APPLIED PHYSICS 295

QUANTUM THEORY OF SOLIDS

NOTES

LECTURE I

Professor: Dr. Henry Ehrenreich
Room: Pierce 304, MWF at 11 AM

Topics to be covered:

1. Lattice Vibrations
2. Electron in a periodic potential
3. Many electron problem; statistics
4. Electron - phonon interaction
5. Transport Theory

Recommended Reading List:

1. Sommerfeld & Bethe, Hand. d. Phys., vol. 24/2, (1933)
2. Mott & Jones, Prop. of Metals & Alloys, (1936)
3. Seitz (1940)
4. Brooks (1950) Lecture Notes
5. Kittel (1953)
6. Wilson (1953) Theory of Metals
7. Born & Hrang (1954)
8. * Peierls (1955)
9. Seitz & Turnbull Series
   vol. I. Reitz
   Pines
   vol. 5. W. Kohn
10. Encyclopedia of Physics (1955) (German)
    Liepfried, vol. 7
    Bardeen, vol. 15 (electron-phonon interaction)
    Slater, vol. 19
    Jones, vol. 19 (transport Theory)
11. * Wannier (1959)
12. * Ziman (1960) Electrons and Phonons

* should buy

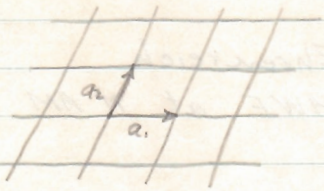
LATTICE VIBRATIONS:

Crystal Lattice:

Lattice vector definition:

$$\bar{l} \equiv \bar{R}_l = l_1 \bar{a}_1 + l_2 \bar{a}_2 + l_3 \bar{a}_3$$

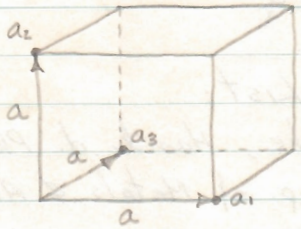
l's are integers less than the number of atoms.



1 atom/unit cell : Bravais lattice
2 or more : Basis Lattice

Cubic Types:

Simple:

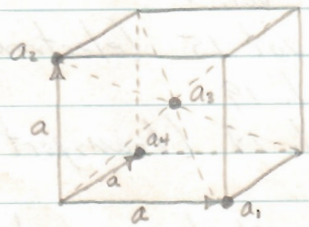


basic co-ordinates: $(a,0,0) = a_1$
$(0,a,0) = a_2$
$(0,0,a) = a_3$

other atomic co-ordinates may be found by a simple translation of these three

Body Centered Cubic (bcc):

basic co-ordinates: $(a,0,0) = a_1$
$(0,a,0) = a_2$
$(\frac{a}{2},\frac{a}{2},\frac{a}{2}) = a_3$



Now the position of a_4 may be found through a translation of the other three, viz,

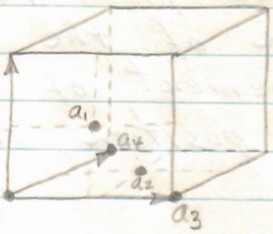
$$a_4 = (0,0,a) = 2a_3 - a_2 - a_1$$

Face Centered Cubic:

basic co-ordinates: $\left(\frac{a}{2}, \frac{a}{2}, 0\right) = a_1$

$\left(\frac{a}{2}, 0, \frac{a}{2}\right) = a_2$

$(a, 0, 0) = a_3$



Now,

$a_4 = (0,0,a) = 2a_2 - a_3$

Assuming Crystal Equilibrium, ie,

a) Equilibrium Configuration

b) Stable

and that atomic displacement is small, that is,

and $\frac{\langle \mu_\ell^2 \rangle^{1/2}}{\langle a \rangle} \ll 1$

we may write the following for the Hamiltonian:

$$H = \tfrac{1}{2} M \sum |\dot{\bar{r}}_\ell|^2 + V(\bar{r}_1, \bar{r}_2, \bar{r}_3, \ldots)$$

The potential function may be expanded by Taylor's expansion as follows:

$$V(\ldots, \bar{R}_\ell + \bar{\mu}_\ell, \ldots) = V_0 + \sum_{l\alpha} \left(\frac{\partial V}{\partial \mu_{l\alpha}}\right)_{\mu=0} \mu_{l\alpha}$$

$$+ \frac{1}{2} \sum_{l\alpha, l'\alpha'} \left(\frac{\partial^2 V}{\partial \mu_{l\alpha} \partial \mu_{l'\alpha'}}\right)_{\mu=0} \mu_{l\alpha} \mu_{l'\alpha'} + \frac{1}{6} \sum_{(\ )} (\quad) \mu\mu'\mu'' \ldots$$

Under Equilibrium, $\left(\frac{\partial V}{\partial \mu_{l\alpha}}\right)_0 = 0$

α is cartesian subscript, not subscript on l.

LECTURE II 9/28/60

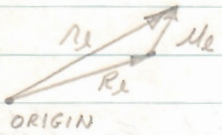
Continuing with the Hamiltonian for an atomic lattice of one atom per unit cell, viz.,

(1) $H = \frac{1}{2} M \sum_l |\dot{\bar{r}}_l|^2 + V(\bar{r}_1, \bar{r}_2, \ldots \bar{r}_l, \ldots)$

in which $\bar{r}_l$ represents the distance at some instant from any arbitrary origin to the lth atom, $\bar{R}_l$ the distance from this origin to the equilibrium position of the lth atom, and $\bar{u}_l$ the displacement of the lth atom from its equilibrium position, that is,

(2) $\bar{r}_l = \bar{R}_l + \bar{u}_l$

with $\frac{\langle u_l^2 \rangle^{1/2}}{\langle a \rangle} << 1$



Expanding the potential in a Taylor series about $u = 0$

(3) $V(\bar{r}_1, \bar{r}_2, \ldots \bar{r}_l, \ldots) = V(\ldots, \bar{R}_l + \bar{u}_l, \ldots)$

$= V_0 + \sum_{l\alpha} \left(\frac{\partial V}{\partial u_{l\alpha}}\right)_{u=0} u_{l\alpha} + \frac{1}{2} \sum'_{l\alpha, l'\alpha'} \left(\frac{\partial^2 V}{\partial u_{l\alpha} \partial u_{l'\alpha'}}\right)_{u=0} u_{l\alpha} u_{l'\alpha'} + \ldots$

in which α is the cartesian co-ordinates of displacement of the lth atom. It is usual to take $V_0 = 0$ for simplicity. Also, by the definition of equilibrium,

(4) $\left(\frac{\partial V}{\partial u_{l\alpha}}\right) = 0$, $u_{l\alpha} = 0$, and the linear terms disappear

The mixed partial in (3) is merely a constant when evaluated for all $u_{l\alpha} = 0$ and can be written

$$(5)\quad \left(\frac{\partial^2 V}{\partial u_{l\alpha}\,\partial u_{l'\alpha'}}\right)_0 = C_{\alpha\alpha'}(l,l')$$

Note that this has the dimensions of a force constant, as in a spring.

If the displacement is small, we may neglect higher order terms in V. However, these terms are called anharmonic terms and really give rise to the following phenomena:

1) thermal expansion
2) specific heat
3) thermal conductivity

The first term is called a harmonic term.

Symmetry Properties of harmonic terms:

a) all cells are physically equivalent with respect to their surroundings, thus,
$C_{\alpha\alpha'}(l,l') = C_{\alpha\alpha'}(l-l')$
that is, the "force constants" are dependent only on the difference between the positions of their atoms rather than on the positions themselves.

b) From (5), then, $C_{\alpha\alpha'}(l-l') = C_{\alpha'\alpha}(l'-l)$

c) For lattices having inversion symmetry, in which opposite directions on the same axis are equivalent, $C_{\alpha\alpha'}(l-l') = C_{\alpha\alpha'}(l'-l)$

d) Under a rigid displacement, $u_{l\alpha} = \text{epsilon}\ (\epsilon)$, the force constants are zero, i.e.,
$\sum_{l'} C_{\alpha\alpha'}(l-l') = 0$, from which follows
$\sum_{l} C_{\alpha\alpha'}(l) = 0$ by taking $l' = 0$ and summing on l.

The Hamiltonian now has the form:

$$(1A)\quad H = \tfrac{1}{2} M \sum_l |\dot{u}_l|^2 + \tfrac{1}{2} \sum_{l\alpha\, l'\alpha'} C_{\alpha\alpha'}(l-l')\, u_{l\alpha}\, u_{l'\alpha'}$$

We will now define the canonical conjugates necessary to set up the equations of motion.

(6) $M_{l\alpha} \rightarrow q$, $M\dot{u}_{l\alpha} \rightarrow p$

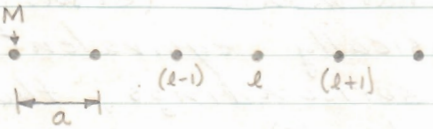
(7) From mechanics, $\dot{p} = -\frac{\partial H}{\partial q}$

Therefore,

(8) $M\ddot{u}_{l\alpha} + \sum_{l'\alpha'} C_{\alpha\alpha'}(l-l')\, u_{l'\alpha'} = 0$

which is an equation of motion corresponding to Hooke's Law:

One Dimensional Case:



Take $C(l-l') = C(l'-l)$ from property (b)
and $\sum_l C(l) = 0$ from property (d)

Now (8) reduces to:

(9) $M\ddot{u}_l + \sum_{l'} C(l'-l)\, u_{l'} = 0$

of which a solution might be

(10) $u_l(t) = u_l(0)\, e^{-i\omega t}$

Substituting (10) into (9):

(11) $-M\omega^2 u_l(0) + \sum_{l'} C(l'-l)\, u_{l'}(0) = 0$

As there is no damping, there will be no exponential rise or decay along the lattice and the displacements will differ from one to the other only by a phase constant.

(12)[a] $u_{l+n}(0) = \Gamma^n u_l(0)$, or, with respect to a "$l=0$" reference,

[b] $u_l(0) = \Gamma^l u^\circ$ where u° denotes the displacement of the zeroth atom at $t=0$.

It is seen that Γ must be complex with modulus unity. Therefore,

(13) $\Gamma = e^{iqa}$, the qa being chosen with "foresight."

Substituting (12)[b] into (11); and using (13):

(14) $$-M\omega^2 e^{iqla} + \sum_{l'} c(l-l') e^{iql'a} = 0$$

(15) $$M\omega^2 = \sum_{l'} c(l-l') e^{-iq(l-l')a}$$

By taking into account the periodicity of the lattice, we may assign $l=0$ as a reference with $c(l') = c(l')$ by (b), then changing l' back to l, we have:

(16) $$M\omega^2 = \sum_{l} c(l) e^{iqla}$$

By using the same process, we could have initially assigned $l'=0$ as reference and obtained

(17) $$M\omega^2 = \sum_{l} c(l) e^{-iqla}$$

Adding (16) and (17) and dividing by two, we have,

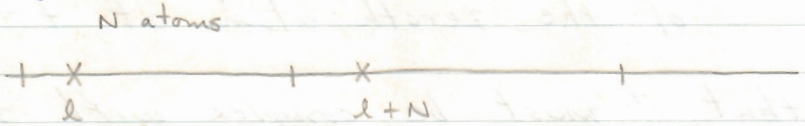
(18) $$M\omega^2 = \tfrac{1}{2} \sum_{l} c(l) \left(e^{iqla} + e^{-iqla}\right) = \sum_{l} c(l) \cos qla$$

From (18), the following important fact is apparent:

(19) $\omega^2(q) = \omega^2(-q)$

Boundary Conditions:

Assume (due to Born) we have periodic boundary conditions, that is,



(20) $u_l = u_{l+N}$

Since the displacements differ only by a phase factor, from (20) the phase factors of the u_l, u_{l+N} must be equal, that is,

(21) $e^{iqla} = e^{iq(l+N)a}$ or $e^{iqNa} = 1$

Thus,

(22) $qNa = 2n\pi$ or $q = \frac{2\pi n}{Na}$

which indicates the important fact that the q's are discrete, and with a bounded number of independent solutions because if $n = N+m$, $q = \frac{2\pi}{a} + \frac{2\pi m}{Na}$ with $n = m = N+m$ by periodicity.

Therefore: $0 \leq n \leq N-1$

N values of q

N values of ω

$0 \leq q \leq \frac{2\pi(N-1)}{Na}$, or, $0 \leq q < \frac{2\pi}{a}$

We may define the principle values of q as lying between $-\frac{\pi}{a}$ and π/a for convenience.

That is,

(23) $-\pi/a \leq q < \pi/a$ and which is the first Brillouin zone containing all the independent wave numbers.

Returning to (18), $M\omega^2 = \sum_l c(l) \cos qla$, we take the limit as $q \to 0$.

(24) $$\lim_{q \to 0} \left| \sum_l c(l) \left[1 - \tfrac{1}{2} q^2 a^2 l^2 + \dots \right] = -\tfrac{1}{2} q^2 a^2 \sum_l l^2 c(l) \right.$$

This indicates that $\omega \sim q$ which is typical of continuum motion, that is, as the wavelength grows larger, the wave moves much as if the lattice were a continuous solid. It is apparent that the condition must be made that $\omega^2 > 0$ as it must be real, and it follows that,

(25) $$\sum_l l^2 c(l) < 0$$

Now consider force constants between nearest neighbors, that is, only three force constants $c(0)$, $c(1)$, $c(-1)$. Now apply symmetry condition (d): $\sum_l c(l) = 0$

(26) $c(0) + c(1) + c(-1) = 0$ and $c(1) = -\tfrac{1}{2} c(0)$ by symmetry condition (b)

Substitute into (18) and sum from $l=0$ to $l=2$ or $l=-1$ to $l=+1$:

(27) $$M\omega^2 = \sum_{l=-1}^{l=+1} c(l) \cos qla = c(0) + 2c(1) \cos qa$$

$$= c(0) \left[1 - \cos qa \right] = 2 c(0) \sin^2 \tfrac{1}{2} qa$$

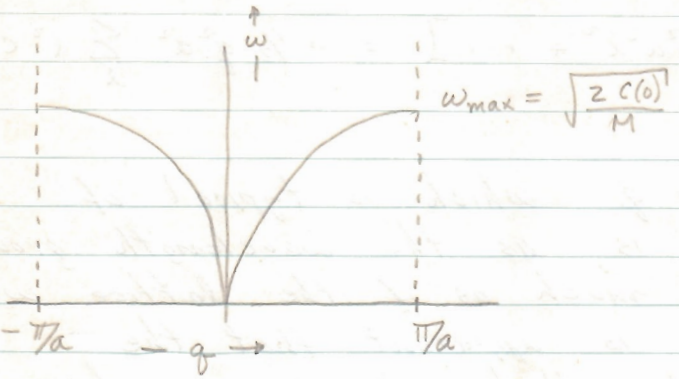
(28) $$\therefore \omega = \sqrt{\frac{2c(0)}{M}} \left| \sin \tfrac{1}{2} qa \right|$$

Taking the limit as $q \to 0$:

(29) $$\lim_{q \to 0} \left| \omega = \sqrt{\frac{c(0)}{2M}}\, a\, q = c\, q \right.$$

where c is the velocity of sound as it is usually taken for a continuous medium.

We plot ω versus q as given by equation (28)



Physical Significance of the Plot:

1) $u_\ell \propto e^{i q \ell a}$

$\therefore \frac{u_{\ell+1}}{u_\ell} = e^{iqa} = e^{i\frac{\pi}{a}a} = -1$ for $q = \pi/a$

2) Shows two different modes for high q.

LECTURE III 9/30/60

Recapitulation on One-Dimensional Case:

(1) $u_\ell(t) \sim e^{i(q\ell a - \omega t)}$; $q = \frac{2\pi}{\lambda}$

(2) $\omega = \left[-\frac{a^2}{2M} \sum_\ell \ell^2 c(\ell)\right]^{1/2} q$, for long λ

with $c(0)$, $c(1) = c(-1)$

For this long wavelength approximation:

(3) $C(1) = -1/2\, C(0)$

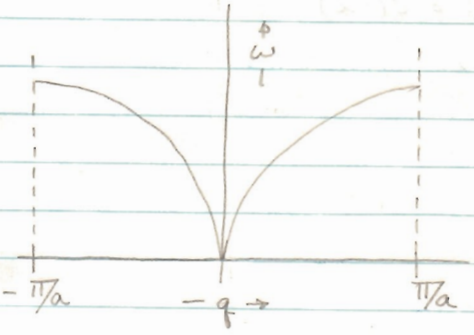
(4) $\sum_{l=-1}^{+1} l^2 C(l) = C(-1) + C(0) + C(1) = 0$

In general:

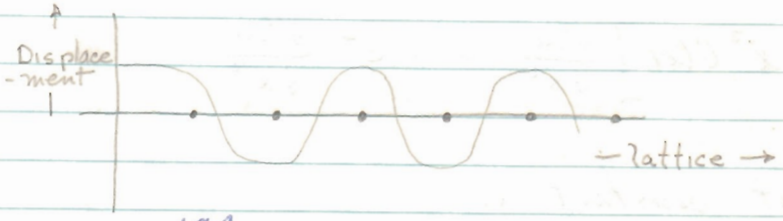
(5) $M\omega^2 = 2C(0)\sin^2 1/2 qa$; $\omega = \omega_{max} \sin \frac{n\pi}{2N}$, $0 \le n < N-1$

with $\omega_{max} = \sqrt{\frac{2C(0)}{M}}$

Graphical Explanation:



for $q = 0$: wave moves in phase
$q = \pi/a$: out of phase



e^{-iqa} → right traveling wave
e^{iqa} → left " "

This diagram represents the shortest possible wavelength of the system, $\lambda = 2a$. Anything shorter would be ridiculous as there would be no atoms there to vibrate.

The group velocity, $v_g = \frac{d\omega}{dq}$, is zero at $q = \pm \pi/a$ as can be seen from the simple diagrams above.

Demonstration That Long-wavelength Approximation Leads to Ordinary Wave Equation:

(6) Take $\sum_{l'} C(l-l')\, u_{l'} = \sum_{l''} C(l'')\, u_{l-l''}$

taking $l - l' = l''$

Expanding $u_{l-l''} = u_l - l'' \frac{du}{dl''} + \frac{1}{2} l''^2 \frac{d^2u}{dl''^2} - \ldots$

in a Taylor series considering u a function of l and substituting:

(7) $\sum_{l''} C(l'')\, u_{l-l''} = u_l \underbrace{\sum C(l'')}_{0} - \frac{du}{dl''} \underbrace{\sum l'' C(l'')}_{0} + \frac{1}{2} \frac{d^2u}{dl''^2} \sum l''^2 C(l'')$

$C(l) = C(-l)$

neglecting higher order terms in $\frac{du}{dl''}$.

Substituting (7) into II (9), viz.,

(8) $M \ddot{u}_l + \sum_{l'} C(l'-l)\, u_{l'} = 0$

we have,

(9) $\frac{\partial^2 u_l}{\partial t^2} = -\left[\frac{a^2}{2M} \sum_{l''} l^2 C(l)\right] \frac{\partial^2 u}{\partial x^2} = -c^2 \frac{\partial^2 u}{\partial x^2}$

Considering $\frac{d^2u}{dl''^2} = \frac{\partial^2 u}{\partial x^2}$ at constant l.

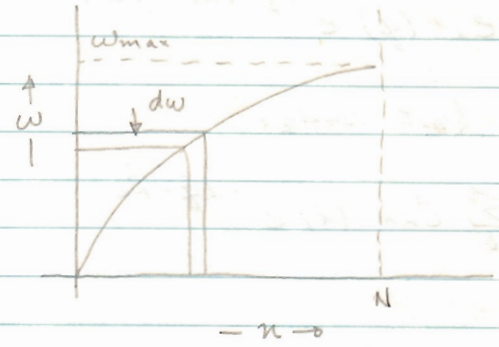
Thus it is right to think of wave motion in a continuum when $\lambda \gg a$. This connects us with elasticity theory. We can measure the elastic constants from which we can determine the force constants.

Density of Oscillators:

We ask the question: How many oscillators in the range $\Delta\omega = \omega + d\omega$. In other words, we want to calculate $\rho(\omega)$:

(10) $$\rho(\omega)\,d\omega = \frac{dn}{d\omega}\,d\omega$$

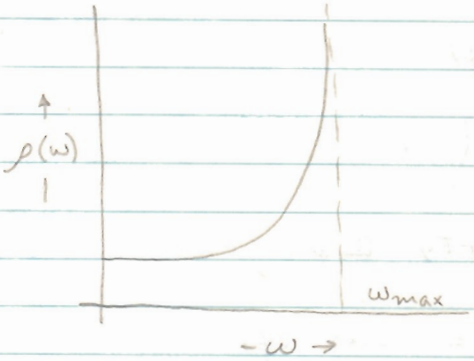
Plot ω versus n from relation (5):



From (5):

(11) $$n = \frac{2N}{\pi}\,\sin^{-1}\frac{\omega}{\omega_{max}}$$

(12) $$\frac{dn}{d\omega} = \frac{2N}{\pi}\,\frac{1}{\sqrt{\omega_{max}^2 - \omega^2}} = \rho(\omega)$$



$\rho(\omega)$ at ω_{max} is infinite because of $\frac{d\omega}{dn} = 0$ from above.

This difficulty disappears in the three dimensional case. Here it means that we have an infinite density of oscillators when $\omega = \omega_{max}$

Three Dimensional Case:

(13) From Before: $M\ddot{u}_{l\alpha} + \sum_{l'\alpha'} C_{\alpha\alpha'}(l-l')\, u_{l'\alpha'} = 0$

Postulate the following solution:

(14) $u_{l\alpha'}(t) = e_{\alpha'}(q)\, e^{i(\bar{q}\cdot\bar{R}_l - \omega(q,j)t)}$

Substituting,

(15) $-M\omega^2 e_\alpha(q) + \sum_{l'\alpha'} C_{\alpha\alpha'}(l-l')\, e_{\alpha'}(q)\, e^{i\bar{q}\cdot(\bar{R}_{l'} - \bar{R}_l)}$

Performing a Fourier inversion: (not really)

(16) $\sum_{l'} C_{\alpha\alpha'}(l-l')\, e^{i\bar{q}\cdot(\bar{R}_{l'} - \bar{R}_l)} = \sum_{l} C_{\alpha\alpha'}(l)\, e^{-i\bar{q}\cdot\bar{R}_l}$

$= \hat{C}_{\alpha\alpha'}(q)$

On Substitution:

(17) $M\omega^2 e_\alpha(q) = \sum_{\alpha'} \hat{C}_{\alpha\alpha'}(q)\, e_{\alpha'}(q)$

Properties of $C_{\alpha\alpha'}(q)$ $[= \hat{C}_{\alpha\alpha'}(q)]$:

a) $C_{\alpha\alpha'}(l) = C_{\alpha'\alpha}(-l)$ from property II b.

b) $C^*_{\alpha\alpha'}(-q) = \sum_l C_{\alpha\alpha'}(l)\, e^{i(-\bar{q})\cdot\bar{R}_l} = C_{\alpha\alpha'}(q)$

from (16).

c) $C_{\alpha'\alpha}(q) = \sum_l C_{\alpha'\alpha}(l)\, e^{-i\bar{q}\cdot\bar{R}_l} = \sum_l C_{\alpha\alpha'}(-l)\, e^{i\bar{q}\cdot\bar{R}_l}$

$= C^*_{\alpha\alpha'}(q)$ which denotes the Hermiticity of the $C_{\alpha\alpha'}$'s.

d) From Inversion Symmetry: $C_{\alpha\alpha'}(l) = C_{\alpha\alpha'}(-l)$:

$C^*_{\alpha\alpha'}(-q) = C_{\alpha\alpha'}(q)$

$C_{\alpha'\alpha}(q) = C^*_{\alpha\alpha'}(q)$

Shifting our basis for l, we may form as before:

$$(18)\quad C_{\alpha\alpha'}(q) = \tfrac{1}{2}\sum_l C_{\alpha\alpha'}(l)\left[e^{-i\bar{q}\cdot\bar{R}_l} + e^{i\bar{q}\cdot\bar{R}_l}\right]$$

$$= \sum_l C_{\alpha\alpha'}(l)\cos\bar{q}\cdot\bar{R}_l$$

$$= -2\sum_l C_{\alpha\alpha'}(l)\tfrac{1}{2}\left[1-\cos\bar{q}\cdot\bar{R}_l\right] \quad \left\{\text{From } \sum_l C_{\alpha\alpha'}(l) = 0\right\}$$

$$= -2\sum_l C_{\alpha\alpha'}(l)\sin^2 \tfrac{1}{2}\bar{q}\cdot\bar{R}_l$$

which is analogous to our one-dimensional case. See equation II (18).

Returning to (15) and (16), we have on substitution:

$$(19)\quad \frac{1}{M}\sum_{\alpha'} C_{\alpha\alpha'}(q)\xi_{\alpha'} - \omega^2 \xi_\alpha = 0$$

We may now write three equations for each three directions:

$$(20)\quad \left(\frac{1}{M}C_{11}(q) - \omega^2\right)e_1 + \frac{1}{M}C_{12}(q)e_2 + \frac{1}{M}C_{13}(q)e_3 = 0$$

$$\frac{1}{M}C_{21}(q)\,e_1 + \left(\frac{1}{M}C_{22}(q) - \omega^2\right)e_2 + \frac{1}{M}C_{23}(q)e_3 = 0$$

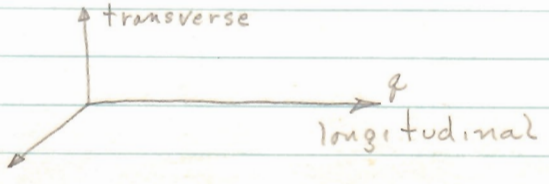
$$\frac{1}{M}C_{31}(q)\,e_1 + \frac{1}{M}C_{32}(q)\,e_2 + \left(\frac{1}{M}C_{33}(q) - \omega^2\right)e_3 = 0$$

Now we must have:

$$(21)\quad \left|\frac{1}{M}C_{\alpha\alpha'}(q) - S_{\alpha\alpha'}\omega^2\right| = 0$$

Thus we get our solution: $\omega(j,q)$ in which j is the index of the eigenvalues. $j = 1, 2, 3$

Also, $e(q,j)$ are the polarization vectors apparently



Significance of Symmetry:

(a) From Hermiticity of $C_{\alpha\alpha'}(q)$, i.e., $C_{\alpha\alpha'}(q) = C^*_{\alpha'\alpha}(q)$, the main diagonal must be real in the secular equation, so ω^2 is real.

(b) $\omega^2(q,j) > 0$, from common sense

(c) $\omega(q,j) = \omega(-q,j)$; because $C_{\alpha\alpha'}(-q) = C_{\alpha\alpha'}(q)$

(d) $e(q,j) = e^*(-q,j)$; see secular equation.

We will now look at the general solution and impose periodic boundary conditions:

(22) $\bar{u}_l = \sum'_{q,j} e(q,j)\, e^{i(\bar{q}\cdot\bar{R}_l - \omega\{q,j\}t)}$

as the sum of all solutions is a solution or as found by Fourier series solution.

Impose Periodic Boundary Conditions:

(23) $u_l = u_{l'}$, $l = (0, l_2, l_3)$
$l' = (G, l_2, l_3)$

considering G atoms per edge of sample. Although it is unrealistic to think of joining the boundarys of a four-dimensional object, we still do it for mathematical convenience.

"q" Space:

In q space there is a corresponding symmetry as in real lattice space.

Reciprocal Lattice Vector:

(24) $K = 2\pi (g_1 \bar{b}_1 + g_2 \bar{b}_2 + g_3 \bar{b}_3)$

with g_i = integers

b_i = co-ordinates of q space

The lattice vector is $\bar{R}_l = (l_1 \bar{a}_1 + l_2 \bar{a}_2 + l_3 \bar{a}_3)$ with the important relation that,

(25) $\bar{a}_i \cdot \bar{b}_j = \delta_{ij}$

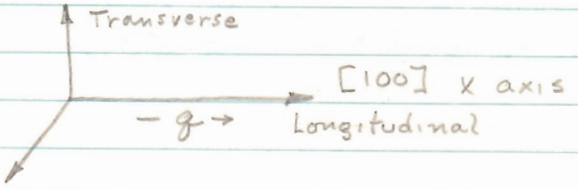
LECTURE IV 10-3-60

Continuation of 3 Dimensional Lattice Study:

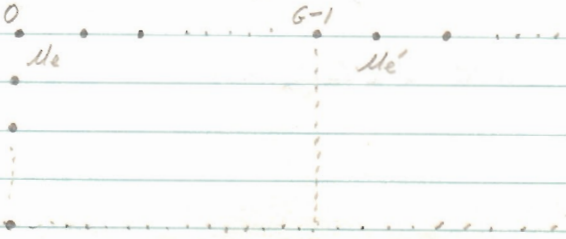
The general equation of a 3-D lattice has been given as:

(1) $\sum_{\alpha'} \left[\frac{1}{M} C_{\alpha\alpha'}(q) - \delta_{\alpha\alpha'} \omega^2(q,j) \right] e_{\alpha'}(q,j) = 0$

in which the eigenvectors are taken as the polarization vectors, with $\bar{u}_l \sim \bar{e}_q$



Taking periodic boundary conditions: $\bar{u}_l = \bar{u}_{l'}$ in all directions.



Reciprocal Lattice; system of axis representing "q" space which is analogous to coordinate space.

It is defined by 3 vectors, $\bar{b}_1, \bar{b}_2, \bar{b}_3$, such that $\bar{a}_\ell \cdot \bar{b}_j = \delta_{\ell j}$. Thus:

(2) $\bar{K}_g = 2\pi \left(g_1 \bar{b}_1 + g_2 \bar{b}_2 + g_3 \bar{b}_3 \right)$

in which the relation to the real lattice is:

(3) $\bar{b}_i = \dfrac{\bar{a}_2 \times \bar{a}_3}{\bar{a}_1 \cdot \bar{a}_2 \times \bar{a}_3}$, etc., with dimensions of reciprocal length

In one dimension, $b = \frac{1}{a}$, $K = \frac{2\pi}{a}$ or the principal values of q, viz., $0 < q < \frac{2\pi}{a}$.

Now,

(4) $\bar{q} = \dfrac{2\pi}{G} \left(g_1 \bar{b}_1 + g_2 \bar{b}_2 + g_3 \bar{b}_3 \right)$ with $M_\ell = M_{\ell'}$

Take $\ell = (0, \ell_2, \ell_3)$
$\ell' = (G, \ell_2, \ell_3)$

(5) $M_\ell \sim e^{i \bar{q} \cdot \bar{R}_\ell}$
$M_{\ell'} \sim e^{i G \bar{q} \cdot \bar{a}_1}$

The periodic boundary conditions are satisfied if:

(6) $e^{i G \bar{q} \cdot \bar{a}_1} = 1$, now

(7) $G \bar{q} \cdot \bar{a}_1 = G \dfrac{2\pi}{G} \left(g_1 \bar{b}_1 + \dots \right) \cdot \bar{a}_1 = 2\pi g_1$

(8) $\therefore e^{i 2\pi g_1} = 1$

The spacing between points in "q" space is $\frac{2\pi}{G} \bar{b}_i$

There is no unique wave vector, i.e.

(9) $\bar{q}' = \bar{q} + K$

(10) $M_e \cong e^{i\bar{q}'\cdot\bar{R}_e} = e^{i\bar{q}\cdot\bar{R}_e} e^{i\bar{K}\cdot\bar{R}_e}$

with $\bar{K}\cdot\bar{R}_e = 2\pi \sum_i l_i q_i$ which is always some integer times π, thus showing $\bar{q}$ not unique. We then confine q so that $|\bar{q}| < |\bar{K}|$

The reciprocal lattice of a bcc is a fcc and vice-versa. Read article on reciprocal lattice in Ziman § 1.5, Rietz, vol. I., SSP.

Brillouin Zone: depends only on translational symmetry which is very important. Contains inversion symmetry.

How many independent eigenvalues are in a region of a crystal? The answer is 3G independent values of q. Thus number of independent eigenvalues equals the number of degrees of freedom.

Density of States in reciprocal space: The "volume" around each point is $\left(\frac{2\pi}{G}\right)^3 \bar{b}_1\cdot\bar{b}_2\times\bar{b}_3$. It can be shown that

(11) $$\bar{b}_1\cdot\bar{b}_2\times\bar{b}_3 = \frac{1}{\bar{a}_1\cdot\bar{a}_2\times\bar{a}_3}$$

Now $G^3[\bar{a}_1\cdot\bar{a}_2\times\bar{a}_3]$ is interpreted in real space as the volume V of the crystal, therefore, the volume in "q" space $= \frac{8\pi^3}{V}$

No. of points in "q" space / per volume $= \frac{V}{8\pi^3}$. This result is important because we can change a sum on q into an integration in "q" space, viz.,

(12) $$\sum_q \rightarrow \frac{V}{8\pi^3}\int d^3q$$

Interpretation of Eigenvectors:

Translational and Longitudinal properties result from the orthogonality of the eigenvectors, e_j.

Theorem: $S = \sum_l e^{i(\bar{q}-\bar{q}')\cdot \bar{R}_l} = G^3 \delta_{q', q+K}$

Proof: Shift origin: $\sum_l e^{i(q-q')\cdot(R_l + R_l')}$

$= S \, e^{i(\bar{q}-\bar{q}')\cdot \bar{R}_l}$

Now $S = 0$ unless $q - q' = K$ $\quad (e^{iK\cdot R_l} = 1)$

Then $S = \sum_l e^{i\bar{K}\cdot \bar{R}_l} = G^3$ (triple directions)

Theorem proved.

We note in all discussions a continual shift of thought between infinite and finite lattices.

Orthogonality of Eigenfunctions:

Orthogonality Condition:

(13) $\sum_l \left\{ e(\bar{q},j)\, e^{i\bar{q}\cdot \bar{R}_l} \right\}^* \left\{ e(\bar{q}',j')\, e^{i\bar{q}'\cdot \bar{R}_l} \right\} = \eta\, \delta_{q,q'}\, \delta_{j,j'}$

where η is a normalization factor. We may write (13) as follows:

(14) $e(\bar{q},j)^* \cdot e(\bar{q}',j') \sum_l e^{i(\bar{q}'-\bar{q})\cdot \bar{R}_l} = \eta\, \delta_{\bar{q},\bar{q}'}\, \delta_{j,j'}$

$\sum_l e^{i(\bar{q}'-\bar{q})\cdot \bar{R}_l} = G^3 \delta_{\bar{q},q'}$ from the above theorem

Choosing $\eta = G^3$, we have,

(15) $e(\bar{q},j)^* \cdot e(\bar{q}',j') = \delta_{j,j'}$

We have thus shown the orthogonality of the eigenvectors from the orthogonality of the eigenfunctions. Thus, the polarization vectors in monatomic unit cell are all mutually orthogonal.

Assumption: $\omega(\bar{q},j)$ are non-degenerate

(16) $M\omega^2(\bar{q},j)\, e_\alpha(\bar{q},j) = \sum_{\alpha'} C_{\alpha\alpha'}(q)\, e_{\alpha'}(q)$

Change $j \to j'$

In tensor notation:

(17) $M\omega^2(\bar{q},j')\, \bar{e}(\bar{q},j') = \mathbb{C}(q)\, \bar{e}(\bar{q},j')$

Take the complex conjugate and transpose, knowing that the matrix $\mathbb{C}(q)$ possesses Hermiticity, that is, $\mathbb{C}(q) = \mathbb{C}^\dagger(q)$ where the dagger ($\dagger$) means complex conjugate and transpose.

(18) $M\omega^2(\bar{q},j')\, \bar{e}^\dagger(\bar{q},j') = \bar{e}^\dagger(\bar{q},j')\, \mathbb{C}(q)$

Multiply (17) by $\bar{e}^\dagger(\bar{q},j)$. Change $j' \to j$ in (18) and multiply by $\bar{e}(\bar{q},j')$. Subtract results:

(19) $M\left[\omega^2(\bar{q},j') - \omega^2(\bar{q},j)\right] \bar{e}^\dagger(\bar{q},j)\, \bar{e}(\bar{q},j')$

$= \bar{e}^\dagger(\bar{q},j)\, \mathbb{C}(q)\, \bar{e}(\bar{q},j') - \bar{e}^\dagger(\bar{q},j')\, \mathbb{C}(q)\, \bar{e}(\bar{q},j')$

$= 0$

Check assumption of non-degeneracy:

(20) For $j \neq j'$; $\bar{e}^\dagger(\bar{q},j) \cdot \bar{e}(\bar{q},j') = 0$

$j = j'$; $\bar{e}^\dagger(\bar{q},j) \cdot \bar{e}(\bar{q},j') \neq 0$

Thus $\omega^2(\bar{q},j)$ is non-degenerate

Evaluation of $\mathbb{C}$ or $C_{\alpha\alpha'}(q)$:

(21) $C_{\alpha\alpha'}(q) = \sum_{\ell} C_{\alpha\alpha'}(\ell)\, e^{i\bar{q}\cdot\bar{R}_\ell}$

$= -2 \sum C_{\alpha\alpha'}(\ell) \sin^2 \tfrac{1}{2}\bar{q}\cdot\bar{R}_\ell$

Now the $C_{\alpha\alpha'}(\ell)$'s form a matrix:

Examine the symmetry of the crystal, for example, the rotation symmetry in a cubic crystal.

(22) $\bar{u}'_{\ell\beta} = \sum_{\alpha} S_{\beta\alpha}\, \bar{u}_{\ell\alpha}$ may be written

(23) $\bar{u}'_{\ell} = \mathbb{S}\, \bar{u}_{\ell}$ and when

(24) $\bar{u}'^{T}_{\ell} = \bar{u}^{T}_{\ell}\, \mathbb{S}^{T}$, then

(25) $\mathbb{S}^{T}\mathbb{S} = \mathbb{1}$ and $\mathbb{S}$ is an orthogonal transformation.

Using the tensor notation, we may write the potential energy as follows:

(26) $\Phi = \frac{1}{2} \sum_{\ell\ell'} u_\ell^{T}\, \mathbb{C}(\ell-\ell')\, u_{\ell'}$ (u_ℓ transposed, see II-1A)

$= \frac{1}{2} \sum_{\ell\ell'} u'^{T}_{\ell}\, \mathbb{C}'(\ell-\ell')\, u'_{\ell'}$ (by rotation or translation in a simple cubic)

$= \frac{1}{2} \sum_{\ell\ell'} u_\ell^{T}\, \mathbb{S}^{T}\, \mathbb{C}'(\ell-\ell')\, \mathbb{S}\, u_{\ell'}$

Then $\mathbb{C}(\ell-\ell') = \mathbb{S}^{T}\, \mathbb{C}'(\ell-\ell')\, \mathbb{S}$

LECTURE V 10-5-60

We have from before:

(1) $\hat{C}_{\alpha\alpha'}(q) = \sum_{\ell} C_{\alpha\alpha'}(\ell)\, e^{-i\bar{q}\cdot\bar{R}_\ell} = -2 \sum_{\ell} C_{\alpha\alpha'}(\ell) \sin^2 \tfrac{1}{2}\bar{q}\cdot\bar{R}_\ell$ (with inversion symmetry)

(2) $\sum_{\alpha'} \left[\frac{1}{M} \hat{C}_{\alpha\alpha'}(q) - \delta_{\alpha\alpha'}\omega^2(q) \right] e_{\alpha'}(q) = 0$

(3) $\Phi = \frac{1}{2} \sum_{\ell}{}' \bar{u}_\ell^{\,T}\, \mathbb{C}(\ell-\ell')\, \bar{u}_{\ell'}$

The transpose is written because of the form necessary for matrix multiplication, viz., $(\ )(\ )^T(\ )(\ )$.

Make a symmetry transformation:

(4) $\Phi = \frac{1}{2} \sum_{\ell}{}' \bar{u}'^{\,T}_{\ell}\, \mathbb{C}'(\ell-\ell')\, \bar{u}'_{\ell'}$

Make the transformation unitary:

(5) $\bar{u}'_\ell = \mathbb{S}\,\bar{u}_\ell$
$\bar{u}'^{\,T}_\ell = \bar{u}_\ell^{\,T}\,\mathbb{S}^T$
with the condition $\mathbb{S}^T\mathbb{S} = \mathbb{I}$

Then:

(6) $\mathbb{C}(\ell-\ell') = \mathbb{S}^T\,\mathbb{C}'(\ell-\ell')\,\mathbb{S}$

We may remove the prime from the right hand side and write it without because the nature of the force constants remain physically unchanged.

Take a simple cubic lattice - compute tensor when there is nearest neighbor interaction. Find $\mathbb{C}(100)$.

[100]
(a, 0, 0)

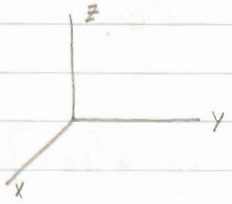
Nearest neighbor distance in simple cubic

(7) $\mathbb{C}(100) = \begin{bmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{bmatrix}$

We would desire a transform such that $x, y, z \rightarrow x', y', z' = x, \pm y, \pm z$, leaving x invariant.

Use the transformation:

(8) $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ z \\ y \end{pmatrix}$



(9) $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ z \\ -y \end{pmatrix} \rightarrow \begin{pmatrix} x \\ z \\ y \end{pmatrix}$

↓ Rotate x axis

↓ Reflect in xz plane

Essentially, we make transformations keeping the direction of interest invariant.

Then:

(10) $\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ z \\ y \end{pmatrix}$

$\Leftrightarrow$ and is also symmetric about the diagonal,

Plug-in equation (6)

(11) $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} c_{11} & x & x \\ x & x & c_{22} \\ x & c_{33} & x \end{pmatrix}$

$= \begin{pmatrix} c_{11} & x & x \\ x & c_{33} & x \\ x & x & c_{22} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix}$

and we can conclude that $c_{33} = c_{22}$

Another transformation: $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$; from this $\Leftrightarrow$ would be:

(12) $\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$

Plug-in equation (6):

(13) $\begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix}\begin{pmatrix} + & + & + \\ + & + & + \\ + & + & + \end{pmatrix}\begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix} = \begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix}\begin{pmatrix} + & - & + \\ + & - & + \\ + & - & + \end{pmatrix}$

$= \begin{pmatrix} + & - & + \\ - & + & - \\ + & - & + \end{pmatrix} = \begin{pmatrix} + & + & + \\ + & + & + \\ + & + & + \end{pmatrix}$, from which we conclude

(14) $C_{12} = -C_{12} = 0$

$C_{21} = -C_{21} = 0$

$C_{23} = -C_{23} = 0$

$C_{32} = -C_{32} = 0$

By performing the transformation $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ y \\ -z \end{pmatrix}$, we find that $C_{13} = -C_{13} = 0$

$C_{31} = -C_{31} = 0$

Thus we have shown that

(15) $\mathbb{C}(100) = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{bmatrix}$; also $\mathbb{C}(010) = \begin{bmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{bmatrix}$

and $\mathbb{C}(001) = \begin{bmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{bmatrix}$

Now we want to find $\hat{C}_{\alpha\alpha'}(q)$. Take nearest neighbors along axis with q propagating along the [100] direction. From (1), we get

(16) $\hat{\mathbb{C}}(q) = -2 \sum_{-1}^{1}{}' \mathbb{C}(l) \sin^2 \frac{qla}{2} = -4\,\mathbb{C}(100) \sin^2 \tfrac{1}{2} qa$

which gives: from (2):

(17) $\begin{bmatrix} -4\alpha \sin^2 \frac{1}{2} qa & 0 & 0 \\ 0 & -4\beta \sin^2 \frac{1}{2} qa & 0 \\ 0 & 0 & -4\beta \sin^2 \frac{1}{2} qa \end{bmatrix} = \hat{\mathbb{C}}(q)$

(18) $\begin{bmatrix} -\frac{4\alpha}{M} \sin^2 \frac{1}{2} qa - \omega^2 & 0 & 0 \\ 0 & -\frac{4\beta}{M} \sin^2 \frac{1}{2} qa - \omega^2 & 0 \\ 0 & 0 & -\frac{4\beta}{M} \sin^2 \frac{1}{2} qa - \omega^2 \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix} = 0$

The Determinant of the matrix must, of course, be zero. We then get:

(19) (a) $\omega^2 = -\frac{4\alpha}{M} \sin^2 \frac{1}{2} qa$

(b) $\omega^2 = -\frac{4\beta}{M} \sin^2 \frac{1}{2} qa$ for eigenvalues

For eigenvectors: Substitute eigenvalue one at a time back into (18): For (19) (a):

(20) $\begin{bmatrix} 0 & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & B \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix} = 0$ It is apparent that e_2 and e_3 are zero, while e_1 may be finite.

$\begin{bmatrix} e_1 \\ 0 \\ 0 \end{bmatrix}$ will give a longitudinal wave

Using eigenvalue (19) (b):

(21) $\begin{bmatrix} A & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix} = 0$, we will get $\begin{bmatrix} 0 \\ e_2 \\ e_3 \end{bmatrix}$ because the transverse mode has two directions. It is to be noted that we may only talk about longitudinal and transverse modes in high symmetry crystals.

Another simplifying assumption: look at long wavelengths, $\omega \sim q$, in a continuum. Measure elastic constants to match to coefficients. Sometimes we have more coefficients than constants. We sometimes search for a model to simulate reality. Use the central force model.

Central Force Model: Force between two atoms depends only on the distance between them.

Then:

(22) $V = \sum_l \varphi_x(r) = \frac{1}{2} k \sum_l (r-l)^2$ assuming a spring type relationship and nearest neighbor case

$$= \sum_l \left[\varphi(l) + \sum_\alpha \left(\frac{\partial \varphi}{\partial x_\alpha}\right)_{eq.} (x_\alpha - l_\alpha) + \frac{1}{2} \sum_{\alpha\alpha'} \left(\frac{\partial^2 \varphi}{\partial x_\alpha \partial x_{\alpha'}}\right)_{eq.} (x_\alpha - l_\alpha)(x_{\alpha'} - l_{\alpha'}) + \cdots \right.$$

with the usual assumptions about equilibrium. It can be shown that:

(23) $C_{\alpha\alpha'}(l) = \left(\frac{\partial^2 \varphi}{\partial x_\alpha \partial x_{\alpha'}}\right)_{eq.} = -k \frac{l_\alpha l_{\alpha'}}{l^2}$ this relation can be used to set up matrices

Look at [100] direction, $\alpha = 1, 2, 3$

$\therefore \quad C(l) = \begin{bmatrix} x & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$; thus reducing two force constants to one.

Important to remember the definition of the central force model.

This concludes the classical approach to lattice vibrations.

RESUME' OF CLASSICAL THEORY OF LATTICE VIBRATIONS

Hamiltonian (KE + V)

↓

Expand V → harmonic & anharmonic

↓

Hamilton's Equation of Motion

↓

Symmetry Properties of C's

- Vanishing of Forces under rigid displacements
- Periodicity of Lattice Fourier Analysis: $u_\ell \sim e^{i\vec{q}\cdot\vec{R}_\ell}$ Separation into different q's
- $C_{\alpha\alpha'}(q) = C_{\alpha'\alpha}(q)$ Hermiticity
  - ↓
  - ω's are real
- $C_{\alpha\alpha'}(q) = C_{\alpha\alpha'}(-q)$
  $\omega(-q) = \omega(q)$
  $e(q,j) = e^*(-q,j)$
  Displacement Real
  - ↓
  - Small q: $\omega \sim q$

} Time Reversibility

↓

Periodic Boundary Conditions

↓

(1) q's discrete
(2) not unique
(3) No. of q's = No. of Degrees of freedom

- Density of States in "q" space $\left(\frac{V}{8\pi^3}\right)$
- Brillouin Zone
  (1) Contains all about q's
  (2) Translational symmetry
  (3) Inversion symmetry

↓

Evaluate C's for specific systems: all symmetry properties

↓

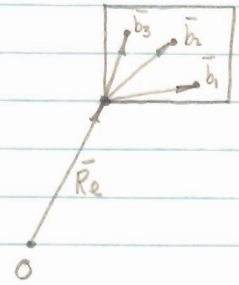
Specific Force Models

↓

$\rho(\omega)$: Density of States

Quantization of Lattice Vibrations

We previously considered only one atom/unit cell, now we will do the general case: Consider the following diagram for the unit cell:



$\bar{R}_\ell$ is the distance from some arbitrary origin to the origin of the unit cell. The $\bar{b}_i$'s are the vectors to the individual atoms in the unit cell from the unit cell origin.

For one atom/unit cell, the Hamiltonian in tensor terminology is:

$$(24)\quad H = V_0 + \frac{1}{2M}\sum_{\ell} \bar{p}_\ell \cdot \bar{p}_\ell + \frac{1}{2}\sum_{\ell\ell'} \bar{u}_\ell^{\,T}\, \mathbb{C}(\ell-\ell')\, \bar{u}_{\ell'}$$

In general:

$$(25)\quad H = V_0 + \frac{1}{2}\sum_{\ell,b} \frac{1}{M_b}\, \bar{p}_{\ell,b} \cdot \bar{p}_{\ell,b} + \frac{1}{2}\sum_{\ell\ell',bb'} \bar{u}_{\ell b}^{\,T}\, \mathbb{C}(\ell b, \ell' b')\, \bar{u}_{\ell' b'}$$

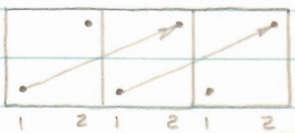
LECTURE VI 10-7-60

Quantum Mechanical Case

Our procedure will be to work with equation I(25) and combine it with the usual commutation rule, viz.,

$$(1)\quad [\bar{u}_{\ell b}, \bar{p}_{\ell b}] = i\hbar\, \delta_{\ell\ell'}\, \delta_{bb'}\, \mathbb{I}$$

The periodicy is such that $\ell-\ell'$ is the same when a particular atom in the unit cell is specified. Thus we have:



$$(2)\quad \mathbb{C}(\ell b, \ell' b') = \mathbb{C}(\ell-\ell', bb')$$

As the force tensor is really a mixed partial derivative, we may also write:

(3) $C_{\alpha\alpha'}(l-l', bb') = C_{\alpha'\alpha}(l'-l, b'b)$

The equation of motion is:

(4) $M\ddot{u}_{lb\alpha} + \sum_{\alpha' l' b'} C_{\alpha\alpha'}(l-l', bb')\, u_{l'b'\alpha'} = 0$

Under rigid displacement:

(5) $\sum_{l'b'} C_{\alpha\alpha'}(l', bb') = 0$

Now, we would like to transform our equations to "q" space. To do this, we need two theorems.

I. $\frac{1}{G^3}\sum_{l} e^{i(\bar{q}-\bar{q}')\cdot\bar{R}_l} = \delta_{q,q'+K}$

II. $\frac{1}{G^3}\sum_{q} e^{i\bar{q}\cdot(\bar{R}_l-\bar{R}_{l'})} = \delta_{ll'}$

Proof: $\bar{q} = \frac{2\pi}{G}\left(q_1\bar{b}_1 + q_2\bar{b}_2 + q_3\bar{b}_3\right)$

$\bar{R}_l - \bar{R}_{l'} = l_1\bar{a}_1 + l_2\bar{a}_2 + l_3\bar{a}_3$

$\therefore\ e^{i\bar{q}\cdot(\bar{R}_l-\bar{R}_{l'})} = e^{\frac{2\pi i}{G}(l_1q_1 + l_2q_2 + l_3q_3)}, \quad 0 \le q_i \le G-1$

$\frac{1}{G^3}\sum_{q} e^{i\bar{q}\cdot(\bar{R}_l-\bar{R}_{l'})} = \left[\frac{1}{G}\sum_{q_i=0}^{G-1} e^{\frac{2\pi i l_i q_i}{G}}\right]^3$

$= \left[\frac{1}{G}\,\frac{1-e^{i2\pi l_i}}{1-e^{i2\pi l_i/G}}\right]^3 = \delta_{ll'}$

$= \begin{cases} 0 & \text{if } l_i \neq 0 \\ 1 & \text{if } l_i = 0 \end{cases} = \delta_{ll'}$

We will use these theorems later.

We may define the following two transforms from coordinate space to q space:

(6) $\bar{u}_{\ell b} = \frac{1}{G^{3/2}} \sum_{q} \hat{\bar{u}}_{qb} e^{i q \cdot R_\ell}$

(7) $\bar{p}_{\ell b} = \frac{1}{G^{3/2}} \sum_{q} \hat{\bar{p}}_{qb} e^{-i q \cdot R_\ell}$, the minus sign being taken for later convenience.

Going back to the Hamiltonians; we shall first consider the kinetic energy term; using equation (7):

(8) $T = \frac{1}{2G^3} \sum_{\ell b} \frac{1}{M_b} \sum_{qq'} \hat{p}_{qb} \hat{p}_{q'b} e^{-i(\bar{q}+\bar{q}')\cdot \bar{R}_\ell}$

$= \frac{1}{2} \sum_{b,qq'} \frac{1}{M_b} \hat{p}_{qb} \hat{p}_{q'b} \delta_{q,-q'}$ (by Theorem I)

$= \frac{1}{2} \sum_{bq} \frac{1}{M_b} \hat{p}_{qb} \hat{p}_{-q,b}$ (removing Kronecker Delta)

Considering the potential energy term and applying equation (6):

(9) $V = \frac{1}{2G^3} \sum_{\substack{\ell\ell' \\ bb' \\ qq'}} \hat{\bar{u}}_{qb} \mathbb{C}(\ell-\ell', bb') \hat{\bar{u}}_{q'b'} e^{i(\bar{q}\cdot\bar{R}_\ell + \bar{q}'\cdot\bar{R}_{\ell'})}$

Now: $e^{i(\bar{q}\cdot\bar{R}_\ell + q'\cdot\bar{R}_\ell)} = e^{i\bar{q}\cdot(\bar{R}_\ell - \bar{R}_{\ell'})} e^{i(\bar{q}+\bar{q}')\cdot\bar{R}_{\ell'}}$

Define: $\bar{R}_\ell - \bar{R}_{\ell'} = \bar{R}_h$

(10) $V = \frac{1}{2G^3} \sum_{\substack{h\ell' \\ bb' \\ qq'}} \bar{u}_{qb} \mathbb{C}(h, bb') e^{i\bar{q}\cdot\bar{R}_h} \underbrace{e^{i(\bar{q}+\bar{q}')\cdot\bar{R}_{\ell'}}}_{G^3 \delta_{q,-q'} \text{ (by Theorem I)}} \bar{u}_{q'b'}$

$= \frac{1}{2} \sum_{\substack{bb' \\ q'}} \left[\underbrace{\sum_{h} \mathbb{C}(h, bb') e^{-i\bar{q}'\cdot\bar{R}_h}}_{\text{Fourier Invert}} \right] \bar{u}_{-q',b} \bar{u}_{q'b}$ (eliminating $\delta_{q,-q'}$)

$= \frac{1}{2} \sum_{\substack{bb' \\ q'}} \bar{u}_{-q'b} \mathbb{C}(q', bb') \bar{u}_{q'b}$

Because of the traveling waves in the "q" space, we find only a change in the sign of the exponent of e for the different directions:

(11) $p_{-q,b} = p^*_{qb}$
$u_{-qb} = u^*_{qb}$

and from the Fourier inversion performed to get (10):

(13) $\tilde{C}(q', bb') = \sum_n C(n, bb')\, e^{-i\bar{q}'\cdot\bar{R}_n}$

Using (11) on (10), we finally get the complete Hamiltonian:

(14) $H = \sum_q \left[\frac{1}{2} \sum_b \frac{1}{M_b} p^*_{qb} p_{qb} + \frac{1}{2} \sum_{bb'} u^*_{qb} C(q, bb') u_{qb} \right]$

$= \sum_q H_q$, changing $q' \to q$ in the potential energy term

We now examine the symmetry of the tensor C:

(15) a. $C^*_{\alpha\alpha'}(-q, bb') = C_{\alpha\alpha'}(q, bb')$ Time Reversal

b. $C^*_{\alpha\alpha'}(q, bb') = C_{\alpha'\alpha}(q, b'b)$ Hermiticity

c. $C_{\alpha\alpha'}(q, bb') = C_{\alpha'\alpha}(-q, b'b)$ From above properties

What are the commutation relations in "q" space? Multiply equation (6) by $\sum_l e^{-i\bar{q}'\cdot\bar{R}_l}$:

(16) $\sum_l \bar{u}_{qb} e^{-i\bar{q}'\cdot\bar{R}_l} = \frac{1}{G^{3/2}} \sum_q u_{qb} \sum_l e^{i(\bar{q}-\bar{q}')\cdot\bar{R}_l}$

$= \frac{1}{G^{3/2}} \cdot G^3 \sum_q u_{qb}\, \delta_{q,q'}$ (by Theorem I)

$= G^{3/2} u_{q'b}$; Finally:

(17) $u_{q'b} = \frac{1}{G^{3/2}} \sum_l \bar{u}_{lb} e^{-i\bar{q}'\cdot\bar{R}_l}$

In a similar manner, we find for the momentum:

$$(18)\quad p_{q'b} = \frac{1}{G^{3/2}} \sum_{l} p_{lb}\, e^{i\bar{q}'\cdot\bar{R}_l}$$

On multiplying (17) and (18) together, we may factor out all terms that commute and get:

$$(19)\quad \left[u_{qb}, p_{q'b'}\right] = \frac{1}{G^3} \sum_{ll'} e^{i(\bar{q}'\cdot\bar{R}_{l'} - \bar{q}\cdot\bar{R}_l)} \left[u_{lb}, p_{l'b'}\right]$$

$$= \frac{i\hbar}{G^3} \sum_{ll'} \delta_{ll'}\,\delta_{bb'}\, \mathbb{1}\, e^{i(\bar{q}'\cdot\bar{R}_{l'} - \bar{q}\cdot\bar{R}_l)}$$

$$= \frac{i\hbar}{G^3} \sum_{l} \delta_{bb'}\, \mathbb{1}\, e^{i(\bar{q}'-\bar{q})\cdot\bar{R}_l}$$

$$= i\hbar\,\delta_{bb'}\,\delta_{qq'}\,\mathbb{1} \quad \text{(by Theorem I)}$$

Thus we see that the commutation rules are analogous in "q" space to those in co-ordinate space. We now must make use of the Heisenberg equation of motion (from Schiff, Sec. 23), viz.,

$$(20)\quad i\hbar \frac{\partial F}{\partial t} = [F, H]$$

in which F is a quantum operator (coordinates or momentum, etc.) and H is the Hamiltonian of the system. We would like to find $\dot{u}$ and then $\dot{p}$. We see from the Hamiltonian (14) that if we choose u_{qb} as our quantum operator, it will commute with all terms of the Hamiltonian except the kinetic energy. Thus, we have:

$$(21)\quad i\hbar\,\dot{u}_{qb} = \left[u_{qb}, \frac{1}{2} \sum_{q'b'} \frac{1}{M_{b'}} p_{-q'b'}\, p_{q'b'}\right]$$

$$= \frac{1}{2} \sum_{q'b'} \frac{1}{M_{b'}} \left(u_{qb}\, p_{-q'b'}\, p_{q'b'} - p_{-q'b'}\, p_{q'b'}\, u_{qb}\right)$$

We now apply the commutation rules of equation (1).

(22) $u_{qb}\, p_{-q'b'}\, p_{q'b'} = (p_{-q'b'}\, u_{qb} + i\hbar\, \delta_{q,-q'}\, \delta_{bb'})\, p_{q'b'}$

(23) $u_{qb}\, p_{-q'b'}\, p_{q'b'} = p_{q'b'}(p_{-q'b'}\, u_{qb} + i\hbar\, \delta_{q,-q'}\, \delta_{bb'}) + i\hbar\, \delta_{q,-q'}\, \delta_{bb'}\, p_{qb}$

Substituting into equation (21), we finally obtain:

(24) $i\hbar\, \dot{u}_{qb} = \frac{1}{2} \sum_{q'b'} \frac{1}{M_{b'}} (2 i\hbar\, \delta_{q,-q'}\, \delta_{bb'})\, p_{q'b'}$

(25) $\dot{u}_{qb} = \frac{p_{qb}}{M_b}$

Equation (25) is just the classical result which one might have expected as we have only operated on the classical kinetic energy term of the Hamiltonian.

The next operation is to find: $M_b \ddot{u}_{qb} = \dot{p}_{qb}$
The proper Hiesenberg equation of motion is:

(26) $i\hbar\, \dot{p}_{qb} = [p_{-qb}, H]$

in which we will evaluate the potential energy part of the term (Hamiltonian).

LECTURE VII 10-10-60

Continuation of the Quantum Mechanical Case:
The following equations are given from before:

(1) $H = \frac{1}{2} \sum_q \left[\sum_b p^{\dagger}_{qb}\, p_{qb} + \sum_{bb'} u^{\dagger}_{qb}\, C(q, bb')\, u_{qb'} \right]$

(2) $u_{-qb} = u^{\dagger}_{qb}$
$p_{-qb} = p^{\dagger}_{qb}$

(3) $[u_{qb}, p_{q'b'}] = \delta_{qq'}\, \delta_{bb'}\, \mathbb{I}\, i\hbar$

(4) $\tilde{C}(q, bb') = \sum_l C(l, bb')\, e^{-iq \cdot R_l}$

(5) $C^{*}_{\alpha\alpha'}(-q, bb') = C_{\alpha\alpha'}(q, bb')$

(6) $C_{\alpha\alpha'}(q, bb') = C_{\alpha'\alpha}(-q, b'b)$

(7) $i\hbar \frac{\partial F}{\partial t} = [F, H]$

Take F to be u_{qb}, we get:

(8) $\dot{u}_{qb} = \frac{1}{M_b} p_{-qb}$, or, $M_b \ddot{u}_{qb} = \dot{p}_{-qb}$

Take F to be p_{-qb}, we then have from (6) and (7):

(9) $i\hbar \dot{p}_{-qb} = \left[p_{-qb} , \frac{1}{2} \sum_{b'b''} u_{-q'b'} C(q'; b'b'') u_{q'b''} \right]$

The following rules can be shown through manipulations in operator algebra:

(10) $[B, A_1 A_2] = -[A_1, B] A_2 - A_1 [A_2, B]$

Let $B \to p_{-qb}$, $A_1 \to u_{-q'b'}$, $A_2 \to u_{q'b''}$

Now:

(11) $i\hbar \dot{p}_{-qb} = -\frac{1}{2} \sum_{q' b'b''} \left\{ \underbrace{\left[u_{-q'b'}, p_{-qb}\right]}_{i\hbar \delta_{qq'}\delta_{bb'}} C(q'; b'b'') u_{q'b''} + u_{-q'b'} C(q'; b'b'') \underbrace{\left[u_{q'b''}, p_{-qb}\right]}_{i\hbar \delta_{qq'}\delta_{bb''}} \right\}$

$= -\frac{1}{2} i\hbar \sum_{b''} C(q, bb'') u_{qb''} - \frac{1}{2} i\hbar \sum_{b'} u_{qb'} C(-q, b'b)$

$= -i\hbar \sum_{b'} C(q, bb') u_{qb'}$

Because:

(12) $\left\{ \sum_{b'} u_{qb'} C(-q, b'b) \right\}_{\alpha} = \sum_{b'\alpha'} u_{qb'\alpha'} C_{\alpha'\alpha}(-q, b'b)$

$= \sum_{b\alpha'} C_{\alpha\alpha'}(q, bb') u_{qb'\alpha'} = \left\{ \sum_{b'} C(q, bb') u_{qb'} \right\}_{\alpha}$

The final result from (8) and (11) is:

$$(13)\quad M_b \ddot{u}_{qb} + \sum_{b'} C(q,bb')\, u_{qb'} = 0$$

which is the classical equation of motion except that the u's are now operators.

We now define a solution:

$$(14)\quad u_{qb} = \frac{1}{\sqrt{M_b}}\, \bar{e}(q,b)\, e^{i\omega t}\, u_q$$

where u_q is a quantum mechanical factor. Substitute this into the equation of motion:

$$(15)\quad \sum_{b'\alpha'} \left\{ \frac{1}{\sqrt{M_b M_{b'}}} C_{\alpha\alpha'}(q,bb') - \omega^2(q)\, \delta_{bb'} \delta_{\alpha\alpha'} \right\} \bar{e}_{\alpha'}(q,b')\, u_q = 0$$

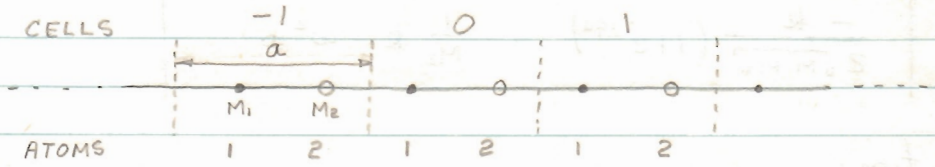
This looks like the corresponding equation for a unit cell without a basis. How many solutions are there? The upper limit on α' is three. Assume that there are k atoms per unit cell, then the upper limit on b' is k. So there are $3kG^3$ number of solutions which is also equal to the degrees of freedom of the system. Label each solution by j, q; that is, we have $\omega(q,j)$, $\bar{e}(q,j)$, u_{qj}. We also have an orthogonality-normality relationship between the $\bar{e}$'s similar to that before.

$$(16)\quad \sum_{b} \bar{e}^*(qbj) \cdot \bar{e}(qbj') = \delta_{jj'}$$

Previously, there was no summation over b.

Example: The Linear Di-atomic Chain:

We will ignore M_q and assume only nearest neighbor forces:



From rigid displacement considerations, we have

(17) $\sum_{\ell bb'} C(\ell, bb') = 0$

For atom #1 of cell #0:

(18) $C(0,11) + C(0,12) + C(-1,12) = 0$

For atom #2 of cell #0:

(19) $C(0,21) + C(0,22) + C(1,21) = 0$

By symmetry considerations and equations (17) and (19):

(20) $C(0,12) = C(-1,12) = -\frac{1}{2} C(0,11)$
$C(0,21) = C(1,21) = -\frac{1}{2} C(0,22)$

Since $C(\ell, bb') = C(-\ell, b'b)$

(21) $C(0,12) = C(0,21) \Rightarrow C(0,11) = C(0,22) = k$ (a constant)

From equation (4):

(22) $\hat{C}(q,11) = C(0,11) = k$
$\hat{C}(q,22) = C(0,22) = k$
$\hat{C}(q,12) = C(0,12) + C(-1,12)\, e^{-iq(-a)} = -\frac{1}{2} k \left[e^{iqa} + 1 \right]$
$\hat{C}(q,21) = C(0,21) + C(1,21)\, e^{-iq(+a)} = -\frac{1}{2} k \left[e^{-iqa} + 1 \right]$

We can check these against the symmetry relationships for Hermiticity.

Setting up the secular equation:

$$(23)\qquad \begin{vmatrix} \frac{1}{M_1}k-\omega^2 & -\frac{k}{2\sqrt{M_1M_2}}\left(1+e^{iqa}\right) \\ -\frac{k}{2\sqrt{M_1M_2}}\left(1+e^{-iqa}\right) & \frac{1}{M_2}k-\omega^2 \end{vmatrix} = 0$$

Upon solution:

$$(24)\qquad \omega^4-\left(\frac{1}{M_1}+\frac{1}{M_2}\right)k\omega^2+\frac{k^2}{M_1M_2}\left[1-\frac{1}{4}\left(1+e^{iqa}\right)\left(1+e^{-iqa}\right)\right]=0$$

$$\left(1+e^{iqa}\right)\left(1+e^{-iqa}\right) = 4\sin^2 \tfrac{1}{2}qa$$

$$(25)\qquad \omega^2(q)=\frac{1}{2}\frac{k}{M_1M_2}\left[(M_1+M_2)\pm\left\{(M_1+M_2)^2-4M_1M_2\sin^2\tfrac{1}{2}qa\right\}^{1/2}\right]$$

Consider the long wavelength approximation: $qa \ll 1$.
Then $\sin^2 \tfrac{1}{2}qa \approx \tfrac{1}{4}q^2a^2 \ll 1$ and

$$(26)\qquad \omega^2(q)=\tfrac{1}{2}k\frac{(M_1+M_2)}{M_1M_2}\left[1\pm\left(1-\frac{1}{2}\frac{M_1M_2}{(M_1+M_2)^2}q^2a^2\right)^{1/2}\right]$$

For the positive solution: ⊕

$$(27)\qquad \omega^2 \approx k\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\quad \text{[optical branch]}$$
(a finite constant)

For the negative solution: ⊖

$$(28)\qquad \omega^2=\frac{k}{4}\frac{q^2a^2}{M_1+M_2}\quad \text{[acoustical branch]}$$

Let us now consider the polarization vectors:
For the ⊕ solution:

$$(29)\qquad -\frac{k}{M_2}e_1-\frac{k}{\sqrt{M_1M_2}}e_2=0$$

$$(30)\qquad \frac{e_1}{e_2}=-\sqrt{\frac{M_2}{M_1}}=\sqrt{\frac{M_1}{M_2}}\frac{M_1}{M_2}\Rightarrow M_1\mu_1+M_2\mu_2=0$$

(from (14))

Physically, the optical branch gives the picture of molecular vibration of two atoms moving against each other or two sublattices moving rigidly against each other. In this branch, ω^2 has the form:

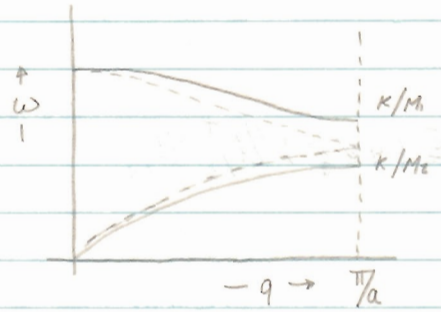
(31) $\omega^2 = A + B q^2$

Thus the group velocity $\frac{d\omega}{dq} = 0$, when $q = 0$ and the phase velocity $\frac{\omega}{q} = \infty$ at $q = 0$. The optical branch is so named because the opposed motion of ionic molecules in an $\mathcal{E}$ field to which case it corresponds.

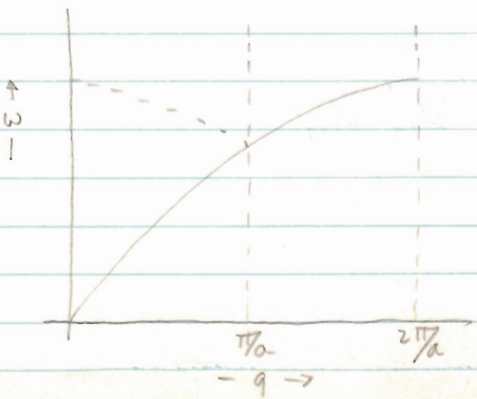
LECTURE VIII 10-14-60

Linear Diatomic Model: Continued:

(A) $\omega^2(q) = \frac{1}{2} \frac{k}{M_1 M_2} \left[(M_1 + M_2) \pm \sqrt{(M_1 + M_2)^2 - 4 M_1 M_2 \sin^2 \tfrac{1}{2} qa} \right]$



If $M_1 = M_2$, the problem reduces to the linear chain and the dotted line occurs in the graph. Why is there apparently an optical mode in the monatomic lattice? This can be explained in the fact the new unit cell has width $a/2$. Thus the new Brillouin zone is $2\pi/a$



Everything will be the same as before when the substitution $a \to \frac{a}{2}$ is made.

Return to Quantum Mechanical Considerations:

The object here will be to obtain a representation in occupation number space so as to quantize the lattice vibrations.

$$(1)\quad H = \frac{1}{2}\sum_{q}\left[\sum_{b}\frac{1}{M_b}p_{qb}^{\dagger}p_{qb} + \sum_{bb'}u_{qb}^{\dagger}\,C(q,bb')\,u_{qb'}\right]$$

with:

$$(2)\quad u_{qb} = \frac{1}{\sqrt{M_b}}\sum_{j}\bar{e}(qbj)\,u_{qj}$$

$$p_{qb} = \sqrt{M_b}\sum_{j}\bar{e}^{*}(qbj)\,p_{qj}$$

} Ignoring the time component or lumping it into the operator.

And the condition that:

$$(3)\quad \sum_{b}\bar{e}^{*}(qbj)\cdot\bar{e}(qbj') = \delta_{jj'}$$

Substitute (2) and make use of (3) in to the Hamiltonian:

$$(4)\quad T = \sum_{b}\frac{1}{M_b}p_{qb}^{\dagger}p_{qb} = \sum_{b}\sum_{jj'}\bar{e}^{*}(qbj)\cdot\bar{e}(qbj')\,p_{qj}^{\dagger}p_{qj'}$$

$$= \sum_{j}p_{qj}^{\dagger}p_{qj}$$

$$(5)\quad V = \sum_{bb'}\sum_{jj'}\frac{1}{\sqrt{M_bM_{b'}}}\bar{e}^{*}(qbj)\,C(q,bb')\,\bar{e}(qb'j')\,u_{qj}^{\dagger}u_{qj'}$$

Recall the secular equation:

$$(6)\quad \sum_{b'}\frac{1}{\sqrt{M_bM_{b'}}}C(q,bb')\,\bar{e}(qb'j') = \omega^2(qj)\,\bar{e}(qbj)$$

Then, upon substitution in (5):

$$(7)\quad V = \sum_{b}\sum_{jj'}\bar{e}^{*}(qbj)\cdot\bar{e}(qbj')\,\omega^2(qj)\,u_{qj}^{\dagger}u_{qj'}$$

$$= \sum_{j}\omega^2(qj)\,u_{qj}^{\dagger}u_{qj'}$$

Thus, finally:

$$(8)\quad H = \frac{1}{2}\sum_{qj}\left[P_{qj}^{\dagger}P_{qj} + \omega^2(qj)\,u_{qj}^{\dagger}u_{qj'}\right]$$

is the new Hamiltonian in terms of our quantum mechanical factors (operators) defined in equation VII (14), as part of the assumed solution.

We must inquire into the commutation rules between these operators. Multiply equations (2) by $\sum_b \bar{e}^*(qbj')$ and $\sum_b \bar{e}(qbj')$ and get:

$$(9)\quad u_{qj} = \sum_b \sqrt{M_b}\,\bar{e}^*(qbj)\cdot u_{qb}$$

$$P_{qj} = \sum_b \frac{1}{\sqrt{M_b}}\,\bar{e}(qbj)\cdot p_{qb}$$

Recall that:

$$(10)\quad [u_{qb\alpha}, p_{q'b'\alpha'}] = i\hbar\,\delta_{\alpha\alpha'}\delta_{bb'}\delta_{qq'}$$

Then, from (9) and (10):

$$(11)\quad [u_{qj}, P_{q'j'}] = \sum_{bb'}\sum_{\alpha\alpha'}\left[\sqrt{\frac{M_b}{M_{b'}}}\left\{\bar{e}_{\alpha}^*(qbj)\,u_{\alpha qb}\,e_{\alpha'}(q'b'j')\,p_{\alpha'q'b'} - e_{\alpha'}(q'b'j')\,p_{\alpha'q'b'}\,e_{\alpha}^*(qbj)\,u_{\alpha qb}\right\}\right]$$

$$= \sum_{bb'}\sum_{\alpha\alpha'}\sqrt{\frac{M_b}{M_{b'}}}\,e_{\alpha}^*(qbj)\,e_{\alpha'}(q'b'j')\left[u_{\alpha qb}, p_{\alpha'q'b'}\right] \quad (i\hbar\,\delta_{\alpha\alpha'}\delta_{bb'}\delta_{qq'})$$

$$= i\hbar\,\delta_{qq'}\sum_b\sum_{\alpha} e_{\alpha}^*(qbj)\,e_{\alpha}(qbj') = i\hbar\,\delta_{qq'}\delta_{jj'}$$

Therefore:

$$(12)\quad [u_{qj}, P_{q'j'}] = i\hbar\,\delta_{qq'}\delta_{jj'}, \text{ or, } [u_q, P_{q'}] = i\hbar\,\delta_{qq'}$$

Thus we have for the Hamiltonian:

(13) $$H = \frac{1}{2} \sum_q \left[P_q^\dagger P_q + \omega^2(q)\, u_q^\dagger u_q \right]$$

with $u_{-q}^\dagger = u_q$

$P_{-q}^\dagger = P_q$

which can be derived from equations (9) and considerations from previous lectures on the u's and e's.

Consider the following operators. We consider these because of their "interesting" properties which will soon be apparent.

(14) $$a_q = \frac{\imath}{\sqrt{2\hbar\omega_q}} P_q^\dagger + \sqrt{\frac{\omega_q}{2\hbar}}\, u_q$$

$$a_q^\dagger = \frac{-\imath}{\sqrt{2\hbar\omega_q}} P_q + \sqrt{\frac{\omega_q}{2\hbar}}\, u_q^\dagger$$

$$a_{-q}^\dagger = \frac{-\imath}{\sqrt{2\hbar\omega_q}} P_q^\dagger + \sqrt{\frac{\omega_q}{2\hbar}}\, u_q$$

Manipulating:

(15) $$u_q = \sqrt{\frac{\hbar}{2\omega_q}} \left(a_q + a_{-q}^\dagger \right)$$

$$P_q^\dagger = \frac{\sqrt{2\hbar\omega_q}}{2\imath} \left(a_q - a_{-q}^\dagger \right)$$

then $P_q = \imath \sqrt{\frac{\hbar\omega_q}{2}} \left(a_q^\dagger - a_{-q} \right)$ and:

(16) $$\left[a_q, a_q^\dagger \right] = \frac{\imath}{\sqrt{2\hbar\omega_q}} \cdot \sqrt{\frac{\omega_q}{2\hbar}} \left\{ \underbrace{\left[P_{-q}, u_{-q} \right]}_{-\imath\hbar} - \underbrace{\left[u_q, P_q \right]}_{\imath\hbar} \right\}$$

$$= 1$$

$$\left[a_q, a_q \right] = 0$$

$$\left[a_q^\dagger, a_q^\dagger \right] = 0 \qquad \text{and in general:}$$

(17) $$\left[a_q, a_{q'}^\dagger \right] = \delta_{qq'}$$

Plugging in the Hamiltonian:

$$(18)\quad H = \frac{1}{2}\sum_q \left[\frac{1}{2}\hbar\omega_q \left(a_q - a_{-q}^\dagger\right)\left(a_q^\dagger - a_{-q}\right) + \omega_q^2 \frac{\hbar}{2\omega_q}\left(a_q^\dagger + a_{-q}\right)\left(a_q + a_{-q}^\dagger\right)\right]$$

$$= \frac{1}{2}\sum_q \frac{\hbar\omega_q}{2}\left[a_q a_q^\dagger + a_{-q}^\dagger a_{-q} + a_q^\dagger a_q + a_{-q}a_{-q}^\dagger\right]$$

We may change $-q$ to $+q$ because we know ω_q is even.

$$(19)\quad H = \frac{1}{2}\sum_q \hbar\omega_q \left(a_q a_q^\dagger + a_q^\dagger a_q\right)$$

$$= \sum_q \hbar\omega_q \left(a_q^\dagger a_q + \frac{1}{2}\right) \quad \text{by application of (16)}$$

Define $N_q \equiv a_q^\dagger a_q$; then:

$$(20)\quad H = \sum_q \hbar\omega_q \left(N_q + \frac{1}{2}\right)$$

We see that this bears a strong resemblence to the usual eigenvalue equation of the quantum mechanical harmonic oscillator.

Occupation Number Representation:

The object of choosing such a representation is to make N_q diagonal. The question is can one be found? At any rate, it must satisfy the commutation rules on the a's. We must prove:

$$(21)\quad \left[N_q, N_{q'}\right] = \left[a_q^\dagger a_q, a_{q'}^\dagger a_{q'}\right] = 0$$

which can be shown from the commutation rules for the a's. Also,

$$(22)\quad \left[a_q, N_q\right] = \left[a_q, a_q^\dagger a_q\right] = a_q$$

$$\left[a_q^\dagger, N_q\right] = \left[a_q^\dagger, a_q^\dagger a_q\right] = -a_q^\dagger$$

Suppose a wave function Ψ_λ describles the states in the occupation space. If:

(23) $N_q \Psi_\lambda = \lambda \Psi_\lambda$

then $a_q \Psi_\lambda$ is an eigenfunction of $\lambda - 1$
also $a_q^\dagger \Psi_\lambda$ is an eigenfunction of $\lambda + 1$
Proof:

$$N_q (a_q \Psi_\lambda) = (a_q N_q - a_q) \Psi_\lambda = (\lambda - 1)(a_q \Psi_\lambda)$$
$$N_q (a_q^\dagger \Psi_\lambda) = (a_q^\dagger N_q + a_q^\dagger) \Psi_\lambda = (\lambda + 1)(a_q^\dagger \Psi_\lambda)$$

LECTURE IX 10-17-60

Occupation Number Representation:

(1) $H = \sum_q \hbar \omega_q (N_q + \frac{1}{2})$; $N_q = a_q^\dagger a_q$

where q is taken to be the sum on q and γ.
Recall:

(2) $[a_q, a_{q'}^\dagger] = \delta_{qq'}$

$[a_q, a_q] = [a_q^\dagger, a_q^\dagger] = 0$

$[N_q, N_{q'}] = 0$ so diagonal representation is possible.

Also:

(3) $[a_q, N_q] = a_q$

$[a_q^\dagger, N_q] = -a_q^\dagger$

We now want to show that N_q's have eigenvalues which are either positive integers or zero. Now:

(4) $N_q (a_q^m \Psi_\lambda) = (\lambda - m)(a_q^m \Psi_\lambda)$, By continuous application of the proof for equation VIII (23).

There are two possibilities that preclude positive integers or zero for the eigenvalues.

1) $\lambda - m$ can be negative
2) one of the Ψ's vanishes

We can eliminate (1) because N_q is a positive, semi-definite number, since:

(5) $\langle N_q \rangle = (\Psi_\mu, a_q^\dagger a_q, \Psi_\mu) = (a_q \Psi_\mu, a_q \Psi_\mu) = \mu (\Psi_\mu, \Psi_\mu) \geq 0,$

therefore $\mu \geq 0$

(2) can be overcome by defining:

(6) $a_q \Psi_0 = 0 \quad , \therefore \lambda_0 = 0$

Now from the above considerations and the proof of equation VIII (23), we see that the states differ only by positive integers or zero.

Recognizitions:

Ψ_0 is the vacuum state : no particles
$N_q (a_q^\dagger \Psi_0) = 1 \cdot a_q^\dagger \Psi_0$, $\therefore$ one particle
Thus $a_q^\dagger$ are "creation" operators
We can then see that a_q are "annihilation" operators.
Therefore, we can associate $\lambda = n_q$, the number of particles and we can say:

(7) $N_q \Psi_{n_q} = n_q \Psi_{n_q}$

We can now find the expectation energy:

(8) $\langle E \rangle = \sum_q \hbar \omega_q \left(n_q + \frac{1}{2}\right) = (\Psi_{n_q}, E, \Psi_{n_q}) = \langle n_q | H | n_q \rangle$

as can be seen because $n_q = \int \Psi_{n_q}^* N_q \Psi_{n_q} \, dq$ (no!)

We can thus associate particles, called phonons, with the energy $\hbar \omega_q$.

The zero point energy is $\frac{1}{2}\sum_q \hbar\omega_q$. In field theory, this quantity is ∞, but finite in a solid because we sum over a number of finite q states.

Find the Matrix Elements:

We introduce the Dirac notation:

$$\langle n_{q'} | a_q | n_q \rangle = (\psi_{n_{q'}}, a_q \psi_{n_q})$$

$$\langle n_{q'} | a_q^\dagger | n_q \rangle = (\psi_{n_{q'}}, a_q^\dagger \psi_{n_q})$$

Consider:

$$(9)\quad \langle n_{q'} | [a_q, N_q] | n_q \rangle = \sum_{q''} \{ \langle n_{q'} | a_q | n_{q''} \rangle \langle n_{q''} | N_q | n_q \rangle - \langle n_{q'} | N_q | n_{q''} \rangle \langle n_{q''} | a_q | n_{q'} \rangle \}$$

Now $\langle n_{q''} | N_q | n_q \rangle = n_q \delta_{qq''}$

$\langle n_{q'} | N_q | n_{q''} \rangle = n_{q'} \delta_{q'q''}$

} because N_q is a diagonal

and $[a_q, N_q] = a_q$

Therefore:

$$(10)\quad (n_q - n_{q'}) \langle n_{q'} | a_q | n_q \rangle = \langle n_{q'} | a_q | n_q \rangle \quad \text{or}$$

$$(11)\quad (n_q - n_{q'} - 1) \langle n_{q'} | a_q | n_q \rangle = 0$$

Now, it is seen that $\langle n_{q'} | a_q | n_q \rangle$ vanishes unless $n_{q'} = n_q - 1$. Thus the matrix elements are:

$$(12)\quad \langle n_q - 1 | a_q | n_q \rangle$$

Also; in the same manner:

$$(13)\quad \langle n_{q'} | [a_q^\dagger, N_q] | n_q \rangle = \langle n_{q'} | a_q^\dagger | n_q \rangle (n_q - n_{q'})$$

$$= - \langle n_{q'} | a_q^\dagger | n_q \rangle$$