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B.Sc (PS) Chemistry VI Sem
Lattice vibrations

Vibrations of 1-dim. Diatomic lattice:-

Consider a 1-dim (linear) primitive lattice with basis consisting of two atoms of masses m and M ($m < M$) which are placed alternatively along the x-axis with an interatomic distance equal to a. In a state of equilibrium, let the atoms be located at sites represented by ... 2n-2, 2n-1, 2n, 2n+1, 2n+2 ... as shown in fig 2. Also let u_{2n} be the displacement of an atom corresponding to the $2n^{th}$ site at any time during the vibratory motion of atoms. Using the assumptions similar to the monoatomic case, we obtain the following different equations of motion, one for the lighter atoms and the other for the heavier ones:

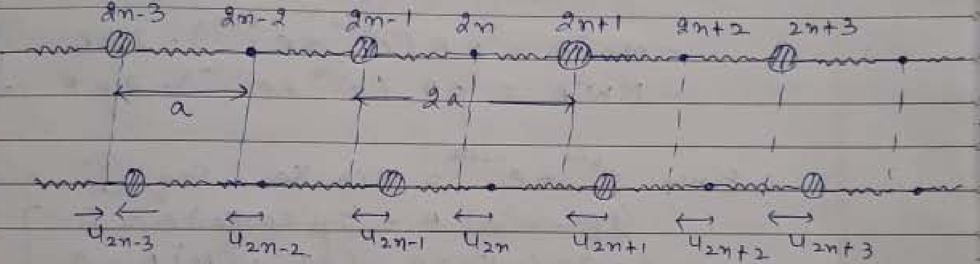

fig2:- State of displacement

$$\left.\begin{aligned} f_{2n} &= m\frac{d^2u_{2n}}{dt^2} = (u_{2n+1}+u_{2n-1}-2u_{2n})\beta \\ f_{2n+1} &= M\frac{d^2u_{2n+1}}{dt^2} = \beta(u_{2n+2}+u_{2n}-2u_{2n+1}) \end{aligned}\right] \text{—(1)}$$

where β is the spring constant

we seek the travelling solutions of the type

~~$u_{2n} = A \exp i[\omega t - 2qna]$~~

$$\left.\begin{aligned} u_{2n} &= A \exp i[\omega t - 2kna] \\ u_{2n+1} &= B \exp i[\omega t - (2n+1)ka] \end{aligned}\right] - (2)$$

where ω is the freq. & k is the wave vector of a particular mode of vibration.

It may be noted that the vibrational freq. of both types of atoms is assumed to be the same because both types of atoms participate in the same wave motion. The amplitudes A and B may, however be different because of different masses of the atoms. Writing similar expressions for u_{2n-1} and u_{2n+2} and substituting these as well as eq. ② into eq. ① we obtain

$$\left.\begin{aligned} -m\omega^2 A &= \beta B(e^{ika} + e^{-ika}) - 2\beta A \\ -M\omega^2 B &= \beta A(e^{ika} + e^{-ika}) - 2\beta B \end{aligned}\right] - ③$$

Since $e^{ika} + e^{-ika} = 2\cos ka$. eq. ③ yield

$$\left.\begin{aligned} (2\beta - \omega^2 m) A - (2\beta \cos ka) B &= 0 \\ (-2\beta \cos ka) A - (2\beta - \omega^2 M) B &= 0 \end{aligned}\right] - ④$$

This set of homogeneous linear equations would give rise to non-zero solutions for A and B only if

$$\begin{vmatrix} 2\beta - \omega^2 m & -2\beta\cos ka \\ -2\beta\cos ka & 2\beta - \omega^2 M \end{vmatrix} = 0$$

or $(2\beta - M\omega^2)(2\beta - m\omega^2) - 4\beta^2\cos^2 ka = 0$

or $\omega^4 - \dfrac{2\beta(m+M)}{mM}\omega^2 + \dfrac{4\beta^2 \sin^2 ka}{mM} = 0$

It gives

$$\omega^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) \pm \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4\sin^2 Ka}{mM}} \quad \text{— (5)}$$

This is the dispersion relation for a linear diatomic lattice. ~~Both eqs~~

Considering only the positive values of ω, we find that, in the monoatomic case, there is only one value of ω for single value of K whereas in the diatomic case there are two values of ω. These two values are written as ω_+ and ω_- and are expressed as

(6) —

$$\omega_+^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) + \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4\sin^2 Ka}{mM}}$$

$$\omega_-^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) - \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4\sin^2 Ka}{mM}}$$

Considering the expression for ω_+, we find that for $K \to 0$, $\sin Ka$ is negligible and therefore, we get

$$\omega_+ = \sqrt{2\beta\left(\frac{1}{m}+\frac{1}{M}\right)} \quad \text{— (7)}$$

for $K \to \frac{\pi}{2a}$, $\sin Ka \to 1$, and we have

$$\omega_+^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) + \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4}{mM}}$$

$$= \beta\left(\frac{1}{m}+\frac{1}{M}\right) + \beta\left(\frac{1}{m}-\frac{1}{M}\right)$$

$$\text{or } \omega_+ = \sqrt{\frac{2\beta}{m}} \quad \text{— (8)}$$

Now consider the expression for ω_- in eq. (6). For $k \to 0$, we write $\sin ka = ka$ (it is not neglected in order to obtain a non-zero value of ω_-). Therefore, we get

$$\omega_-^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) - \beta\left(\frac{1}{m}+\frac{1}{M}\right) \times \sqrt{1-\frac{4k^2a^2}{mM}\left(\frac{mM}{m+M}\right)^2}$$

$$= \beta\left(\frac{1}{m}+\frac{1}{M}\right)\left[1-\sqrt{1-\frac{mM}{(m+M)^2}4k^2a^2}\right]$$

$$= \beta\left(\frac{1}{m}+\frac{1}{M}\right)\left[1-1+\frac{mM}{(m+M)^2}2k^2a^2+\cdots\right]$$

using binomial theorem

$$= \frac{2\beta k^2a^2}{m+M}$$

$$\therefore \quad \omega_- = ka\sqrt{\frac{2\beta}{m+M}} \quad \text{—— (9)}$$

for $k \to \frac{\pi}{2a}$, we get solution similar to eq. (8) with m replaced by M, i.e

$$\omega_- = \sqrt{\frac{2\beta}{M}} \quad \text{—— (10)}.$$

The plots of dispersion relation eq. (6) along with the solutions eq. (7) through eq. (10) are shown in fig. (3). The following points should be observed:

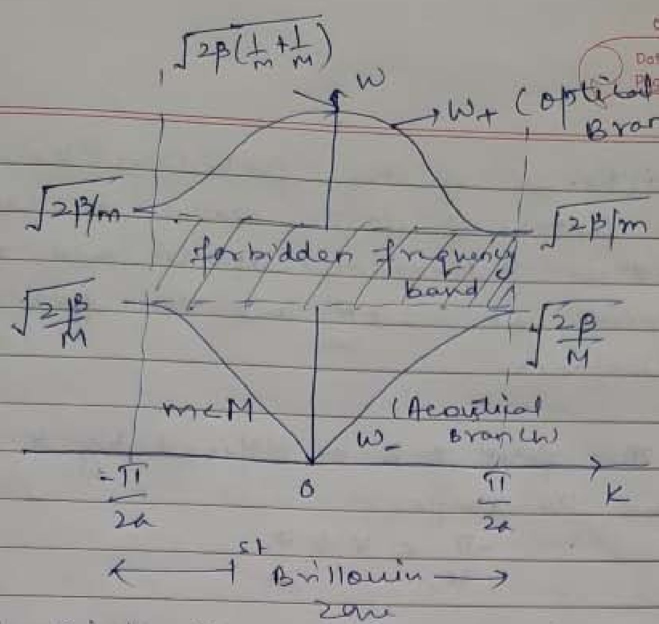

fig 3:- Dispersion relations for linear diatomic lattice showing acoustical & optical modes.

(i) The allowed frequency range of propagation is split into two branches - an upper branch called the <u>optical</u> <u>branch</u> and a lower branch called the <u>acoustical</u> <u>branch</u>. The acoustical branch resembles the dispersion relationship curve for a monoatomic lattice, whereas the optical branch represents an entirely different type of wave motion.

(ii) There exists a band of frequencies between these two branches for which the wave-like solutions of the type eq. (2) are not possible. It means that it is not possible to excite vibrations in a lattice at a frequency which lies inside this band. This band is called <u>forbidden</u> <u>band</u>. The width of this band depends on the mass ratio $\frac{M}{m}$. The larger the ratio $\frac{M}{m}$, the greater the width of the forbidden band. The

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existence of the forbidden band is a characteristic feature of elastic waves in case of diatomic lattices. If $M=m$, the optical and acoustical branches coincide at $K=\pm\frac{\pi}{2a}$ and the forbidden band disappears.

(iii) The first B.Z is defined by K-values which lie in the range

$$-\frac{\pi}{2a} < K < \frac{\pi}{2a}.$$

Therefore, the smallest possible wavelength of this zone is $4a$ which corresponds to $K=\frac{\pi}{2a}$ at the zone boundary.

Now we investigate the physical difference between the vibrations represented by the optical and acoustical branches and determine the origin of the names of these branches. For the optical branch, as $K\to 0$, $\cos Ka \to 1$ and the eq. 4 yield

$$-\omega^2 mA = 2\beta B - 2\beta A \quad \text{or} \quad \frac{\omega^2}{2\beta} = \frac{A-B}{mA}$$

$$\text{and} \quad -\omega^2 MB = 2\beta A - 2\beta B \quad \text{or} \quad \frac{\omega^2}{2\beta} = -\frac{A-B}{MB}$$

$$1 = -\frac{MB}{mA}$$

$$\text{or} \quad \frac{A}{B} = -\frac{M}{m} \quad \text{— (11)}$$

This indicates that the two atoms move in opposite directions and their amplitudes are inversely proportional to their masses so that the centre of mass of the unit cell remains unchanged. Such a mode of vibration is shown in fig. 4(a).