

Vibrations of crystals with diatomic basis in one-dimension:

When two or more atoms per primitive basis is considered (like NaCl, or diamond structure), the dispersion relation shows new features in crystals. Consider a linear chain of identical atoms of mass M per unit cell with equilibrium positions na and $na + d$, where

d is taken $d \leq \frac{a}{2}$ such that the force between neighboring atoms

depends on whether this separation is d or $a - d$. Since $a - d$ is more than d , the force is stronger for the pairs separated by d than that separated by $a - d$ as long as only nearest neighbor interactions are concerned. We will assume that the diatomic linear chain is connected by springs of alternating strengths C_1 and C_2 such that $C_1 \geq C_2$ as shown in figure 64. The displacements of the atoms that oscillates about the sites na and $na + d$, are $u_1(na)$ and $u_2(na)$, respectively.

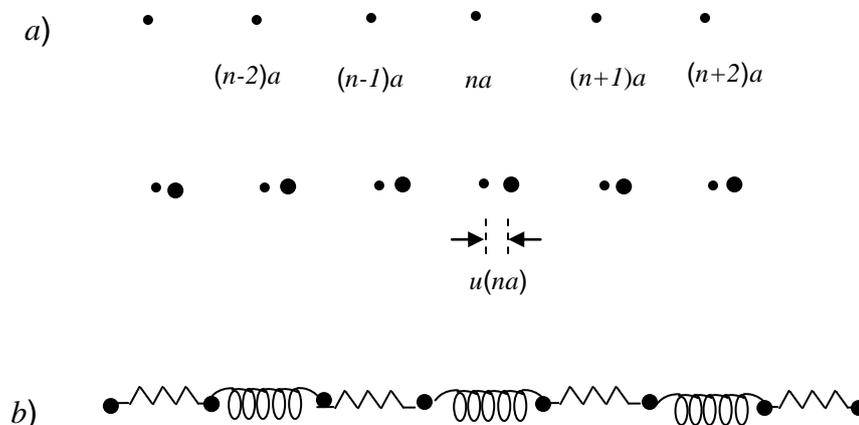


Figure 64: a) The displacement $u(na)$ of an ion from its equilibrium position at na , at any instant.

b) The harmonic approximation for 1-D Bravais lattice describes a model in which each ion is tied to its nearest-neighbor by two perfect springs with spring constants C_1 and C_2 .

The harmonic potential energy can be written as;

$$U^{quad} = \frac{1}{2}C_1 \sum_n [u_1(na) - u_2(na)]^2 + \frac{1}{2}C_2 \sum_n [u_2(na) - u_1((n+1)a)]^2 .$$

The equations of motion

$$M\ddot{u}_1(na) = -\frac{\partial U^{quad}}{\partial u_1(na)}$$

and

$$M\ddot{u}_2(na) = -\frac{\partial U^{quad}}{\partial u_2(na)}$$

can be expressed as:

$$M\ddot{u}_1(na) = -C_1[u_1(na) - u_2(na)] - C_2[u_1(na) - u_2((n-1)a)] ,$$

and

$$M\ddot{u}_2(na) = -C_1[u_2(na) - u_1(na)] - C_2[u_2(na) - u_1((n+1)a)] .$$

Again we are seeking for solutions in the form of traveling waves, with angular frequency ω and wave vector k , like:

$$u_1(na) = \varepsilon_1 e^{i(kna - \omega t)} ,$$

$$u_2(na) = \varepsilon_2 e^{i(kna - \omega t)} .$$

Here ε_1 and ε_2 are the amplitudes of the traveling waves and needed to be determined within each primitive cell.

By substituting these solutions into the equations of motion, we get the following coupled homogenous equations:

$$[M\omega^2 - (C_1 + C_2)]\varepsilon_1 + (C_1 + C_2 e^{-ika})\varepsilon_2 = 0$$

$$[(C_1 + C_2 e^{ika})\varepsilon_1 + [M\omega^2 - (C_1 + C_2)]\varepsilon_2 = 0 .$$

The homogenous linear equations have a solution only if the determinant of the coefficients of the unknowns ε_1 and ε_2 vanishes:

$$\begin{vmatrix} M\omega^2 - (C_1 + C_2) & C_1 + C_2 e^{-ika} \\ C_1 + C_2 e^{ika} & M\omega^2 - (C_1 + C_2) \end{vmatrix} = 0 .$$

Expanding the determinant to get:

$$[M\omega^2 - (C_1 + C_2)]^2 = |C_1 + C_2 e^{-ika}|,$$

or

$$[M\omega^2 - (C_1 + C_2)]^2 = C_1^2 + C_2^2 + 2C_1C_2 \cos ka,$$

$$(M\omega^2)^2 - 2M\omega^2(C_1 + C_2) + (C_1 + C_2)^2 - [C_1^2 + C_2^2 + 2C_1C_2 \cos ka] = 0.$$

Use the quadratic formula to get the roots:

$$\omega^2 = \frac{C_1 + C_2}{M} \pm \frac{1}{M} [C_1^2 + C_2^2 + 2C_1C_2 \cos ka]^{1/2}.$$

Or

$$\omega_1^2 = \frac{C_1 + C_2}{M} + \frac{1}{M} [C_1^2 + C_2^2 + 2C_1C_2 \cos ka]^{1/2},$$

and

$$\omega_2^2 = \frac{C_1 + C_2}{M} - \frac{1}{M} [C_1^2 + C_2^2 + 2C_1C_2 \cos ka]^{1/2}.$$

Here ω_1 and ω_2 represent the frequencies near the optical and acoustical regions of the electromagnetic spectrum (optical and acoustical branches). (See figure 65).

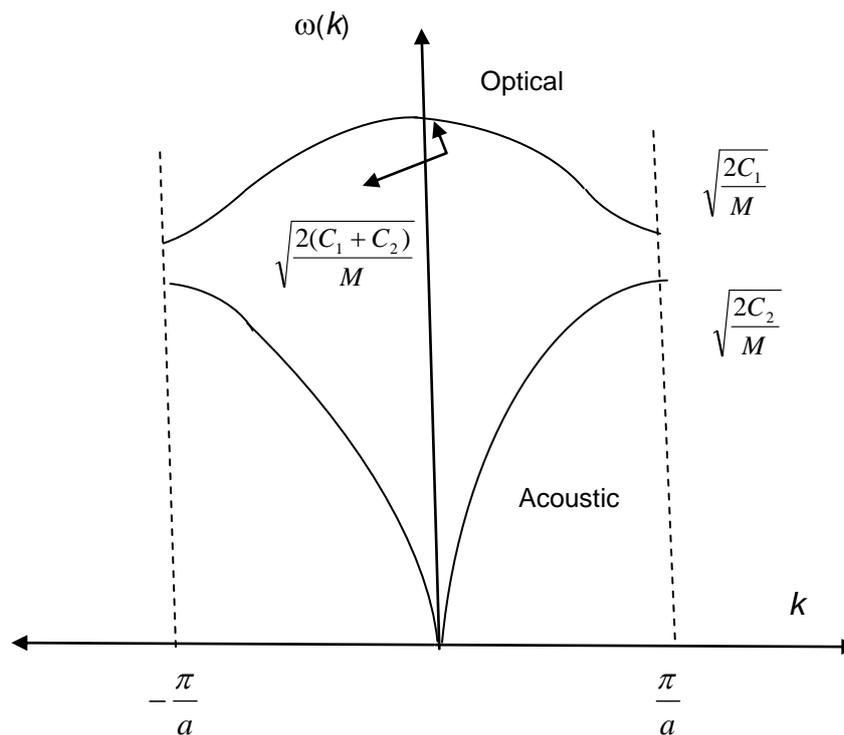


Figure 65: The dispersion plot for the diatomic linear chain with only nearest-neighbor interactions. The lower branch is the acoustic branch. The upper branch is the optical branch.

Notes:

1. Any frequency in the gap between the two branches or above the optical branch will be attenuated so that only atoms near the source oscillate with appreciable amplitude.
2. It must be emphasized that for each of the N values of k there are two solutions which then give $2N$ normal modes. The number of branches is attributed to the number of degrees of freedom of atoms (*i.e.* with two atoms in the primitive cell and N primitive cells in the crystal we have $2N$ degrees of freedom). Each atom has three degrees of freedom (one for each direction in the space).

3. Thus for two atoms in the primitive cell we have $6N$ degrees of freedom in the crystal. But the number of allowed k values in a single branch is just N for one Brillouin zone. In the acoustical branch there are $3N$ normal modes (one longitudinal plus two transverse). While in the optical branch there are also $3N$ normal modes (one longitudinal plus two transverse).

Limitations of the frequencies in the optical branch:

- a) The lower limit of k (i.e. $k \rightarrow 0$)

$$\omega_1 = \omega_{\max} \Rightarrow \sqrt{\frac{2(C_1 + C_2)}{M}}$$

- b) In the limit when $k = \frac{\pi}{a}$

$$\omega_1 = \omega_{\min} \Rightarrow \sqrt{\frac{2C_1}{M}}$$

Exercise:

- a) Use the equation $[M\omega^2 - (C_1 + C_2)]\varepsilon_1 + (C_1 + C_2e^{-ika})\varepsilon_2 = 0$ and take the lower limit of k (assuming $k=0$) to find the ratio $\frac{\varepsilon_1}{\varepsilon_2}$. Describe the

motion of atoms with respect to each other.

- b) Find the ratio $\frac{(\omega_1)_{\max}}{(\omega_2)_{\min}}$. Can you decide when the optical branch

is narrow and when it is wide, in terms of C_1 and C_2 ?

Limitations of the frequencies in the acoustical branch:

- a) When $k = \frac{\pi}{a}$ we get the maximum limit of the frequency, i.e.

$$\omega_2^2 = \frac{C_1 + C_2}{M} - \frac{1}{M}[C_1^2 + C_2^2 - 2C_1C_2]^{1/2}$$

$$\omega_2 = \omega_{\max} \Rightarrow \omega_2^2 = \frac{2C_2}{M}$$

$$\therefore (\omega_2)_{\max} = \sqrt{\frac{2C_2}{M}}$$

b) For very small k we get $\omega_2 = \omega_{\min}$. Use $\cos ka \approx 1 - \frac{k^2 a^2}{2}$.

Substitute this into $\omega_2^2 = \frac{C_1 + C_2}{M} - \frac{1}{M} [C_1^2 + C_2^2 + 2C_1 C_2 \cos ka]^{\frac{1}{2}}$ to get

$$\omega_2^2 = \frac{C_1 + C_2}{M} - \frac{1}{M} [C_1^2 + C_2^2 + 2C_1 C_2 - C_1 C_2 k^2 a^2]^{\frac{1}{2}}$$

$$\omega_2^2 = \frac{C_1 + C_2}{M} - \frac{1}{M} [(C_1 + C_2)^2 - C_1 C_2 k^2 a^2]^{\frac{1}{2}}$$

$$\omega_2^2 = \frac{C_1 + C_2}{M} - \frac{(C_1 + C_2)}{M} \left[1 - \frac{C_1 C_2 k^2 a^2}{(C_1 + C_2)^2} \right]^{\frac{1}{2}}$$

Expand $\left[1 - \frac{C_1 C_2 k^2 a^2}{(C_1 + C_2)^2} \right]^{\frac{1}{2}} \Rightarrow \left[1 - \frac{C_1 C_2 k^2 a^2}{2(C_1 + C_2)^2} \right]$ we get

$$\omega_2^2 = \frac{C_1 C_2 k^2 a^2}{2M(C_1 + C_2)^2}$$

$$(\omega_2)_{\min} = \sqrt{\frac{C_1 C_2 a^2}{2M(C_1 + C_2)}} k$$

Put $T = \frac{C_{eq} a^2}{2}$ and $\eta = \frac{M}{a}$ where $C_{eq} = \frac{C_1 C_2}{C_1 + C_2}$ such that $v = \sqrt{\frac{T}{\eta}}$.

Thus $\omega = vk$ and this is the straight line equation, as plotted in figure 66, from which the velocity of sound can be determined.

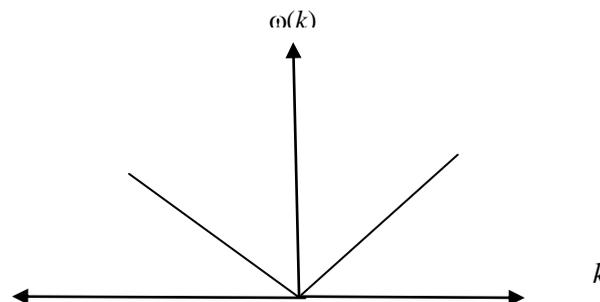


Figure 62: The linear part of the dispersion plot at very small values of k for a diatomic linear chain with only nearest-neighbor interactions.

The width of the gap between the branches at $k = \pm \frac{\pi}{a}$ is:

$$\Delta\omega = (\omega_1)_{\min} - (\omega_2)_{\max}$$

$$\Delta\omega = \sqrt{\frac{C_1 C_2 a^2}{2M(C_1 + C_2)}} k - \sqrt{\frac{2C_2}{M}}$$

Exercise:

- At what values of C_1 and C_2 does the gap get narrower and at what values does it get wider?
- Describe the motion of the two atoms in this diatomic crystal at very small values of k . Use the relation

$$\omega_2^2 = \frac{C_1 + C_2}{M} - \frac{1}{M} [C_1^2 + C_2^2 + 2C_1 C_2 \cos ka]^{1/2}$$