Phys. 460 Lecture 15

Crystal vibrations: phonons

We have seen that the interatomic interactions responsible for the cohesion of solids can be represented by a potential energy of the form:

$$U = \frac{1}{2} \sum_{i,j}{}' V(\vec{r}_i - \vec{r}_j).$$

The equilibrium positions of the atoms are determined by the conditions

$$\left. \frac{\partial U}{\partial \vec{r}_i} \right|_{\{\vec{r}_j^{(0)}\}} = 0$$

in the static lattice approximation. For a crystal not too far from its ground state, i.e., at not too high

a temperature, we can thus expand U to quadratic order in the displacements $\vec{x}_i = \vec{r}_i - \vec{r}_i^{(0)}$:

$$U(\{\vec{r}_i\}) \simeq U(\{\vec{r}_i^{(0)}\}) + \frac{1}{2} \sum_{ij} \vec{x}_i \cdot \left. \frac{\partial^2 U}{\partial \vec{r}_i \partial \vec{r}_j} \right|_{\{\vec{r}_k^{(0)}\}} \cdot \vec{x}_j$$

To describe the dynamics of the lattice, we must add to this potential energy the kinetic energy of the ions/atoms:

$$H = \sum_i \frac{\vec{p}_i^{\,2}}{2M} + \frac{1}{2} \sum_{i,j} \vec{x}_i \cdot \left. \frac{\partial^2 U}{\partial \vec{r}_i \partial \vec{r}_j} \right|_{\{\vec{r}_k^{(0)}\}} \cdot \vec{x}_j$$

$$+ U_0 .$$

Here $U_0 = U(\{\vec{r}_i^{(0)}\})$ is the cohesive energy of the crystal in the static lattice approximation. To simplify the notation in the following, let us consider a crystal in one dimension

and with a single atom per unit cell. We will return to the 3D problem and non monatomic bases later. The Hamiltonian is then

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,j} C_{ij} x_i x_j + U_0,$$

where $$C_{ij} = \left. \frac{\partial^2 U}{\partial r_i \partial r_j} \right|_{\{r_k^{(0)}\}}.$$

Let us first consider this Hamiltonian classically. Hamilton's equations are

$$\dot{x}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial x_i}$$

$$\dot{x}_i = \frac{p_i}{m} \qquad \dot{p}_i = -\sum_{j=1}^{N} C_{ij} x_j$$

$$\Rightarrow \quad m \ddot{x}_i = -\sum_{j=1}^{N} C_{ij} x_j$$

To solve these equations of motion, let us make the ansatz

$$x_n(t) = A e^{i(kna - \omega t)} \quad \text{(travelling wave)}$$

$$-m\omega^2 A e^{i(kna-\omega t)} = -\sum_l C_{nl} A e^{i(kla-\omega t)}$$

$$m\omega^2 = \sum_l C_{nl} e^{ik(l-n)a}$$

Note that due to the translational invariance of the Bravais lattice, $C_{nl} = C(n-l)$. Also, inversion symmetry implies $C(n) = C(-n)$. Consequently, we may write

$$m\omega^2 = \sum_n C(n) e^{ikna} \equiv \tilde{C}(k)$$

or $$\boxed{\omega^2(k) = \frac{\tilde{C}(k)}{m}}.$$

Note that $\tilde{C}(k)$ is real:

$$\tilde{C}^*(k) = \sum_n C(n) e^{-ikna} = \sum_{n'} C(-n') e^{ikn'a}$$

$$= \sum_{n'} C(n') e^{ikn'a} = \tilde{C}(k).$$

Note also that $\tilde{C}\left(k + \frac{2\pi}{a}\right) = \tilde{C}(k)$:

$$\tilde{C}\left(k + \frac{2\pi}{a}\right) = \sum_n C(n) e^{ikna} e^{i2\pi n} = \tilde{C}(k)$$

Thus $\omega\left(k + \frac{2\pi}{a}\right) = \omega(k)$; the dispersion relation is periodic in $k \to k + G$, where $G = \frac{2\pi n}{a}$ is a reciprocal lattice vector in 1D.

This follows trivially from the definition of k:

$$x_n(t) = A e^{i(kna - \omega t)}$$

$k \to k + G$

$$x_n(t) = A e^{i(kna - \omega t)} e^{iGna}$$

But na is a 1D Bravais lattice vector, so $e^{iGna} = 1$. Thus the waves with wavenumber k and $k+G$ are physically indistinguishable.

- Group velocity These wave solutions of the equations of motion represent acoustic waves which propagate at a velocity

$$\vec{V}(\vec{k}) = \frac{\partial \omega}{\partial \vec{k}}.$$

For our one dimensional crystal, this becomes $V(k) = \partial\omega/\partial k$.

- Finite crystal These waves are reflected at the boundaries of the crystal. The eigenstates are then standing waves. For many purposes, it is useful to

impose periodic boundary conditions so that travelling waves remain eigenstates:

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

$$A e^{i(k(n+L)a - \omega t)} = A e^{i(kna - \omega t)}$$

$$\Rightarrow e^{ikLa} = 1$$

$$k = \frac{2\pi j}{La} \quad \text{where } j \in \mathbb{Z}.$$

- First Brillouin Zone

Since k and $k+G$ represent the same wave, it is convenient to restrict k to the first Brillouin zone of the reciprocal lattice:

$$-\frac{\pi}{a} < k \leq \frac{\pi}{a}$$

$$k = \frac{2\pi n}{La} \qquad -\frac{L}{2} < n \in \mathbb{Z} \leq \frac{L}{2}$$

There are exactly L distinct values of k allowed by boundary conditions: The number of wavevectors in the 1st Brillouin zone is equal to the number of points in the direct lattice.

- Example consider a lattice with interactions between nearest neighbors only:

$$U = U_0 + \frac{1}{2} \sum_n C (x_n - x_{n-1})^2$$

Then $C(0) = C_{nn} = 2C$

$C(1) = C_{n,n-1} = -C$

$C(-1) = C_{n-1,n} = -C$

all others are zero.

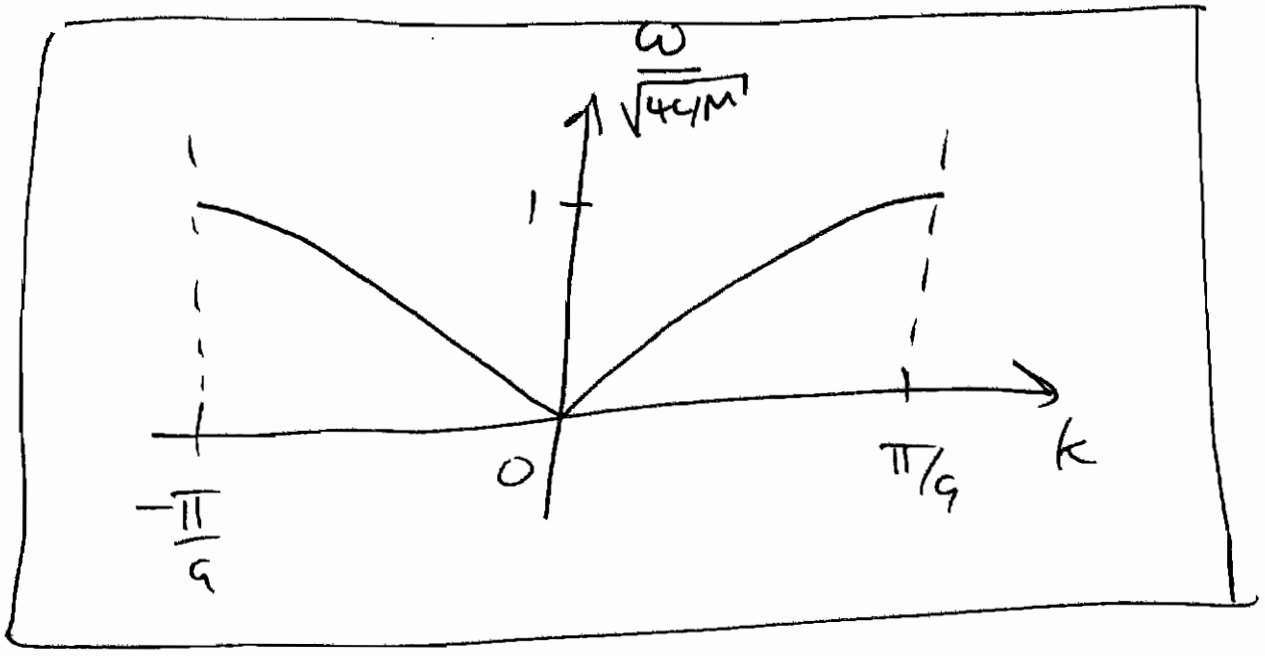
$$\mathcal{C}(k) = C(2 - e^{ikq} - e^{-ikq})$$

$$= 2C(1 - \cos kq)$$

$$\omega^2(k) = \frac{2C}{m}(1-\cos kq)$$

$$= \frac{4C}{m}\sin^2\frac{kq}{2}$$

$$\omega(k) = \sqrt{\frac{4C}{M}}\left|\sin\frac{kq}{2}\right|$$



The group velocity is

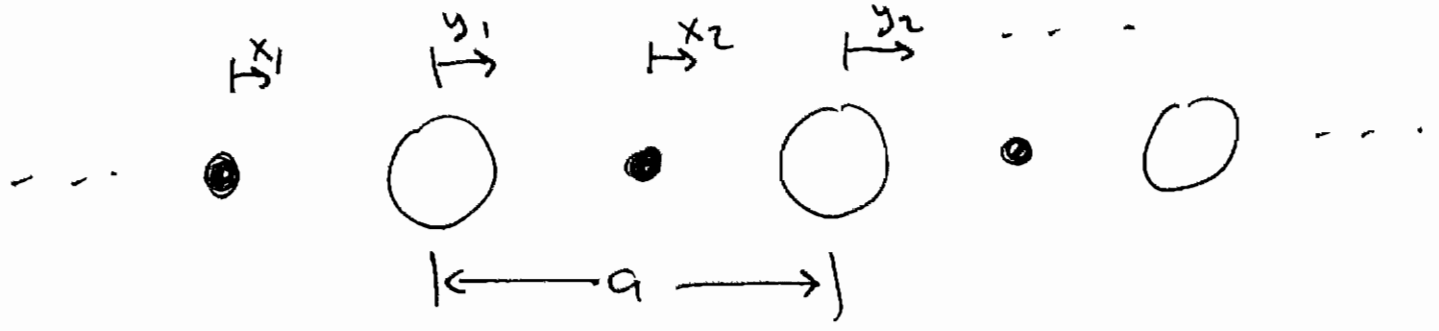
$$|V| = \left|\frac{\partial\omega}{\partial k}\right| = \sqrt{\frac{Cq^2}{m}}\left|\cos\frac{kq}{2}\right|$$

In the long wavelength limit $kq \ll 1$,

$$V_s = \sqrt{\frac{Cq^2}{m}} \quad \text{(speed of sound)}.$$

• Optical phonons

Consider a 1D lattice with a basis of two atoms, of mass m and M, respectively:



Assuming nearest neighbor interactions of the form

$$\frac{1}{2} C (X_1 - y_1)^2$$

between atoms labeled by their displacements X_1 and y_1, the equations of motion are

$$m \ddot{x}_n = C(y_n + y_{n-1} - 2x_n)$$

$$M \ddot{y}_n = C(x_{n+1} + x_n - 2y_n)$$

Ansatz:

$$x_n(t) = A\, e^{i(kna - \omega t)}$$

$$y_n(t) = B\, e^{i(kna - \omega t)}$$

$$-m\omega^2 A = C\left(1 + e^{-ika}\right)B - 2C\,A$$

$$-M\omega^2 B = C\left(e^{ika} + 1\right)A - 2C\,B$$

Such a solution exists if

$$0 = \begin{vmatrix} 2C - m\omega^2 & -C\left(1 + e^{-ika}\right) \\ -C\left(e^{ika} + 1\right) & 2C - M\omega^2 \end{vmatrix}$$

or

$$0 = mM\omega^4 - 2C(m+M)\omega^2 + 2C^2(1 - \cos ka)$$

Solution:

$$\omega_{\pm}^2 = \frac{C}{mM}\left(m+M \pm \sqrt{m^2+M^2+2mM\cos kq}\right)$$

For $|kq| \ll 1$, we have

$$\omega_{\pm}^2 \simeq \frac{C}{mM}\left(m+M \pm \sqrt{(m+M)^2 - mM k^2 q^2}\right)$$

$$\omega_-^2 \underset{kq\ll 1}{\simeq} \frac{1}{2}\frac{C}{m+M}(kq)^2 \qquad \text{(acoustic mode)}$$

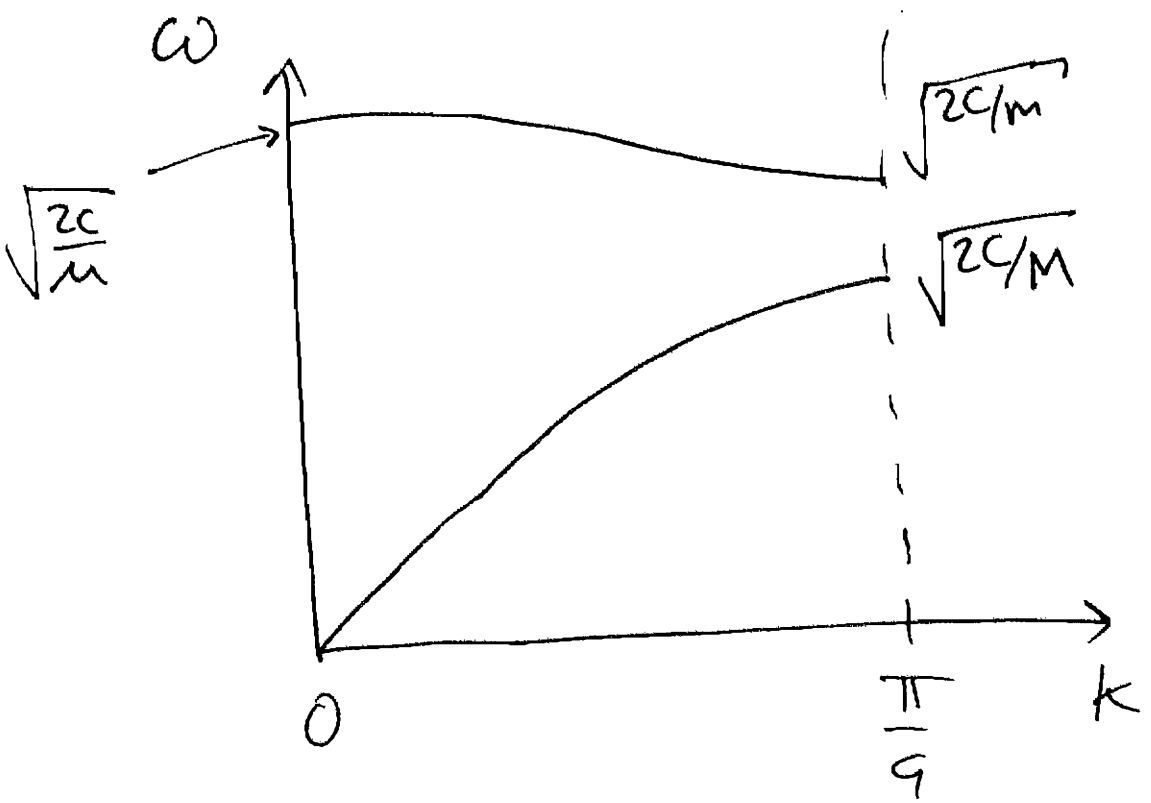
$$\omega_+^2 \underset{kq\ll 1}{\simeq} 2C\left(\frac{1}{m}+\frac{1}{M}\right) \qquad \text{(optical mode)}$$

At the Brillouin zone boundary $k = \pm\frac{\pi}{q}$, the modes have

frequencies

$$\omega_+^2 = \frac{2C}{m}$$

$$\omega_-^2 = \frac{2C}{M}$$



The displacement amplitudes $A_\pm$, $B_\pm$ are solutions of

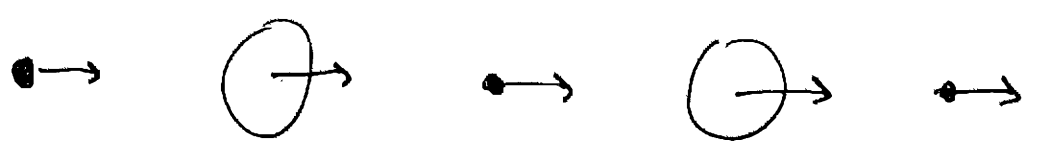
$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 2C - m\omega_\pm^2 & -C(1+e^{-ika}) \\ -C(1+e^{ika}) & 2C - M\omega_\pm^2 \end{pmatrix} \begin{pmatrix} A_\pm \\ B_\pm \end{pmatrix}$$

Consider the modes for $k = 0$:

Acoustic mode $\omega_-(0) = 0$:

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 2C & -2C \\ -2C & 2C \end{pmatrix} \begin{pmatrix} A_- \\ B_- \end{pmatrix}$$

$$A_- - B_- = 0 \qquad A_- = B_-$$



(overall translation)

Optical mode:

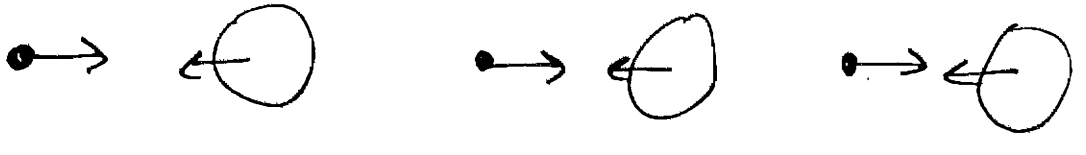
$$\omega_+^2(0) = 2C\left(\frac{1}{m} + \frac{1}{M}\right)$$

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 2C - 2C\left(1 + \frac{m}{M}\right) & -2C \\ -2C & 2C - 2C\left(1 + \frac{M}{m}\right) \end{pmatrix} \begin{pmatrix} A \\ B_+ \end{pmatrix}$$

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{pmatrix} -\frac{2Cm}{M} & -2C \\ -2C & -2C\frac{M}{m} \end{pmatrix} \begin{pmatrix} A_+ \\ B_+ \end{pmatrix}$$

$$\frac{m}{M} A_+ + B_+ = 0$$

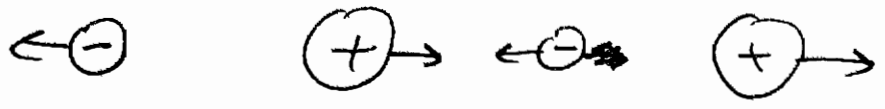
$$\Rightarrow \quad B_+ = -\frac{m}{M} A_+$$

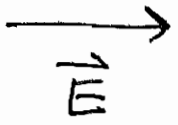


"molecular" vibration

In the optical mode at k=0, each unit cell vibrates independently like a diatomic molecule.

If it is an ionic crystal, such a mode will be induced





by the electric field of an electromagnetic wave. The wavelength of the phonon will be determined by the wavelength of the E&M wave. Hence the origin of the term "optical phonon."