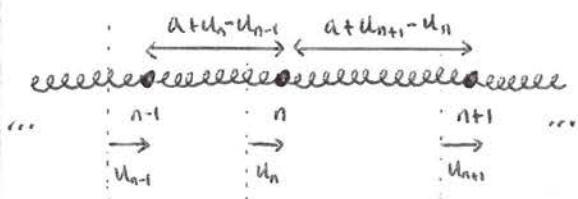
← displacement from equilibrium (m)

↑
spring const. (Nm⁻¹)

Hooke's Law

• Atoms in a lattice may be modelled as masses attached by springs. Since, by Taylor's theorem, the oscillation of an atom about its equilibrium is simple harmonic to a very good approximation (provided the perturbation is relatively small). The masses represent atoms and the springs represent atomic bonds.

Example 1) **Atomic Chain** Consider a 1D chain of "masses on springs" each of mass M.



NB: mass n is perturbed (small perturbation ⇒ only take nearest-neighbours into account)

The equilibrium separation is a and u_n is the displacement of the nth atom in the chain.

For mass n, apply "F=ma" (→):

$$M \frac{d^2 u_n}{dt^2} = \gamma (u_{n-1} - u_n) + \gamma (u_{n+1} - u_n)$$

EoM

(to the right)

Notice that, keeping all other atoms stationary and moving mass n^v will result in a leftwards force. Hence the minus sign attached to all u_n terms. However moving masses n+1 and n-1 to the right will both result in a rightwards force on mass n, hence the plus signs.

2nd order ODE \Rightarrow wave ansatz
 time-dependence $\propto e^{-i\omega t}$
 space-dependence $\propto e^{ik(an)}$ integer distance along the chain

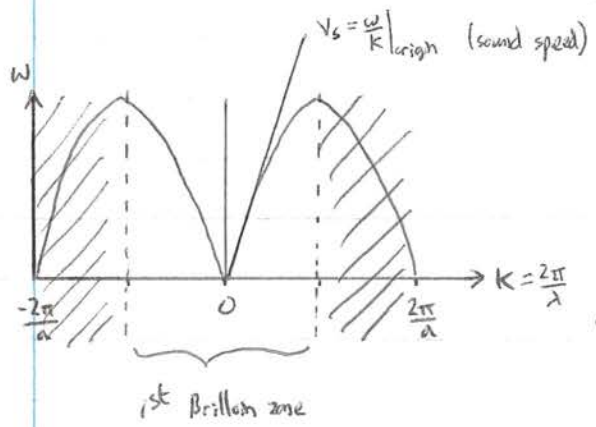
Now we simply solve the EoM... $M \ddot{u}_n = -\gamma (2u_n - u_{n-1} - u_{n+1})$

Ansatz $u_n(t) = u e^{i(kan - \omega t)}$ is a wave (defined only on lattice sites, hence u_n)

where wave-number $k = \frac{2\pi}{\lambda}$.

Upon substitution, we find $\omega = \sqrt{\frac{2\gamma(1 - \cos(ka))}{M}}$. (using $e^{ika} + e^{-ika} = 2 \cos ka$)

Using " $\cos \theta \equiv 1 - 2 \sin^2 \frac{\theta}{2}$ " \Rightarrow $\omega(k) = 2 \sqrt{\frac{\gamma}{M}} \left| \sin \frac{ka}{2} \right|$ dispersion relation

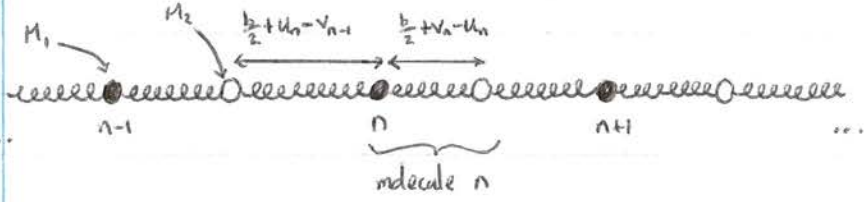


NB: It is common to just show the 1st BZ or even just the positive half of the 1st BZ.

- For an infinite chain, the possible frequency of oscillations is continuous \Rightarrow infinite number of possible propagating waves/phonons.
- Finite chain \Rightarrow discrete number of phonons.

Example 2) **Molecular Chain** Consider a 1D chain of diatomic molecules with masses M_1 and M_2 .

b = equilibrium separation of atoms
 v_n = displacement of the n^{th} secondary atom in the chain.



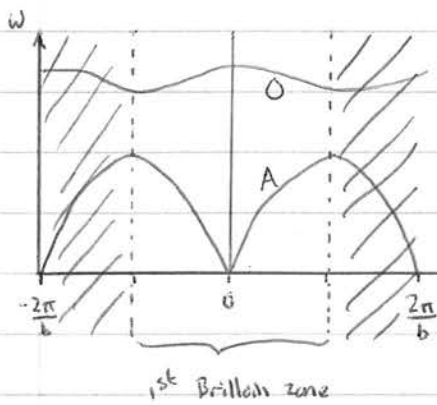
As before, apply " $F=ma$ " (\Rightarrow) to molecule n : $\begin{cases} M_1 \ddot{u}_n = -\gamma (2u_n - v_{n-1} - v_n) \\ M_2 \ddot{v}_n = -\gamma (2v_n - u_n - u_{n+1}) \end{cases}$

Ansatz $\begin{cases} u_n(t) = u e^{i(kb_n - \omega t)} \\ v_n(t) = v e^{i(kb_n - \omega t)} \end{cases} \Rightarrow \begin{cases} -\omega^2 M_1 u = \gamma v (1 + e^{-ikb}) - 2\gamma u \\ -\omega^2 M_2 v = \gamma u (e^{ikb} + 1) - 2\gamma v \end{cases}$

$$\begin{pmatrix} 2\gamma - \omega^2 M_1 & -\gamma(e^{ikb} + 1) \\ -\gamma(1 + e^{-ikb}) & 2\gamma - \omega^2 M_2 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \underline{0}$$

This only has a non-trivial solution when the matrix is non-invertible i.e. singular

$$\begin{vmatrix} 2\gamma - \omega^2 M_1 & -\gamma(e^{ikb} + 1) \\ -\gamma(1 + e^{-ikb}) & 2\gamma - \omega^2 M_2 \end{vmatrix} = 0 \Rightarrow \omega^2 = \gamma \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm \gamma \left[\left(\frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4}{M_1 M_2} \sin^2 \frac{kb}{2} \right]^{\frac{1}{2}}$$



optical branch

acoustic branch

$$\rightarrow k = \frac{2\pi}{\lambda}$$

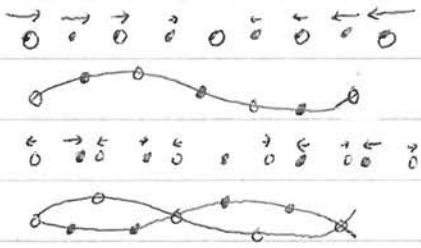
now the dispersion relation has a higher frequency (optical) branch and a lower frequency (acoustic) branch.

In general, for a crystal that has at least two atoms in its primitive cell (which may or may not be different), the dispersion relation exhibits two types of phonon (optical & acoustic).

acoustic mode - M_1 and M_2 oscillate in phase
 - corresponds to sound wave in long wavelength limit, hence the name. ($k \rightarrow 0$)

optical mode - M_1 and M_2 oscillate in antiphase
 - interact strongly with EM radiation in polar crystals, hence the name.

- A { longitudinal acoustic (LA)
- transverse acoustic (TA)
- O { longitudinal optical (LO)
- transverse optical (TO)



(very rough sketches!)

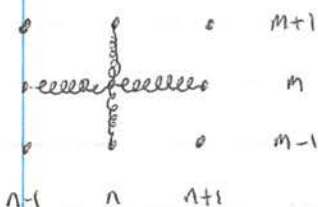
So often the optical/acoustic branches are degenerate.

NB: For a crystal with $N \geq 2$ atoms in the primitive cell, there are...
 { 3 acoustic modes (1x LA, 2x TA) (or d=dimension)
 3N-3 optical modes
 (or d(N-1))

dN modes in total

Example 3) **Square Atomic Lattice** Consider a 2D lattice of atoms each of mass M .

Note that there is only one atom in the primitive cell this time, so we don't expect optical and acoustic branches in the dispersion relation.



As before, consider only nearest neighbour interactions.
This time atom can oscillate in x and y directions.
(a = equilibrium separation)

$$F = ma \text{ (} \rightarrow \text{): } F_x = \gamma(u_{n+1,m} - u_{n,m}) - \gamma(u_{n,m} - u_{n-1,m})$$

$$F = ma \text{ (} \uparrow \text{): } F_y = \gamma(u_{n,m+1} - u_{n,m}) - \gamma(u_{n,m} - u_{n,m-1})$$

$$\text{Since } M \frac{d^2 u_{n,m}}{dt^2} = F_x + F_y \Rightarrow \boxed{M \ddot{u}_{n,m} = \gamma [(u_{n+1,m} - 2u_{n,m} + u_{n-1,m}) + (u_{n,m+1} - 2u_{n,m} + u_{n,m-1})]}$$

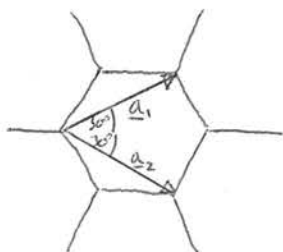
Ansatz $u_{n,m}(t) = \underline{A}_k e^{i(nk_x a + mk_y a - \omega t)}$ is a plane wave (as usual, defined only on lattice sites)

$$\Rightarrow \boxed{\omega = \pm \sqrt{\frac{2\gamma}{M} (2 - \cos(k_x a) - \cos(k_y a))}} \text{ dispersion relation (only positive root is physical)}$$

NB: For $k \equiv k_x, k_y = 0$; $\omega = \pm \sqrt{\frac{2\gamma}{M} (1 - \cos(ka))}$ (same as for the atomic chain)

For $k \equiv k_x = k_y$; $\omega = \pm \sqrt{\frac{2\gamma}{M} (2 - 2\cos(ka))}$ (same form)

Example 4) **Hexagonal Atomic Lattice (i.e. Graphene)** Consider a 2D hexagonal lattice of atoms each of mass M .



First, let us define primitive lattice vectors such that $|a_1| = |a_2| = a$

$$\underline{a}_1 = a \cos 30^\circ \hat{x} + a \sin 30^\circ \hat{y} = \frac{\sqrt{3}}{2} a \hat{x} + \frac{1}{2} a \hat{y}$$

$$\underline{a}_2 = a \cos 30^\circ \hat{x} - a \sin 30^\circ \hat{y} = \frac{\sqrt{3}}{2} a \hat{x} - \frac{1}{2} a \hat{y}$$

As with the molecular chain, $u_{n,m}$ = displacement of the $(n,m)^{\text{th}}$ primary atom

$v_{n,m}$ = displacement of the $(n,m)^{\text{th}}$ secondary atom

NB: Each atom has 3 bonds.

As we saw with the atomic chain, the displacement of the atom under consideration will come with a minus sign in Hooke's Law, following in the spirit of example 1 (except now with 3 bonds per atom):

$$\begin{cases} M \ddot{u}_{n,m} = \gamma (v_{n,m} - u_{n,m}) + \gamma (v_{n,m+1} - u_{n,m}) + \gamma (v_{n-1,m} - u_{n,m}) \\ M \ddot{v}_{n,m} = \gamma (u_{n,m} - v_{n,m}) + \gamma (u_{n+1,m} - v_{n,m}) + \gamma (u_{n,m+1} - v_{n,m}) \end{cases}$$

Now there are 2 atoms per unit cell, so we expect optical and acoustic branches in the dispersion relation.

$$\text{Ansatz } \begin{cases} u_{n,m}(t) = u_{\mathbf{k}} e^{i(n\mathbf{k}\cdot\mathbf{a}_1 + m\mathbf{k}\cdot\mathbf{a}_2 - \omega t)} = u_{\mathbf{k}} \exp \left[i \left(n \frac{\sqrt{3}}{2} k_x a + n \frac{k_y a}{2} + m \frac{\sqrt{3}}{2} k_x a - \frac{m k_y a}{2} \right) \right] e^{-i\omega t} \\ v_{n,m}(t) = v_{\mathbf{k}} e^{i(n\mathbf{k}\cdot\mathbf{a}_1 + m\mathbf{k}\cdot\mathbf{a}_2 - \omega t)} = v_{\mathbf{k}} \exp \left[i \left(n \frac{\sqrt{3}}{2} k_x a + n \frac{k_y a}{2} + m \frac{\sqrt{3}}{2} k_x a - \frac{m k_y a}{2} \right) \right] e^{-i\omega t} \end{cases}$$

Now we need to solve to find the dispersion relation...

$$\begin{aligned} \dot{u}_{n,m} &= -i\omega u_{n,m} & \text{and same for } v_{n,m} \\ \ddot{u}_{n,m} &= -\omega^2 u_{n,m} \end{aligned}$$

$$\begin{aligned} u_{n+1,m} &= e^{i(\mathbf{k}\cdot\mathbf{a}_1)} u_{n,m} & \text{and same for } v_{n,m} \\ u_{n,m+1} &= e^{i(\mathbf{k}\cdot\mathbf{a}_2)} u_{n,m} \end{aligned}$$

$$\therefore \begin{cases} -M\omega^2 u_{n,m} = \gamma (v_{n,m} - u_{n,m}) + \gamma (e^{-i\mathbf{k}\cdot\mathbf{a}_2} v_{n,m} - u_{n,m}) + \gamma (e^{-i\mathbf{k}\cdot\mathbf{a}_1} v_{n,m} - u_{n,m}) \\ -M\omega^2 v_{n,m} = \gamma (u_{n,m} - v_{n,m}) + \gamma (e^{i\mathbf{k}\cdot\mathbf{a}_1} u_{n,m} - v_{n,m}) + \gamma (e^{i\mathbf{k}\cdot\mathbf{a}_2} u_{n,m} - v_{n,m}) \end{cases}$$

Let us drop the subscripts for clarity...

$$\begin{pmatrix} -M\omega^2 + 3\gamma & -\gamma(1 + e^{-i\mathbf{k}\cdot\mathbf{a}_2} + e^{-i\mathbf{k}\cdot\mathbf{a}_1}) \\ -\gamma(1 + e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{i\mathbf{k}\cdot\mathbf{a}_2}) & -M\omega^2 + 3\gamma \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \underline{0} \quad \text{NB: only non-trivial solution when } \det \underline{M} = 0$$

$$(3\gamma - M\omega^2)^2 - \gamma^2 (1 + e^{-i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2})(1 + e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{i\mathbf{k}\cdot\mathbf{a}_2}) = 0$$

$$1 + e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{i\mathbf{k}\cdot\mathbf{a}_2} + e^{-i\mathbf{k}\cdot\mathbf{a}_1} + 1 + e^{i\mathbf{k}\cdot(\mathbf{a}_2 - \mathbf{a}_1)} + e^{-i\mathbf{k}\cdot\mathbf{a}_2} + 1 + e^{i\mathbf{k}\cdot(\mathbf{a}_1 - \mathbf{a}_2)} =$$

$$3 + 2 \cos(\mathbf{k}\cdot\mathbf{a}_1) + 2 \cos(\mathbf{k}\cdot\mathbf{a}_2) + 2 \cos(\mathbf{k}\cdot(\mathbf{a}_1 - \mathbf{a}_2)) \equiv X$$

$$\text{So } (3\gamma - M\omega^2)^2 - \gamma^2 X = 0$$

$$3\gamma - M\omega^2 = \pm \gamma \sqrt{X}$$

$$M\omega^2 = 3\gamma \pm \gamma \sqrt{X}$$

$$\omega^2 = \frac{3\gamma}{M} \pm \frac{\gamma}{M} \sqrt{X}$$

$$\omega = \sqrt{\frac{3\gamma}{M} \pm \frac{\gamma}{M} \sqrt{X}}$$

Now we just need a simplified expression for X ...

$$X = 1 + \underbrace{e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{i\mathbf{k}\cdot\mathbf{a}_2} + e^{-i\mathbf{k}\cdot\mathbf{a}_2} + e^{-i\mathbf{k}\cdot\mathbf{a}_1}}_{\left(e^{i\frac{\sqrt{3}}{2}k_x a} + e^{-i\frac{\sqrt{3}}{2}k_x a}\right)\left(e^{i\frac{k_y a}{2}} + e^{-i\frac{k_y a}{2}}\right)} + \underbrace{e^{i\mathbf{k}\cdot(\mathbf{a}_1 - \mathbf{a}_2)} + 1 + 1 + e^{-i\mathbf{k}\cdot(\mathbf{a}_1 - \mathbf{a}_2)}}_{\left(e^{i\mathbf{k}\cdot\frac{(\mathbf{a}_1 - \mathbf{a}_2)}{2}} + e^{-i\mathbf{k}\cdot\frac{(\mathbf{a}_1 - \mathbf{a}_2)}{2}}\right)^2}$$

$$= 1 + 4 \cos\left(\frac{\sqrt{3}}{2}k_x a\right) \cos\left(\frac{k_y a}{2}\right) + \left(e^{i\frac{k_y a}{2}} + e^{-i\frac{k_y a}{2}}\right)^2$$

$$= 1 + 4 \cos\left(\frac{\sqrt{3}}{2}k_x a\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right)$$

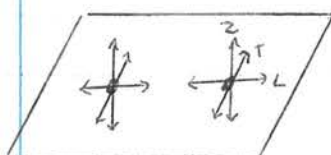
$$\Rightarrow \omega = \sqrt{\frac{3\gamma}{M} \pm \frac{\gamma}{M} \left[1 + 4 \cos\left(\frac{\sqrt{3}}{2}k_x a\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right) \right]} \quad \text{dispersion relation}$$

higher $\omega \Rightarrow$ optical branch
lower $\omega \Rightarrow$ acoustic branch

Let us consider a sheet of graphene in 3D space ...

We have 2 atoms per unit cell and 3 dimensions \Rightarrow $\begin{cases} 3 \text{ acoustic modes} \\ 3 \text{ optical modes} \end{cases}$
(say a & b)

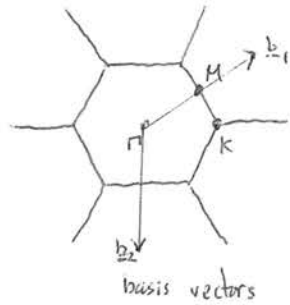
The modes are now associated with $\begin{cases} \text{out-of-plane} & (Z) \\ \text{in-plane longitudinal} & (L) \\ \text{in-plane transverse} & (T) \end{cases}$



a b

So now not only do we have optical and acoustic branches but each branch is degenerate into 3 (Z, L and T).

Let us sketch the Brillouin zone of graphene and mark the points of high symmetry...



$$\begin{aligned} \Gamma &: \begin{pmatrix} 0 \\ 0 \end{pmatrix} && \text{(in reciprocal space)} \\ K &: \frac{2\pi}{a} \begin{pmatrix} \frac{1}{\sqrt{3}} \\ \frac{1}{3} \end{pmatrix} \\ M &: \frac{2\pi}{a} \begin{pmatrix} \frac{1}{\sqrt{3}} \\ 0 \end{pmatrix} \end{aligned}$$

where $\underline{b}_1 = \frac{2\pi}{a\sqrt{3}} \begin{pmatrix} 1 \\ \sqrt{3} \end{pmatrix}$, $\underline{b}_2 = \frac{2\pi}{a\sqrt{3}} \begin{pmatrix} 1 \\ -\sqrt{3} \end{pmatrix}$ and $b = |\underline{b}_1| = |\underline{b}_2| = \frac{4\pi}{a\sqrt{3}}$

These high symmetry k-values are often marked on the dispersion relation

NB: Due to the symmetry of graphene, the ZA/ZO and LA/LO branches cross at K.
(D6h point group sym.)

Example 5) **Bilayer Graphene** The analytic treatment of bilayer graphene is publication territory. It was actually published in 2013 by McClann & Koshino.