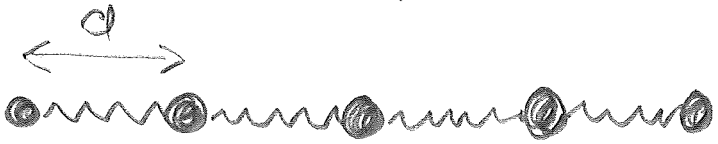
Lecture 12 | Phonons

Crystal vibrations classic theory

Consider a simple harmonic chain of atoms



$$H = \sum_n \frac{P_n^2}{2M} + \frac{\alpha}{2} \sum (x_n - x_{n+1} + a)^2$$

In general for any interaction between the atoms for small displacement we can expand it near equilibrium

$$V(x - x') = V(a) + V'(a)(x - x') + V''(a)\frac{(x - x')^2}{2} + \dots$$

Linear term in $x - x'$ should vanish if without displacement lattice is in equilibrium. Thus we have quadratic Hamiltonian written above.

Equation of motion is then

$$M \ddot{x}_n = \alpha (x_{n-1} + x_{n-1} - 2x_n)$$

Such kind of equations are solved by going to a Fourier space

$$X_n = X_0 e^{-i\omega t + ikna}$$

If we choose periodic boundary conditions with N atom on length L then

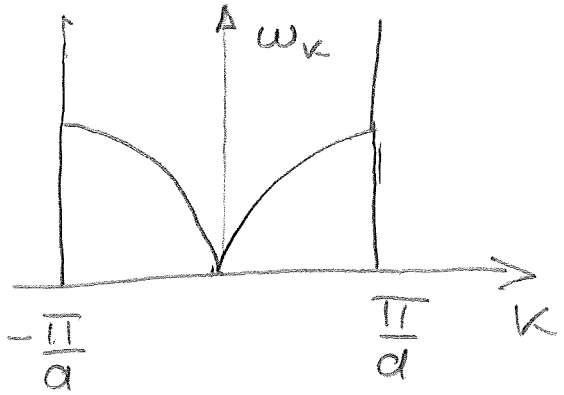
$$K = K_n = \frac{2\pi}{L} n = \frac{2\pi}{a} \frac{n}{N}$$

Changing K by $\frac{2\pi}{a}$ doesn't change coordinate of the atoms (compare to Bloch's waves).

$$M\omega^2 X_n = \varkappa (2X_n - X_{n-1} - X_{n+1}) =$$
$$= \varkappa e^{-i\omega t + ikna} \left(2 - e^{-ika} - e^{ika}\right) \Rightarrow$$

$$M\omega^2 X_n = \varkappa X_n (2 - 2\cos ka) \Rightarrow$$

$$\omega_K^2 = \frac{\varkappa}{M} 2(1 - \cos ka) = \frac{4\varkappa}{m} \sin^2 \frac{ka}{2}$$



The interval $-\frac{\pi}{a} < K < \frac{\pi}{a}$ corresponds to the Brillouin zone

For $K \to 0$ we have linear spectrum

$\omega = \sqrt{\frac{\varkappa}{M}}\, Ka = cK$ with the sound velocity $c = a\sqrt{\frac{\varkappa}{M}}$. This can be easily understood if for slowly varying displacement we replace $X_n - X_{n+1} = u_n - u_{n+1} = \frac{du}{dn} = a\frac{du}{dx}$

Then replacing $\sum_n \to \frac{1}{a}\int dx$ we get the Lagrangean

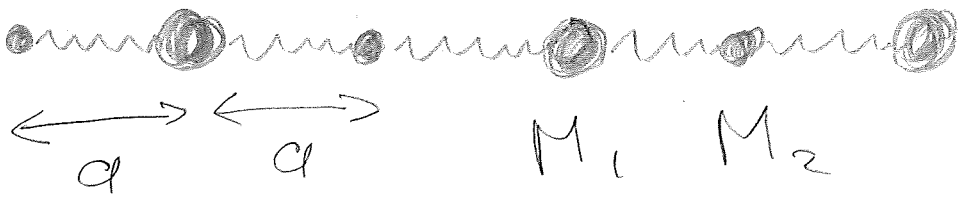
$$\int \frac{dx\,dt}{a}\left(\frac{M}{2}\left(\frac{\partial u}{\partial t}\right)^2 - \frac{\varkappa}{2}a^2\left(\frac{\partial u}{\partial x}\right)^2\right)$$

which gives the wave equation

$$\frac{M}{2}\frac{\partial^2 u}{\partial t^2} - \frac{\varkappa}{2}a^2\frac{\partial^2 u}{\partial x^2} = 0.$$

The mode with $\omega \propto K$ is called acoustic mode

Let us consider more complicated lattice with basis



For simplicity we consider the same distance a between the particles and the same elastic constants. Only the masses M_1 and M_2 are different. Denoting by $u_1(2n)$ and $u_2(2n+1)$ displacements of the first and second atom in the n-th cell we obtain

$$M_1 \ddot{u}_1(2n) = \varkappa \left[u_2(2n+1) + u_2(2n-1) - 2u_1(2n)\right]$$

$$M_2 \ddot{u}(2n+1) = \varkappa \left[u_1(2n+2) + u_1(2n) - 2u_1(2n+1)\right]$$

or in Fourier space

$$M_1 \omega^2 u_1(k) = 2\varkappa u_1(k) - 2\varkappa \cos(ka) \cdot u_2(k)$$

$$M_2 \omega^2 u_2(k) = 2\varkappa u_2(k) - 2\varkappa \cos(ka) \cdot u_1(k)$$

To find the frequency ω we should solve

$$\begin{vmatrix} M_1\omega^2 - 2\varkappa & 2\varkappa\cos ka \\ 2\varkappa\cos ka & M_2\omega^2 - 2\varkappa \end{vmatrix} = 0$$

This gives two roots

$$\omega_\pm^2 = \varkappa\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \varkappa\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2 ka}{M_1 M_2}}$$

ω_- is acoustic mode with

$$\omega_-^2(k\to 0) = \frac{2\varkappa\, \sin^2 ka}{M_1+M_2}$$

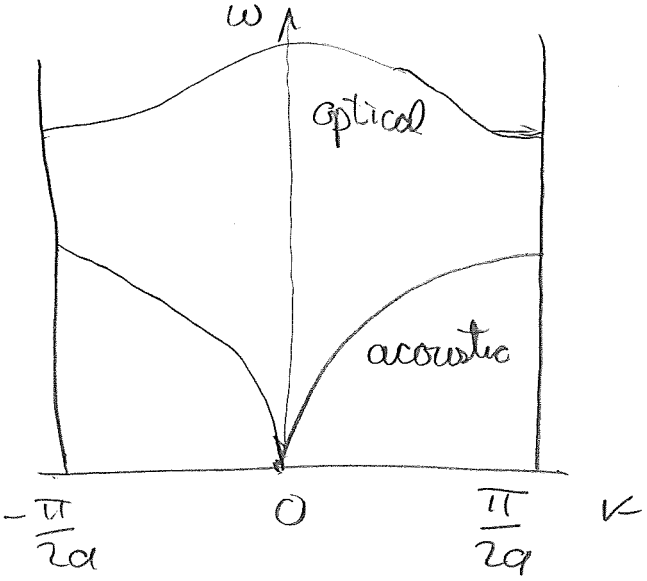
Another branch $\omega_+^2(k\to 0) = 2\varkappa\left(\frac{1}{M_1}+\frac{1}{M_2}\right)$ doesn't go to zero for $k\to 0$. It is called optical mode. Taking $k=0$ in the original system of equations we obtain

$$M_1\omega^2 u_1 = 2\varkappa(u_1-u_2) = -M_2\omega^2 u_2$$

Acoustic branch corresponds to $u_1 = u_2$, $\omega = 0$ particles are moving together

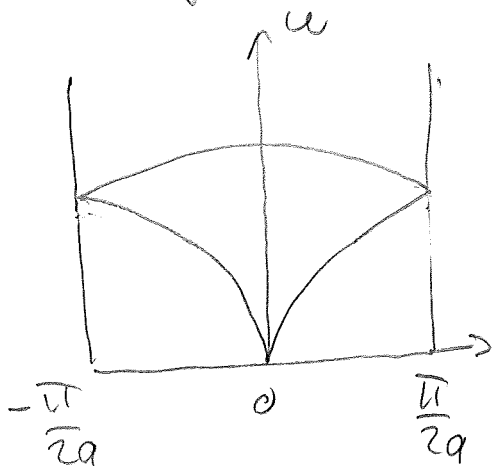
In the optical branch particles move in the opposite directions 

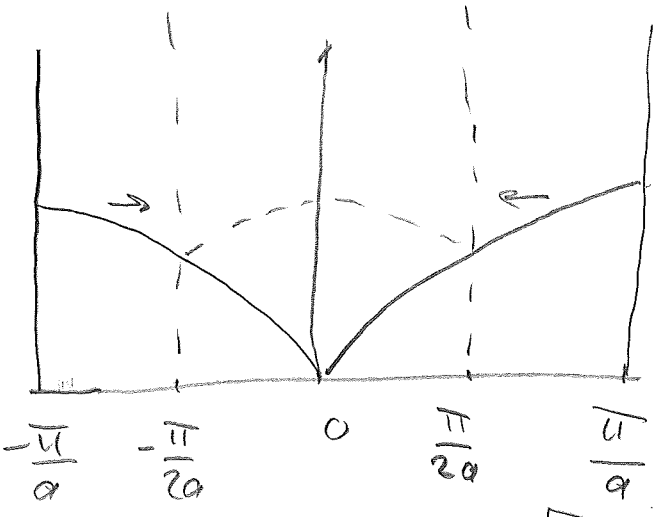
The name optical is because in ionic crystals (like NaCl) two type of atoms have opposite charge that gives oscillating dipole moment. Then these oscillations can interact with electromagnetic radiation



These $\omega(\kappa)$ spectra reminds us electronic band structure. The analogy would be more transparent if we look what happens with these modes when $M_1 \to M_2$

For $M_1 = M_2$ the optical and acoustic modes will join at $K = \frac{\pi}{2a}$





But for $M_1 = M_2$ the real period of the lattice is a rather than $2a$. and the Brillouin zone is from $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$

Folding it to half corresponds to doubling of unit cell which gives spectra of the left figure. The effect of changing the masses of alternating atoms of the chain is to introduce new zone boundaries at $\pm\frac{\pi}{2a}$

The frequency is no longer continuous across this boundary - a gap appears

In general 3-d case energy is

$$E = \sum_i \frac{M}{2}\left(\frac{\partial u_i}{\partial t}\right)^2 + \frac{1}{2}\sum_{i\neq j} V(R_i - R_j + u_i - u_j)$$

expanding in u_i, u_j we obtain

$$E = \sum_i \frac{M}{2}\left(\frac{\partial u_i}{\partial t}\right)^2 + \frac{1}{4}\sum_{ij} \Phi_{\mu\nu}(R_i - R_j)(u_i - u_j)_\mu (u_i - u_j)_\nu$$

where $\Phi_{\mu\nu}(R) = \dfrac{\partial^2 V(R)}{\partial R_\mu \partial R_\nu}$

We can rewrite it as

$$E = \sum_i M\left(\frac{\partial u_i}{\partial t}\right)^2 + \frac{1}{2}\sum_{ij} D_{\mu\nu}(R_i - R_j)\, u_{\mu i}\, u_{\nu j}$$

with $D_{\mu\nu}(R_i - R_j) = \delta_{ij} \sum_e \Phi_{\mu\nu}(R_i - R_e) - \Phi_{\mu\nu}(R_i - R_j)$

Equations of motion are

$$M\frac{\partial^2 u_{i\mu}}{\partial t^2} = -\sum_j D_{\mu\nu}(R_i - R_j)\, u_{j\nu}$$

Substituting $u_{i\mu}(t) = e_\mu e^{iKR_i - i\omega t}$

where e_μ are components of the polarization vector we get the eigenvalue problem

$$M\omega^2 e_\mu = D_{\mu\nu}(K)\, e_\nu$$

with $D_{\mu\nu}(K) = \sum_i D_{\mu\nu}(R_i)\, e^{-i\vec{K}\cdot\vec{R}_i}$

For small values of K $D_{\mu\nu}(K)$ can be expressed through elastic constants

$$D_{\mu\nu}(K) = \lambda K_\mu K_\nu + 2\mu K_\gamma K_\gamma \delta_{\mu\nu}$$

where λ and μ are Lamé coeffitients

$$E_{ee} = \int d^3r \left[\frac{\lambda}{2} \frac{\partial u_\alpha}{\partial r_\alpha} \frac{\partial u_\beta}{\partial r_\beta} + \mu \left(\frac{\partial u_\alpha}{\partial r_\beta} \right)^2 \right]$$

Quantization of lattice vibrations

Let us refresh the physics of harmonic oscilator in operator formalism.

$$H = \frac{p^2}{2m} + \frac{\varkappa x^2}{2} \quad \text{with momentum } p = -i\hbar\frac{\partial}{\partial x}$$

$$[p, x] = -i\hbar$$

Let us introduce raising and lowering operators

$$a^+ = \left(\frac{m\omega_0}{2\hbar}\right)^{1/2}\left[x - \frac{ip}{m\omega_0}\right] \qquad \omega_0 = \sqrt{\frac{\varkappa}{m}}$$

$$a = \left(\frac{m\omega_0}{2\hbar}\right)^{1/2}\left[x + \frac{ip}{m\omega_0}\right]$$

Multiplying we obtain

$$a^+ a = \frac{m\omega_0}{2\hbar}\left(x^2 + \frac{p^2}{m\omega_0} - i\frac{1}{m\omega_0}[p, x]\right) =$$

$$= \frac{m\omega_0}{2\hbar}\left(x^2 + \frac{p^2}{m\omega_0} - \frac{\hbar}{m\omega_0}\right)$$

$$a\,a^+ = \frac{m\omega_0}{2\hbar}\left(x^2 + \frac{p^2}{m\omega_0} + \frac{\hbar}{m\omega_0}\right)$$

a and a^+ satisfy Bose commutation relations ...

$$[a, a^+] \equiv a a^+ - a^+ a = 1 \,, \quad [a,a] = [a^+, a^+] = 0$$

Hamiltonian can be rewritten as

$$H = \hbar \omega_0 \left(a^+ a + \frac{1}{2} \right)$$

Let us define the ground (vacuum) state

$|0\rangle$ as $a|0\rangle = 0 \Leftrightarrow \left(x + \frac{\hbar}{m\omega_0} \frac{\partial}{\partial x} \right) \psi(x) = 0 \Rightarrow$

$$\psi(x) \propto e^{-\frac{m\omega_0}{\hbar} \frac{x^2}{2}}$$

Then $|n\rangle = \dfrac{(a^+)^n}{(n!)^{1/2}} |0|$

Indeed

$$a^+ a |n\rangle = (n!)^{-1/2} a^+ a \underbrace{a^+ a^+ \ldots a^+}_{n \text{ times}} |0\rangle =$$

$$= (n!)^{-1/2} a^+ a^+ a \underbrace{a^+ \ldots a^+}_{n-1 \text{ times}} + |n\rangle =$$

$$= (n!)^{-1/2} a^+ a^+ a^+ a \underbrace{a^+ \ldots a^+}_{n-2 \text{ times}} + 2n = \ldots$$

$$= \ldots = n|n\rangle. \text{ Thus } H|n\rangle = \sum \omega_k \left(n_k + \frac{1}{2} \right)$$

$$n_k = a_k^+ a$$

We also can rewrite x and p through a and a^+

$$x = \left(\frac{\hbar}{2m\omega_0}\right)^{1/2}(a + a^+), \quad p = i\left(\frac{\hbar m\omega_0}{2}\right)^{1/2}(a^+ - a)$$

Quantum harmonic chain] Fourier:

$$x_n = \frac{1}{N^{1/2}}\sum_k e^{ikan} x_k, \quad x_k = \frac{1}{N^{1/2}}\sum_n e^{-ikan} x_n$$

$$k = \frac{2\pi}{N}\frac{l}{a}$$

$$p_l = \frac{1}{N^{1/2}}\sum_k e^{ikal} p_k, \quad p_k = \frac{1}{N^{1/2}}\sum_m e^{ikam} p_m$$

In real space $[x_l, p_m] = i\hbar\,\delta_{lm}$

In Fourier space

$$[x_k, p_{k'}] = \frac{1}{N}\sum_{l,m} e^{-ikal} e^{ik'am} [x_l, p_m] =$$

$$= \frac{i\hbar}{N}\sum_l e^{ial(k-k')} = i\hbar\,\delta_{k,k'}$$

Thus commutation relations are the same

$$\sum_e (x_e - x_{e+1})^2 = \frac{1}{N} \sum_{e,k,k'} x_k e^{ikal} (1 - e^{ika}) x_{k'} e^{ik'al} (1 - e^{ik'a})$$

$$= \sum_k x_k x_{-k} (1 - e^{ika})(1 - e^{-ika}) =$$

$$= \sum_k x_k x_{-k} \, 2(1 - \cos ka)$$

In the same way $\sum_e p_e^2 = \sum_k p_k p_{-k}$

and the Hamiltonian

$$H = \frac{1}{2M} \sum p_k p_{-k} + \frac{M}{2} \sum \omega_k^2 x_k x_{-k}$$

with $\omega_k = \sqrt{\frac{\varepsilon}{M} 2(1 - \cos ka)}$

We define like for the single harmonic oscilator

$$a_k = \left(\frac{m\omega_k}{2\hbar}\right)^{1/2} \left(x_k + \frac{i}{m\omega_k} p_{-k} \right)$$

$$a_k^+ = \left(\frac{m\omega_k}{2\hbar}\right)^{1/2} \left(x_{-k} - \frac{i}{m\omega_k} p_k \right)$$

They satisfy Bose commutation relations

$$[a_k, a_{k'}^+] = \delta_{k,k'} \; ; [a_k, a_{k'}] = [a_k^+, a_{k'}^+] = 0$$

and the Hamiltonian

$$H = \sum_k \omega_k \left(a_k^+ a_k + \frac{1}{2}\right)$$

These collective modes are called phonons

and the energy is $E = \sum \omega_k \left(n_k + \frac{1}{2}\right)$

We say that the operators a_k^+ (a_k) create (annihilate) a phonon, a quasiparticle with well defined energy - momentum relation. ω_k

The position operator:

$$X_k(t) = \left(\frac{\hbar}{2m\omega_k}\right)^{1/2} \left(a_k e^{-i\omega_k t} + a_{-k}^+ e^{i\omega_k t}\right)$$

$$X_e(t) = \sum \left(\frac{\hbar}{2mN\omega_k}\right)^{1/2} e^{ikal} \left(a_k e^{-i\omega_k t} + a_{-k}^+ e^{i\omega_k t}\right)$$

In 3d solids theory is similar

For interatomic interaction $\sum_{ij} V(R_i - R_j)$

we expand around the lattice points

$$R = R_i^0 + X_i$$

$$Q_\ell(t) = \sum_{k,\lambda} \left(\frac{\hbar}{2NM\omega_{k\lambda}} \right)^{1/2} \vec{e}_{k,\lambda} e^{i\vec{k}\cdot R_\ell} \left(a_{\vec{k},\lambda} e^{-i\omega_{k\lambda}t} + \right.$$

$$\left. + a^{+}_{-\vec{k},\lambda} e^{i\omega_{k\lambda}t} \right)$$

Here M is the ion mass $\vec{e}$ polarization vector

$\lambda = 1, \ldots 3z$, where z - number of atoms per unit cell