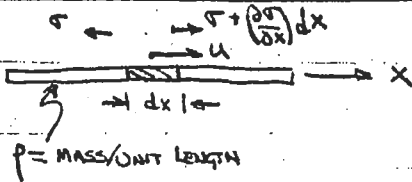# 3.60 Symmetry, Structure and Tensor Properties of Materials

A CRYSTAL IS NOT A CONTINUUM, BUT IS COMPOSED of DISCREET ATOMS. HOW DOES THIS INFLUENCE THE PROPAGATION of ELASTIC WAVES? WE WILL HERE CONSIDER ONLY A ONE DIMENSIONAL CRYSTAL IN ORDER TO KEEP THE ALGEBRA TRACTABLE. THIS IS NOT A SWINDLE! NO NEW NOTIONS ARE REQUIRED TO EXTEND THE DISCUSSION TO A TWO- OR THREE-DIMENSIONAL PROBLEM.

① WAVE PROPAGATION IN A CONTINUOUS ONE-DIMENSIONAL MEDIUM

$$\epsilon = \frac{\partial u}{\partial x} \qquad \sigma = c\epsilon = c\frac{\partial u}{\partial x}$$

$$\rho\, dx\, \frac{\partial^2 u}{\partial t^2} = \left[\sigma + \left(\frac{\partial \sigma}{\partial x}\right)dx\right] - \sigma$$
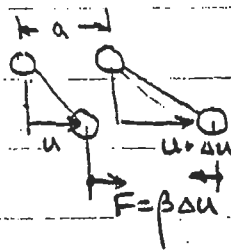
$$\rho\frac{\partial^2 u}{\partial t^2} = \frac{\partial \sigma}{\partial x} = c\frac{\partial^2 u}{\partial x^2}$$

SOLUTION $u = u_0\, e^{-2\pi i/\lambda\,(Vt - x)}$

SUBTITION IN WAVE EQUATION GIVES $\boxed{V = \sqrt{\dfrac{c}{\rho}}}$

CONSIDER A ONE-DIMENSIONAL CRYSTAL WITH ONE KIND of ATOM of MASS M SEPARATED BY LATTICE CONSTANT a. LET THE RESTORING FORCE WHICH ACTS WHEN AN ATOM IS DISPLACED BE DESCRIBED BY THE FORCE CONSTANT β SUCH THAT

$$F = \beta\,\Delta u$$

$$F = \beta\,\Delta u$$

LET US NOW RELATE THE MACROSCOPIC PARAMETERS c AND ρ TO ATOMIC PARAMETERS.

$$\rho = \text{No. of ATOMS}/\text{UNIT LENGTH} \cdot M$$

$$\boxed{\rho = \frac{1}{a}\cdot M}$$

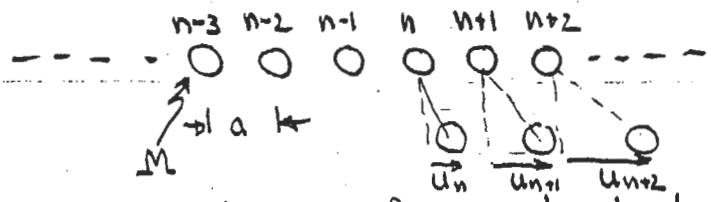$$F = \beta\,\Delta u \qquad \text{BUT } F \equiv c\epsilon = c\frac{\Delta u}{a}$$

$$\therefore \boxed{\frac{c}{a} = \beta}$$

THE WAVE VELOCITY IN TERMS of ATOMIC QUANTITIES IS

$$V = \sqrt{\frac{c}{\rho}} = \sqrt{\frac{\beta a^2}{M}} \qquad \text{INDEPENDENT of } \lambda.$$

② WAVE MOTION ON A ROW OF IDENTICAL ATOMS

CONSIDER A CRYSTAL OF ONE DIMENSION CONTAINING ONE TYPE OF ATOM OF MASS M PER UNIT CELL a. NUMBER THE ATOMS:

n-3 n-2 n-1 n n+1 n+2

LET AN ELASTIC WAVE PROPAGATE ALONG THE CHAIN. AT ONE INSTANT OF TIME EACH ATOM HAS A DISPLACEMENT U_n. CONSIDER ONLY NEAREST NEIGHBOR FORCES (BUT SEE DIGRESSION LATER)

WITH $F = \beta \Delta u$

$$\therefore F_n = \beta(U_{n+1} - U_n) - \beta(U_n - U_{n-1})$$

$$= \beta(U_{n+1} - 2U_n + U_{n-1}) = M\frac{\partial^2 U_n}{\partial t^2}$$

WE AGAIN LOOK FOR A WAVE SOLUTION OF THE FORM $U_n = U_0 e^{i(\omega t - kx)}$

BUT THIS EXACT FORM WILL NOT SUFFICE: X IS NO LONGER A CONTINUOUS VARIABLE. DISPLACEMENT IS DEFINED ONLY AT ATOM LOCATIONS. LET $kx \to k\,na$

AND $U_n = U_0 e^{i(\omega t - kna)}$ IS AN ACCEPTABLE EXPRESSION $\left[U_{n+1} = U_0 e^{i[\omega t - k(n+1)a]}\text{ etc.}\right]$

SUBSTITUTION OF THIS EXPRESSION IN THE EQUATION OF MOTION AS A TRIAL SOLUTION GIVES:

$$M U_0 (i\omega)^2 e^{i(\omega t - kna)} = \beta U_0 e^{i\omega t}\left[e^{-i[k(n+1)a]} - 2e^{-ikna} + e^{-ik[n-1]a}\right]$$
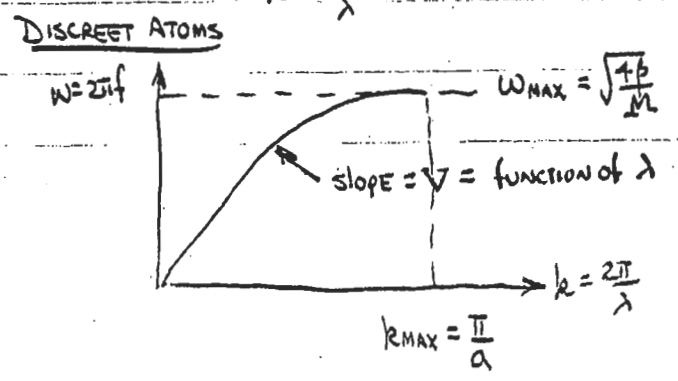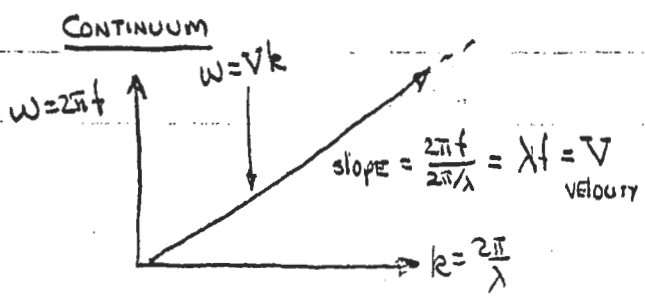
$$-M\omega^2 = \beta\left\{ e^{-ika} - 2 + e^{+ika}\right\}$$

$$= \beta\left(e^{-ika/2} - e^{+ika/2}\right)^2$$

BUT $-\frac{1}{2}i(e^{ix} - e^{-ix}) = \sin x$

$$\therefore -M\omega^2 = \beta\left(-\frac{2}{i}\sin\frac{ka}{2}\right)^2 = -4\beta\sin^2\frac{ka}{2}$$

$$\boxed{\omega = \left(\frac{4\beta}{M}\right)^{\frac{1}{2}}\sin\frac{ka}{2}}$$

NOTE THAT $\omega = 2\pi f$ IS A FUNCTION OF $k = \frac{2\pi}{\lambda}$

CONTINUUM

$\omega = 2\pi f$ $\omega = Vk$

slope $= \frac{2\pi f}{2\pi/\lambda} = \lambda f = V$ VELOCITY

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

DISCREET ATOMS

$\omega = 2\pi f$ $\omega_{MAX} = \sqrt{\frac{4\beta}{M}}$

slope $= V =$ function of λ

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

$k_{MAX} = \frac{\pi}{a}$

FOR THE CONTINUUM, VELOCITY IS A CONSTANT $\sqrt{\frac{c}{\rho}}$, INDEPENDENT of λ AND A WAVE of ANY FREQUENCY OR ANY λ SHOULD BE PROPAGATABLE IN THE CRYSTAL

TAKING INTO ACCOUNT THE DISCREET NATURE of THE CRYSTAL WE FIND

→ THERE IS A MAXIMUM ANGULAR FREQUENCY $W_{MAX} = \sqrt{\frac{4\beta}{M}}$ WHICH CAN BE PROPAGATED IN THE CRYSTAL

→ VELOCITY IS A FUNCTION of WAVELENGTH AND NOT A CONSTANT (NOTE THAT V SLOWS TO <u>ZERO</u> AT k_{MAX}!)

[ALL THIS IS RATHER UNEXPECTED! NOTE: NO RAZZLE-DAZZLE QUANTUM MECHANICS OR ANYTHING FANCY HERE! THIS IS PURELY CLASSICAL MECHANICS!]

<u>DIGRESSION A</u> DOES THIS RESULT REDUCE TO WHAT WE OBTAINED FOR THE CONTINUUM FOR WAVELENGTHS $>> a$? THE WAVE SHOULDN'T BE ABLE TO TELL THAT ATOMS ARE THERE FOR THIS SITUATION!

$$W = \left(\frac{4\beta}{M}\right)^{\frac{1}{2}} \sin\frac{ka}{2}$$

FOR LARGE λ $k = \frac{2\pi}{\lambda}$ IS VERY SMALL $\therefore \sin\frac{ka}{2} \approx \frac{ka}{2}$

THEN $W \approx \left(\frac{4\beta}{M}\right)^{\frac{1}{2}} \frac{ka}{2}$

$$\approx \sqrt{\frac{\beta a^2}{M}} \, k \qquad \text{EXACTLY WHAT WE OBTAINED EARLIER!}$$

WHAT IS "SMALL" k?

CONSIDER $k_{MAX} = \frac{\pi}{a}$ a IS of THE ORDER of $3 \cdot 10^{-8}$ cm

SO $k_{MAX} \approx 10^8$ cm^{-1}

CONSIDER A k ONLY $\underline{1\%}$ of THE WAY TOWARDS k_{MAX},

ie $k \approx 10^6$ cm^{-1}. A TYPICAL VELOCITY of AN ELASTIC WAVE IN A SOLID IS $\approx 5 \cdot 10^5$ cm^2/sec

$$V = f\lambda = f\frac{2\pi}{k} \qquad \text{SO } f = \frac{kV}{2\pi} = \frac{10^6 \cdot 5 \cdot 10^5}{2\pi}$$

$$\approx 10^5 \text{ MEGACYCLES , AN}$$

ENORMOUSLY HIGH FREQUENCY!

<u>INTERLUDE B</u> IN A "REAL" 1-DIMENSIONAL CRYSTAL WE SHOULD CONSIDER INTERACTIONS BEYOND MERELY NEAREST NEIGHBORS! HOW WILL THIS INFLUENCE THE RESULT?

IN THE FORCE BALANCE ON THE nth ATOM WE WROTE

$$M\frac{\partial^2 u_n}{\partial t^2} = F = \beta_1 (u_{n+1} - 2u_n + u_{n-1})$$

NOW INCLUDE THESE HIGHER-ORDER TERMS $\begin{cases} + \beta_2 (u_{n+2} - 2u_n + u_{n-2}) \\ + \beta_3 (u_{n+3} - 2u_n + u_{n-3}) + ----- \end{cases}$
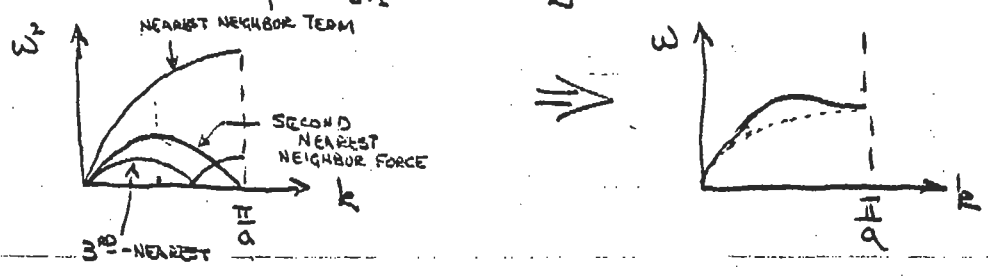
SUBSTITUTING OUR TRIAL SOLUTION:

$$-MW^2 = \beta_1 \left\{ e^{-ika} - 2 + e^{ika} \right\} + \beta_2 \left\{ e^{-i2ka} - 2 + e^{+i2ka} \right\} + \beta_3 \left\{ e^{-i3ka} - 2 + e^{+i3ka} \right.$$

EACH HIGHER ORDER TERM MAY NOW BE CONDENSED TO GIVE A $\sin^2$ TERM AS BEFORE:

$$\omega^2 = \frac{4\beta_1}{M} \sin^2 \frac{ka}{2} + \frac{4\beta_2}{M} \sin^2 \frac{2ka}{2} + \frac{4\beta_3}{M} \sin^2 \frac{3ka}{2} + \cdots$$

SO THAT

$$\omega^2 = \sum_p \frac{4\beta_p}{M} \sin^2 \frac{pka}{2} \qquad p = \text{AN INTEGER}$$

EFFECT OF HIGHER-NEIGHBOR INTERACTIONS IS TO IMPOSE SMALL PERTURBATIONS ON THE $\sin \frac{ka}{2}$ BEHAVIOR. THIS MIGHT APPEAR TO BE A MINOR HIGHER-ORDER EFFECT BUT IT IS ENORMOUSLY IMPORTANT IN CALCULATING SPECIFIC HEAT! (THE EXPRESSION WILL INVOLVE $\partial k/\partial \omega$ WHICH BLOWS UP AT THE POINT WHERE $\omega(k)$ HAS ZERO SLOPE!!)

$$= (\text{FINIS DIGRESSIONS}) =$$

LET US NOW EXAMINE THE MEANING OF THE WAVE WITH $k_{MAX} = \frac{\pi}{a}$ FOR WHICH ω ASSUMES THE MAXIMUM ANGULAR FREQUENCY FOR WHICH A VIBRATIONAL MODE MAY BE SUPPORTED BY THE CRYSTAL.
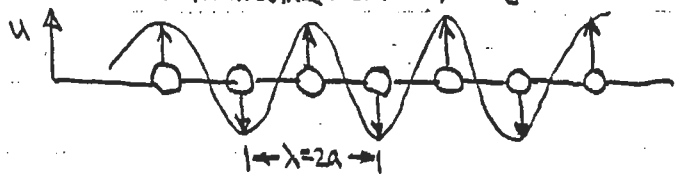
$$\omega = \sqrt{\frac{4\beta}{M}} \sin \frac{ka}{2} \quad \text{HAS MAXIMUM VALUE WHEN} \quad \sin \frac{ka}{2} = 1$$

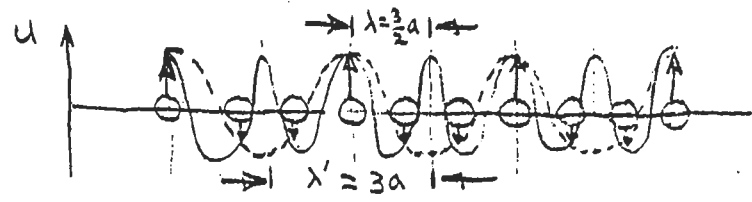$$\frac{ka}{2} = \frac{\pi}{2}$$

$$\therefore k_{MAX} = \frac{\pi}{a}$$

THIS CORRESPONDS TO A WAVE WITH $\lambda_{MIN} = \frac{2\pi}{k_{MAX}} = \frac{2\pi a}{\pi} = 2a$ AND, AS $\partial\omega/\partial k = V = 0$, A WAVE WITH ZERO VELOCITY.

LET'S PLOT THE DISPLACEMENT OF THE ATOMS FOR SUCH A WAVE AS A FUNCTION OF DISTANCE ALONG THE CHAIN AT ONE PARTICULAR INSTANT OF TIME

THE PATTERN OF DISPLACEMENTS ARE EQUAL BUT OPPOSITE IN DIRECTION.

THIS TURNS OUT TO BE THE SMALLEST WAVELENGTH ONE CAN DEFINE PHYSICALLY IN THE CRYSTAL! WHY? DISPLACEMENT MAY BE DEFINED ONLY AT THE LOCATIONS WHERE THE ATOMS SIT! IT CLEARLY MAKES NO PHYSICAL SENSE TO TALK ABOUT A WAVE OF $\lambda \ll a$

ANY PATTERN OF DISPLACEMENTS WHICH WE MIGHT DRAW WITH $\lambda < 2a$ MAY BE EQUALLY WELL DEFINED IN TERMS OF SOME $\lambda' \geq 2a$. LET'S SHOW THIS SPECIFICALLY FOR $\lambda = \frac{3}{2}a$

SO THAT A WAVE WITH $\lambda = \frac{3}{2}a$ IS COMPLETELY INDISTINGUISHABLE FROM ONE WITH $\lambda' = 3a > 2a$!

WHAT IS THE REASON FOR THIS? WELL, ALL WE CAN REALLY TALK ABOUT WITH MEANING IS THE RELATIVE DISPLACEMENT OF NEIGHBORING ATOMS

$$\frac{U_n}{U_{n+1}} = \frac{U_0 \, e^{i(\omega t - kna)}}{U_0 \, e^{i[\omega t - k(n+1)a]}} = e^{ika}$$
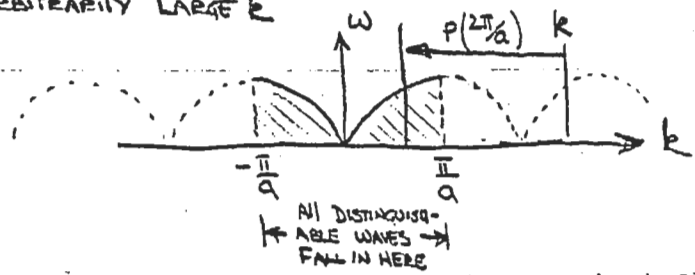
WE CAN THEREFORE ADD OR SUBTRACT ANY INCREMENT TO k WHICH CHANGES PHASE OF e^{ika} BY 2π AND NOTHING WILL HAVE CHANGED. Δk SHOULD BE SUCH THAT

$$\Delta k \, a = 2\pi$$
$$\text{OR } \Delta k = \frac{2\pi}{a}$$

THUS IF k IS SUCH THAT $k > k_{MAX} = \frac{\pi}{a}$, WE CAN ALWAYS DEFINE WAVE IN TERMS OF A NEW k'

$$k' = k \pm p\left(\frac{2\pi}{a}\right) \quad (p = \text{AN INTEGER})$$

SUCH THAT $|k'| < \frac{\pi}{a}$, EVEN THOUGH, FORMALLY, ONE HAS $\omega = \left(\frac{4\beta}{M}\right)^{\frac{1}{2}} \sin\frac{ka}{2}$ DEFINED FOR ARBITRARILY LARGE k

$-\frac{\pi}{a}$ $\frac{\pi}{a}$

All DISTINGUISH-ABLE WAVES FALL IN HERE

[NOTICE THAT SOMETIMES, UPON SUBTRACTING OFF A MULTIPLE OF $\frac{2\pi}{a}$, ONE GETS A $|k'| < \frac{\pi}{a}$, BUT A VALUE WHICH IS NEGATIVE! A NEGATIVE k MERELY MEANS A WAVE WHICH IS TRAVELING IN THE OPPOSITE DIRECTION. IT IS AMUSING TO SHOW THIS TO ONESELF; YOU CAN DO IT WITH THE EXAMPLE SHOWN ABOVE IN WHICH

$$\lambda = \frac{3}{2}a \qquad k = \frac{4}{3}\frac{\pi}{a}$$
$$\lambda = 3a \qquad k' = -\frac{2}{3}\frac{\pi}{a} = \frac{4}{3}\frac{\pi}{a} - \frac{6}{3}\frac{\pi}{a} \quad]$$

FINALLY, WHAT IS THE MEANING OF ZERO VELOCITY FOR THE WAVE WITH $k = k_{MAX} = \frac{\pi}{a}$?

$$U_n = U_0 \, e^{i(\omega t - kna)}$$

SUBSTITUTING $k = \frac{\pi}{a}$

$$U_n = U_0 \, e^{i(\omega t - \frac{\pi}{a}na)} = U_0 \, e^{i(\omega t)} \underbrace{e^{-n\pi}}$$

$+1$ FOR n EVEN
-1 FOR n ODD

THIS REPRESENTS A STANDING WAVE; AMPLITUDE BUILDS UP AND DECAYS WITH TIME FOR A GIVEN ATOM BUT THE WAVE DOESN'T GO ANYWHERE!

SUCH A STANDING WAVE PATTERN WOULD BE PRODUCED BY TWO EQUAL WAVES MOVING IN OPPOSITE DIRECTIONS. THE NODES STAY FIXED! IN FACT, ONE CAN CONSIDER THIS AS ONE-DIMENSIONAL DIFFRACTION À LA BRAGG'S LAW

PATH DIFF $= 2a = n\lambda$
$\therefore \lambda = 2a$ FOR $n = 1$!!!

$k_{MAX} = \frac{\pi}{a}$ IS THEN NOTHING MORE THAN THE λ FOR WHICH DIFFRACTION OCCURS (CONSTRUCTIVE INTERFERENCE) THIS IS A PHENOMENON WHICH OCCURS WHEN EVER A WAVE (ELASTIC, X-RAY, ELECTRON DEBROGLIE WAVE) MOVES THROUGH A PERIODIC MEDIUM.
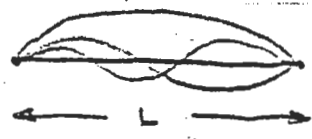
YOU PROBABLY ARE MORE FAMILIAR WITH THIS SITUATION IN CONNECTION WITH X-RAY DIFFRACTION OR ENERGY LEVELS OF ELECTRONS IN CRYSTALS BUT THEY ARE ALL THE SAME EFFECT

THE BOUNDARY TO k AT $k_{max} = \frac{\pi}{a}$ IS CALLED THE FIRST <u>BRILLOUIN ZONE</u>.

TOTAL NUMBER OF VIBRATIONAL MODES WHICH MAY BE SUPPORTED BY THE CRYSTAL

WE HAVE SHOWN THAT THERE IS A LOWER LIMIT, $\lambda_{min} = 2a$, TO THE WAVES WHICH MAY BE SUPPORTED BY A CRYSTAL COMPOSED OF DISCREET ATOMS.

FOR A FINITE-SIZED CHUNK OF CRYSTAL THERE WILL ALSO BE AN <u>UPPER</u> LIMIT TO λ DETERMINED BY THE DIMENSIONS OF THE SAMPLE. FOR A ONE-DIMENSIONAL CRYSTAL OF LENGTH L

$$\lambda = 2L, L, \tfrac{2}{3}L \cdots \cdots 2a$$

$$i.e., \quad \boxed{\lambda = \frac{2L}{m}} \qquad m = \text{AN INTEGER} = 1, 2 \cdots$$

WHAT ARE THE VALUES OF k FOR THESE WAVES?

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{2L}, \frac{2\pi}{L}, \frac{2\pi}{\tfrac{2}{3}L} \cdots \cdots \cdots \frac{\pi}{a}$$

$$\boxed{k = m\frac{\pi}{L}}$$

NOW, HOW MANY DISTINCT VIBRATIONAL MODES CAN THE CRYSTAL SUPPORT?

$$m_{MAX}\frac{\pi}{L} = \frac{\pi}{a}$$

$$m_{MAX} = \frac{L}{a} \approx N \qquad \text{THE NUMBER OF ATOMS IN THE CRYSTAL!}$$

THEREFORE, OUR ONE DIMENSIONAL CRYSTAL WITH ONE KIND OF ATOM MAY SUPPORT <u>A NUMBER OF VIBRATIONAL MODES WHICH IS EQUAL TO THE NUMBER OF ATOMS IN THE CRYSTAL</u>

OUR PLOT OF ω AS A FUNCTION OF k SHOULD THEREFORE NOT BE REGARDED AS A CONTINUOUS FUNCTION, BUT RATHER A SET OF DISCRETE / CLOSELY-SPACED STATES — EACH SEPARATED EQUALLY BY AN AMOUNT $\Delta k = \frac{\pi}{L}$