

CURTAROLO

PHONON THEORY

+ MADELUNG

- INTRO
- DIAGONALIZATION
 - < ID MONOATOMIC
 - < ID BIATOMIC
- ENERGIES
 - QUANTUM, ZERO POINT ENERGY
- DEBYE MODEL
- EINSTEIN MODEL
- DENSITY OF STATES

PHONONS

~~CLASSIC~~ THEORY

- Temperature shakes materials causing vibrations
- Vibrations can be decomposed, with some approximations, in regular oscillations, called phonons (in periodic BRAVAIS lattices)

Within approximations
(harmonic)

$$\text{Vibration} = \sum_i (\text{phonons})_i \dot{q}_i$$

\uparrow "modes" \uparrow amplitude

Sum up phonon decomposition
if possible.

ASSUMPTIONS ARE REASONABLE

- Equilibrium positions are the Bravais lattice points \bar{R}_n

$$\Rightarrow \langle \bar{r}(t) \rangle = \bar{R}_n + \bar{R}_q$$

\uparrow basis observation;

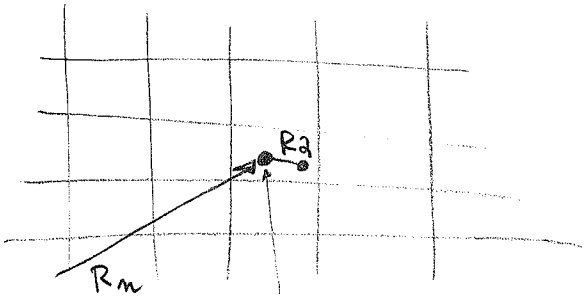
This effect is due to observation; at finite T we still see x-ray patterns but they get wider meaning that oscillation grows with T but they are around the $T \rightarrow 0$ limit (no diffusion).

- excursions from equilibrium is small with respect to interionic spacings; Small ~~was~~ guarantees Taylor expansion which makes the treatment doable.

A full treatment (big excursion) is necessary (harmonic, quasi-harmonic) for ~~low~~ the only and it is a formidable task

DEFINITIONS

need to define coordinates



R_m Eq point in WS cell
(can be representative atom)

$R_m \in \text{BL}$ by choosing n

$R_q =$ internal vector spanning basis $q=1 \dots$ (basis = e)

$u_q =$ displacement from equilibrium

$$\Rightarrow \bar{r}_{nq} = \bar{R}_m + \bar{R}_q + \bar{u}_{nq} \Rightarrow r_{nqi} = (R_m + R_q + u_{nq})_i \begin{matrix} x,y,z \\ 1,2,3 \end{matrix}$$

$\dot{r}_{nqi} = \dot{u}_{nqi}$ *erweiterung else is given later*

$$\# \Rightarrow T = \sum_{nqi} \frac{M_q}{2} \dot{u}_{nqi}^2 \quad \text{KINETIK ENERGY}$$

$$V(\{\bar{r}\}) = \min V \text{ with } u_{nq} = 0 \\ + \text{ higher orders in } (\{u_{nqi}\})$$

HARMONIC APPROXIMATION

Taylor expansion around \bar{r}

$$f \in C^\infty(\mathbb{R}^3)$$

$$f: \mathbb{R}^3 \rightarrow \mathbb{R}$$

$$f(\bar{r} + \bar{a}) = f(\bar{r}) + (\bar{a} \cdot \bar{\nabla}) f(\bar{r}) +$$

$$+ \frac{1}{2} (\bar{a} \cdot \bar{\nabla})^2 f(\bar{r}) + \frac{1}{6} (\bar{a} \cdot \bar{\nabla})^3 f(\bar{r}) + \dots$$

$$f(\bar{r} + \bar{a}) = \sum_{n=0}^{\infty} \frac{(\bar{a} \cdot \bar{\nabla})^n}{n!} f(\bar{r}) \Big|_{\bar{r}}$$

for \bar{V} along $\bar{R} - \bar{R}'$, with distance $(\mu(R) - \mu(R'))$

Let's expand V (potential energy, $a = \mu_{nq} a_i$ (Forget double

around $\bar{R}_m + \bar{R}_q - \bar{R}_{m'} - \bar{R}_{q'}$

this is quadratic

$$V = V_{\text{const}}(\mu_{sa_i} = 0) + \sum_{nq} \mu_{nq} \cdot \nabla_{R_{nq}} V \Big|_{\mu=0} +$$

no contribution just shift

- total force applied to atom n, q for zero distortions \Rightarrow eq 50

$$+ \frac{1}{2} \sum_{\substack{nq \\ n'q'}} (\mu_{nq} \cdot \nabla_{R_{nq}}) (\mu_{n'q'} \cdot \nabla_{R_{n'q'}}) V \Big|_{\mu=0} + O(\mu^3)$$

$$\mu_{nai} \partial_{R_{nai}} \quad \mu_{n'q'j} \partial_{R_{n'q'j}}$$

$$= \frac{1}{2} \sum_{\substack{nai \\ n'q'i'}} \frac{\partial^2 V}{\partial R_{nai} \partial R_{n'q'i'}} \mu_{nai} \mu_{n'q'i'}$$

corrections later

+ NEGLECT

$\Phi_{nai}^{n'q'i'}$ = MATRIX $N \times N \times 3$ rows & columns
 $\downarrow \quad \downarrow \quad \downarrow$
 $m \quad \text{basis } x, y, z \quad \text{PC3}$

LAGRANGIAN

$$L = T - V$$

\Downarrow
 \dot{q}
 \parallel
 i

\Downarrow
 q
 \parallel
 n

$$L = \sum_{n, a, i} \frac{M_a}{2} \dot{r}_{n a i}^2 - \frac{1}{2} \sum_{\substack{n, a, i \\ n', a', i'}} \phi_{n a i}^{n' a' i'} \mu_{n a i} \mu_{n' a' i'}$$

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{r}_{n a i}} - \frac{\partial L}{\partial r_{n a i}} = 0 \Rightarrow$$

$$M_a \ddot{r}_{n a i} + \sum_{n', a', i'} \phi_{n a i}^{n' a' i'} \mu_{n' a' i'} = 0$$

ATOMIC FORCE CONSTANT

$$\phi_{n a i}^{n' a' i'}$$

+ Force expressed in i -direction on a atom in n -unit cell by elementary displacement in i' -direction of a' -atom in n' -unit cell

SIMMETRIES (MANY)

$$\phi_{n a i}^{n' a' i'} = \frac{\partial V(\bar{R}_{n a} - \bar{R}_{n' a'})}{\partial R_{n a i} \partial R_{n' a' i'}}$$

1) Since $V(\mu_{n a i}, \mu_{n' a' i'}) > 0$ that is a quadratic form, semi positive $\forall \mu_{n a i}$

In addition $R \leftrightarrow R'$ in sum \Rightarrow write integrating variables

$$\phi_{n a i}^{n' a' i'} = \frac{\partial V(\bar{R}_{n a} - \bar{R}_{n' a'})}{\partial R_{n a i} \partial R_{n' a' i'}} \leftrightarrow \frac{\partial V(\bar{R}_{n' a'} - \bar{R}_{n a})}{\partial R_{n' a' i'} \partial R_{n a i}} = \phi_{n' a' i'}^{n a i}$$

$$\phi_{n a i}^{n' a' i'} = \phi_{n' a' i'}^{n a i}$$

no prob order derivative

PC4

2) global translation & ROTATIONS $\delta s_i = s_{mai} \quad \forall m, a \Rightarrow$ no force

$$s_{mai} = \sum_k R_{mak} \delta w_{ki} \quad \delta w_{ki} = -\delta w_{ik}$$

general rotation \Rightarrow no force

$$0 = \sum_{m'a'i'} \phi_{mai}^{m'a'i'} \delta s_i = \sum_{i'} \delta s_i \sum_{m'a'} \phi_{mai}^{m'a'i'} = 0$$

$$\sum_{m'a'} \phi(R)_i = 0 \quad \forall \text{ion } m'a'$$

$\Rightarrow \sum_{m'a} \phi_{mai}^{m'a'i'} = 0$

TRANSLATION $\begin{matrix} \uparrow \uparrow \\ \Sigma \\ \downarrow \downarrow \\ \Sigma \end{matrix}$

Total sum Forces constants

ROTATIONS

$$\sum_{m'a} \phi_{mai}^{m'a'i'} R_{mak} = \sum_{m'a} \phi_{mai}^{mak} R_{mai}$$

$$0 = \sum_{i'ki} \delta w_{ki} \sum_{m'a'} \phi_{mai}^{m'a'i'} R_{m'a'k'} \Rightarrow$$

$i \leftrightarrow k$ gets a (-)

3) Every BRAVAILL LATTICE has inversion symmetry
 Energy in which the ion @ $R_{m'a}$ has displacement $\bar{\mu}_{m'a}(R_{m'a})$
 must be the same if ion $-R_{m'a}$ has displacement $-\bar{\mu}_{m'a}(R_{m'a})$

$$\Rightarrow E \left\{ \bar{\mu}(R) \right\} = E \left\{ -\bar{\mu}(-R) \right\}$$

\Rightarrow in $E \mu \rightarrow -\mu$ $(-\mu)^2$ gets + \Rightarrow

$$\phi_{mai}^{m'a'i'} = \frac{\partial V(\bar{R}_{m'a} - \bar{R}_{m'a'})}{\partial R_{m'a} \partial R_{m'a'}} = \frac{\partial V(\bar{R}_{m'a'} - \bar{R}_{m'a})}{\partial R_{m'a} \partial R_{m'a'}} = \frac{\partial V(\bar{R}_{m'a} - \bar{R}_{m'a'})}{\partial R_{m'a'} \partial R_{m'a}} = \phi_{mai}^{m'a'i'}$$

EQUIV

$$\phi_{mai}^{m'a'i'}(R) = \phi_{mai}^{m'a'i'}(-R)$$

m, a
 $R \leftrightarrow R$
 variables

PCS

$$\phi_{mai}^{m'a'i'} = \phi_{mai}^{m'a'i'}$$

$$(\phi_{m'a}^{m'a'})_i = []_i$$

PERIODIC SOLUTIONS $\mu \leftrightarrow s$ change more

$$M_q \ddot{s}_{mai} + \sum_{n'q'i'} \phi_{n'q'i'}^{m'q'i'} s_{m'q'i'} = 0$$

let's get solutions like $s_{mai} = \frac{1}{\sqrt{M_q}} \mu_{mai} e^{-i\omega t}$

$e^{i(kx - \omega t)}$

\downarrow
t = uniform lat

$$-\frac{M_q}{\sqrt{M_q}} \mu_{mai} \omega^2 = - \sum_{n'q'i'} \phi_{n'q'i'}^{m'q'i'} \frac{1}{\sqrt{M_{q'}}} \mu_{m'q'i'}$$

$$\omega^2 \mu_{mai} = \sum_{n'q'i'} \frac{\phi_{n'q'i'}^{m'q'i'}}{\sqrt{M_q M_{q'}}} \mu_{m'q'i'} = \sum_{n'q'i'} D_{n'q'i'}^{m'q'i'} \mu_{m'q'i'}$$

$$D_{n'q'i'}^{m'q'i'} \equiv \phi_{n'q'i'}^{m'q'i'} / \sqrt{M_q M_{q'}}$$

Real, symmetric (1)
with 3.r.N eigenvalues ω_j

\downarrow
all real (no \mathbb{I} otherwise explosion on s)

eigenvalues ω_j & eigenvectors $\mu_{mai}^{(j)}$

NORMAL MODES

\Rightarrow 3.r.N $\mu_{mai}^{(j)}$ orthonormal

TRANSLATIONAL SYMMETRY, $U(a)$

Lattice is ∞ ~~and~~ periodic so $\phi_n^{m'}$ & $D_n^{m'}$ depend only on difference $(m'-n)$

\Rightarrow SI

$$\phi_{n'q'i'}^{m'q'i'} = \phi_{q'i'}^{q'i'}(m-n')$$

quanti BLOCK LIKE theorem

$$\mu_{m'q'i'} = \mu_{n'q'i'} e^{+iq(\bar{R}_m - \bar{R}_{n'})}$$

&

$$\mu_{m'q'i'} = C_{q'i'} e^{iq \cdot \bar{R}_m}$$

then equation becomes

$$\omega^2 c_{2i} e^{i\bar{q} \cdot \bar{R}_m} = \sum_{m' \neq i} D_{m'2i}^{m'2i} c_{2i'} e^{i\bar{q} \cdot \bar{R}_{m'}}$$

$$\omega^2 c_{2i} = \sum_{2i'} \underbrace{\sum_{m'} D_{m'2i}^{m'2i} e^{i\bar{q} \cdot (\bar{R}_{m'} - \bar{R}_m)}}_{\text{Sum depends on distance } m-m'} c_{2i'}$$

Sum depends on distance $m-m'$
 $D_m^{m'} = D(m-m') \Rightarrow$

$$D_{2i}^{2i'}(\bar{q}) \equiv \sum_{m'} \frac{\phi_{2i}^{2i'}(m'-m)}{\sqrt{M_2 M_{2'}}} e^{i\bar{q} \cdot (\bar{R}_{m'} - \bar{R}_m)}$$

$$D_{2i}^{2i'}(\bar{q}) \equiv \sum_m \frac{\phi_{2i}^{2i'}(m)}{\sqrt{M_2 M_{2'}}} e^{i\bar{q} \cdot \bar{R}_m} \equiv D^{\bar{q}}$$

DYNAMICAL MATRIX

Translation has reduced $3rN$ eq to $3r$ not much
 ↓
 dimensionality

$$\omega^2 c_{2i} = \sum_{2i'} D_{2i}^{2i'}(\bar{q}) c_{2i'} \quad 3r \text{ equations}$$

periodic in
 unit cell,
 total phase $e^{i\bar{q} \cdot \bar{R}_m}$
 take real part, get ω ,
 get s & plot

$3r$ eigenvalues $\rightarrow \omega_j(\bar{q}) \quad j=1, \dots, 3r$
 depends on \bar{q}

$$c_{2i} = e_{2i}^{(j)}(\bar{q})$$

MODES

$$S_{m2i}^{(j)}(\bar{q}, t) = \frac{1}{\sqrt{M_2}} e_{2i}^{(j)}(\bar{q}) e^{i(\bar{q} \cdot \bar{R}_m - \omega_j(\bar{q})t)}$$

PHONONS OVER ALL LATTICE

DISPERSION $j=1 \dots 3r$

$\omega_j(q)$ is frequency $\hbar \omega_j(q)$ is energy ω vs q is dispersion relation

Properties $\omega_j(q)$ same meaning that $E_n(k)$
 \downarrow \uparrow
 momenta for phonons momenta for electron

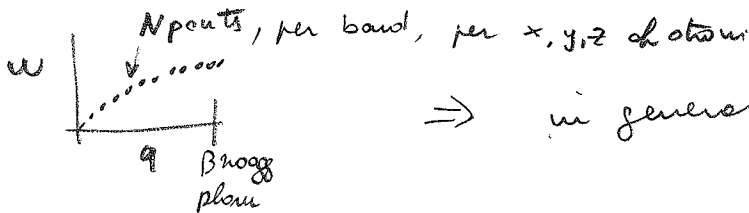
Periodicity is the same: B.Z.

1) $\omega_j(q)$ periodic in q space
 study in B.Z, $C^{q\text{-space}}$ given
 by the symmetry (point group)
 of crystal

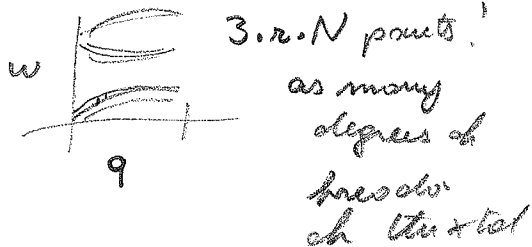
$$e^{i q \cdot R_m} = 1 \quad \text{need to study } \bar{q}\text{-space in B.Z}$$

\downarrow \downarrow
 R.L. $\underbrace{\hspace{2cm}}$ B.O.L. $2\pi m$

2) Like electrons for every band there are N points
 (in MA \vec{r} has N unit cells) \Rightarrow



\Rightarrow in general



3) $\omega_j(q)$ is analytical as $E_n(k)$

but $n=1, \dots, \infty$

& $j=1, \dots, 3r$ ω has $3r$ branches

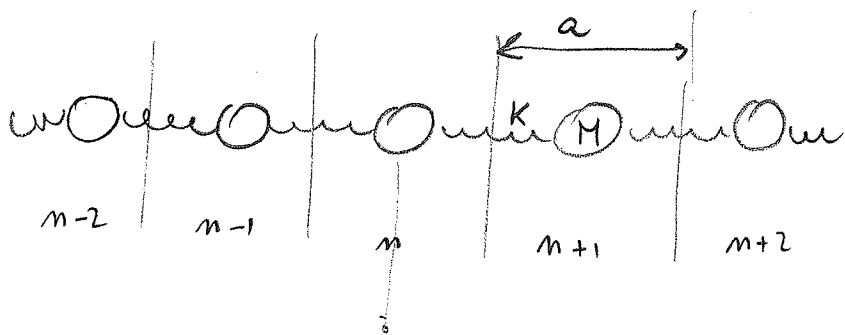
4) $\omega_j(q)$ has same symmetry of $E_n(k)$ in B.Z.
 due to space group of the crystal

in addition since time-reversal we have $\omega(q) = \omega(-q)$

(slope B.Z = point group symmetry with B.Z space group)

ONE DIMENSIONAL CHAIN NO BASIS

~~WITH/WITHOUT BASIS~~



MONOATOMIC HOMOGENEOUS

Forces: spring $K \Rightarrow F = A/SS$

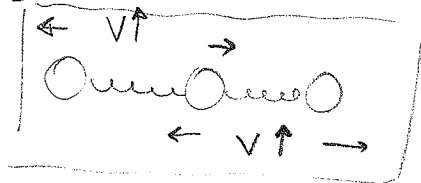
lattice $a = \infty$

Mass M

Lagrangian T-V around n

$$T = \frac{M}{2} \dot{s}_n^2$$

$$V = \frac{1}{2} K (s_n - s_{n-1})^2 + \frac{1}{2} K (s_{n+1} - s_n)^2$$



$$L(s_n) = \frac{M}{2} \dot{s}_n^2 - \frac{1}{2} K [(s_n - s_{n-1})^2 + (s_{n+1} - s_n)^2]$$

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{s}_n} - \frac{\partial L}{\partial s_n} = 0 \Rightarrow M \ddot{s}_n + K [(s_n - s_{n-1}) - (s_{n+1} - s_n)] = 0$$

$$M \ddot{s}_n + K [(s_n - s_{n-1}) + (s_n - s_{n+1})] = 0$$

$$s_n = \frac{1}{\sqrt{M}} u_n e^{-i\omega t}$$

PERIODIC $\rightarrow \omega$

envelopes

Block

$$u = c e^{iqma}$$

$$R_m = m \cdot a \quad (\text{ID BL})$$

$$s_n = \frac{1}{\sqrt{M}} c e^{i(qma - \omega t)}$$

$c_{2i} \Rightarrow i=1$ 1 direction

$c_q \Rightarrow q=1$ 1 BASIS

$\Rightarrow c$

\rightarrow

$$M\ddot{s}_m + K[s_m - s_{m-1} + s_m - s_{m+1}] = 0$$

$$s_m = \frac{1}{\sqrt{M}} c e^{i(qna - \omega t)}$$

$\Rightarrow \frac{c}{\sqrt{M}}$ everywhere \Rightarrow

$$e^{i(qna - \omega t)}$$

$$s_{m-1} = e^{iq(-1)a} s_m$$

$$s_{m+1} = e^{iq(+1)a} s_m$$

\Rightarrow

$$-M\omega^2 s_m + K[2s_m - e^{-iqa} s_m - e^{iqa} s_m] = 0$$

$$\Rightarrow -M\omega^2 + K\left[2 - 2 \frac{e^{iqa} + e^{-iqa}}{2}\right] = 0$$

$\cos qa$

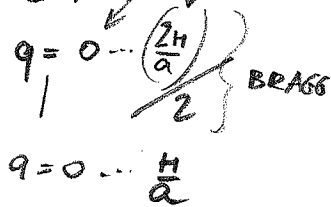
$$M\omega^2 = 2K[1 - \cos qa]$$

$$\sin \frac{\alpha}{2} = \pm \sqrt{\frac{1 - \cos \alpha}{2}}$$

$$M\omega^2 = 4K \left(\frac{1 - \cos qa}{2}\right) = 4K \sin^2 \frac{qa}{2}$$

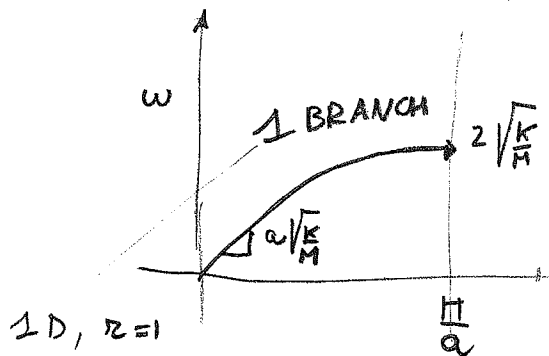
$$M\omega^2 = 4K \sin^2 \frac{qa}{2}$$

$$\Rightarrow \omega = 2\sqrt{\frac{K}{M}} \left| \sin \frac{qa}{2} \right|$$



DISPERSION

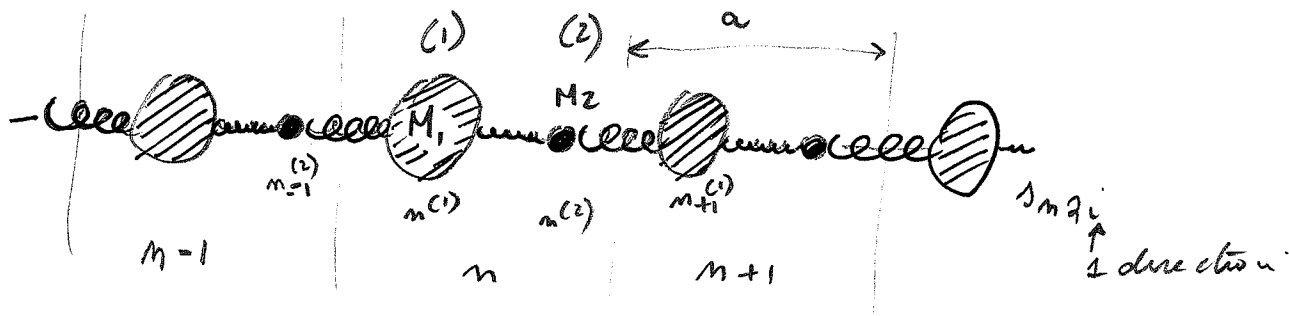
$$\omega = 2\sqrt{\frac{K}{M}} \left| \sin \left(\frac{qa}{2} \right) \right| \quad q \in [0, \frac{\pi}{a}]$$



$\sin x \sim x$
low q $2\sqrt{\frac{K}{M}} \frac{qa}{2}$
 $a\sqrt{\frac{K}{M}}$ slope

$$\frac{\pi a}{2} = \frac{\pi}{2} \Rightarrow \sin 1$$

ONE DIMENSIONAL CHAIN WITH BASIS



$$s_m \rightarrow s_m^{(1)}, s_m^{(2)}$$

$$R_m = ma$$

Lagrangian of n cell

$$\frac{1}{2} M_1 \dot{s}_m^{(1)2} + \frac{1}{2} M_2 \dot{s}_m^{(2)2} - \frac{1}{2} K \left[(s_m^{(1)} - s_{m-1}^{(2)})^2 + (s_m^{(2)} - s_m^{(1)})^2 + (s_{m+1}^{(1)} - s_m^{(2)})^2 \right]$$

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{s}_m^{(i)}} - \frac{\partial L}{\partial s_m^{(i)}} = 0 \quad (i=1,2) \Rightarrow$$

$$M_1 \ddot{s}_m^{(1)} + K \left[(s_m^{(1)} - s_{m-1}^{(2)}) + (s_m^{(1)} - s_m^{(2)}) \right] = 0$$

$$M_2 \ddot{s}_m^{(2)} + K \left[(s_m^{(2)} - s_m^{(1)}) + (s_m^{(2)} - s_{m+1}^{(1)}) \right] = 0$$

$$\Rightarrow \text{Solutions } s_m^{(i)} = \frac{1}{\sqrt{M_i}} \mu_m^{(i)} e^{-i\omega t}$$

Block $\mu_m^{(i)} = c^{(i)} e^{iqma}$
 periodic case

$$s_m^{(i)} = \frac{1}{\sqrt{M_i}} c^{(i)} e^{i(qma - \omega t)}$$

$$s_m^{(2)} = s_m^{(1)} \frac{c^{(2)}}{c^{(1)}} \sqrt{\frac{M_1}{M_2}}$$

$$\begin{cases} M_1 \ddot{s}_m^{(1)} + K [2s_m^{(1)} - s_{m-1}^{(2)} - s_m^{(2)}] = 0 \\ M_2 \ddot{s}_m^{(2)} + K [2s_m^{(2)} - s_m^{(1)} - s_{m+1}^{(1)}] = 0 \end{cases}$$

$$\Delta_{n+1}^{(1)} = e^{iqa} \Delta_n^{(1)} \quad \Delta_{n-1}^{(2)} = e^{-iqa} \Delta_n^{(2)} \Rightarrow$$

$$\left\{ \begin{array}{l} -\omega^2 M_1 \Delta_n^{(1)} + K \left[2\Delta_n^{(1)} - \Delta_n^{(2)} \left[e^{-iqa} + 1 \right] \right] = 0 \\ -\omega^2 M_2 \Delta_n^{(2)} + K \left[2\Delta_n^{(2)} - \Delta_n^{(1)} \left[e^{iqa} + 1 \right] \right] = 0 \end{array} \right.$$

$$S_m^{(2)} = S_m^{(1)} \frac{C_2}{C_1} \sqrt{\frac{M_1}{M_2}}$$

plug and divide by $S_m^{(1)}$

$$\left\{ \begin{array}{l} -\omega^2 M_1 + K \left[2 - \frac{C_2}{C_1} \sqrt{\frac{M_1}{M_2}} \left[e^{-iqa} + 1 \right] \right] = 0 \\ -\omega^2 M_2 + K \left[2 - \frac{C_1}{C_2} \sqrt{\frac{M_2}{M_1}} \left[e^{iqa} + 1 \right] \right] = 0 \end{array} \right.$$

$$\left\{ \begin{array}{l} -\omega^2 M_1 + K \left[2 - \frac{C_2}{C_1} \sqrt{\frac{M_1}{M_2}} \left[e^{-iqa} + 1 \right] \right] = 0 \\ -\omega^2 M_2 + K \left[2 - \frac{C_1}{C_2} \sqrt{\frac{M_2}{M_1}} \left[e^{iqa} + 1 \right] \right] = 0 \end{array} \right.$$

$$\begin{aligned} e^{-iqa/2} (e^{-iqa/2} + e^{iqa/2}) &= e^{-iqa/2} 2 \cos(qa/2) \\ e^{iqa/2} (e^{iqa/2} + e^{-iqa/2}) &= e^{iqa/2} 2 \cos(qa/2) \end{aligned}$$

$$\left\{ \begin{array}{l} -\omega^2 M_1 + K \left[2 - \frac{C_2}{C_1} \sqrt{\frac{M_1}{M_2}} e^{-iqa/2} 2 \cos(qa/2) \right] = 0 \\ -\omega^2 M_2 + K \left[2 - \frac{C_1}{C_2} \sqrt{\frac{M_2}{M_1}} e^{iqa/2} 2 \cos(qa/2) \right] = 0 \end{array} \right.$$

$$\left\{ \begin{array}{l} -\omega^2 \sqrt{M_1} C_1 = +2K \frac{C_1}{\sqrt{M_1}} - 2K \frac{C_2}{\sqrt{M_2}} e^{-iqa/2} \cos\left(\frac{qa}{2}\right) = 0 \\ -\omega^2 \sqrt{M_2} C_2 = +2K \frac{C_2}{\sqrt{M_2}} - 2K \frac{C_1}{\sqrt{M_1}} e^{iqa/2} \cos\left(\frac{qa}{2}\right) = 0 \end{array} \right.$$

\Rightarrow ω are eigenvalues

det $\neq 0$

$$\begin{pmatrix} \frac{2K}{\sqrt{M_1}} - \omega^2 \sqrt{M_1} & -\frac{2K}{\sqrt{M_2}} e^{-iqa/2} \cos\left(\frac{qa}{2}\right) \\ -\frac{2K}{\sqrt{M_1}} e^{iqa/2} \cos\left(\frac{qa}{2}\right) & \frac{2K}{\sqrt{M_2}} - \omega^2 \sqrt{M_2} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\det = 0$$

$\neq 0$

$$0 = \det = \left(\frac{2K}{\sqrt{M_1}} - \omega^2 \sqrt{M_1} \right) \left(\frac{2K}{\sqrt{M_2}} - \omega^2 \sqrt{M_2} \right) - \frac{4K^2}{\sqrt{M_1 M_2}} e^{-iqa/2} e^{iqa/2} \cos^2\left(\frac{qa}{2}\right) = 0$$

$$= \left(\frac{2K}{M_1} - \omega^2 \right) \left(\frac{2K}{M_2} - \omega^2 \right) - \frac{4K^2}{M_1 M_2} \cos^2\left(\frac{qa}{2}\right) = 0$$

$$\omega^4 - \omega^2 \left[2K \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right] + \frac{4K^2}{M_1 M_2} \left(1 - \cos^2\left(\frac{qa}{2}\right) \right) = 0$$

$$\cos^2 + \sin^2 = 1 \Rightarrow \sin^2$$

$$ax^2 + bx + c = 0 \Rightarrow \sqrt{b^2 - 4ac}$$

$$x_{\pm} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\omega_{\pm}^2 = K \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm K \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4}{M_1 M_2} \sin^2\left(\frac{qa}{2}\right)}$$

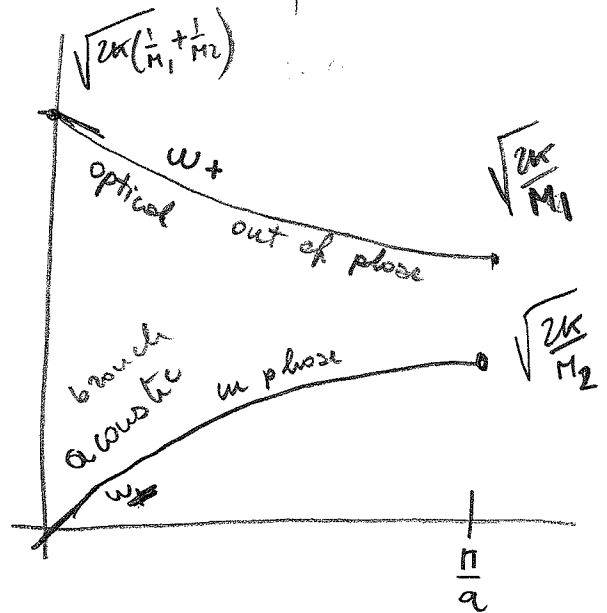
Two branches

$$q = 0$$

$$\omega_{\pm}^2 = K \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm K \left(\frac{1}{M_1} + \frac{1}{M_2} \right)$$

$$= 0, 2K \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \omega_{+}$$

$$\omega_{\pm} = 0, \sqrt{2K \left(\frac{1}{M_1} + \frac{1}{M_2} \right)}$$



$$q = \frac{\pi}{a}$$

$$\omega_{\pm}^2 = K \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm K \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4}{M_1 M_2}} = K \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm K \left(\frac{1}{M_1} - \frac{1}{M_2} \right)$$

$$\left(\frac{1}{M_1} - \frac{1}{M_2} \right)^2$$

$$= \frac{2K}{M_1}, \frac{2K}{M_2} \Rightarrow \omega = \sqrt{\frac{2K}{M_1}}, \sqrt{\frac{2K}{M_2}}$$

EIGENVECTORS

$$-\omega^2 M_1 + 2K \left[1 - \frac{c_2}{c_1} \sqrt{\frac{M_1}{M_2}} e^{-iqa/2} \cos\left(\frac{qa}{2}\right) \right] = 0$$

$$-\frac{\omega^2 M_1}{2K} + 1 - \frac{c_2}{c_1} \sqrt{\frac{M_1}{M_2}} e^{-iqa/2} \cos\left(\frac{qa}{2}\right) = 0$$

$$\frac{c_2}{c_1} = \left(1 - \frac{\omega^2 M_1}{2K} \right) \sqrt{\frac{M_2}{M_1}} e^{iqa/2} \cos^{-1} \frac{qa}{2}$$

$$q=0 \quad \omega = \omega_- = 0 \quad \rightarrow \quad c_2/c_1 = \sqrt{\frac{M_2}{M_1}} \quad \text{in phase}$$

$$q=0 \quad \omega = \omega_+ = \sqrt{2K \left(\frac{1}{M_1} + \frac{1}{M_2} \right)} \quad \rightarrow \quad c_2/c_1 = -\sqrt{\frac{M_1}{M_2}} \quad \text{out of phase.}$$

$$q = \frac{\pi}{a} \quad \omega = \omega_- = \sqrt{\frac{2K}{M_1}} \quad \rightarrow \quad c_2/c_1 = \infty \quad (\text{need to do limit } q \rightarrow \frac{\pi}{a})$$

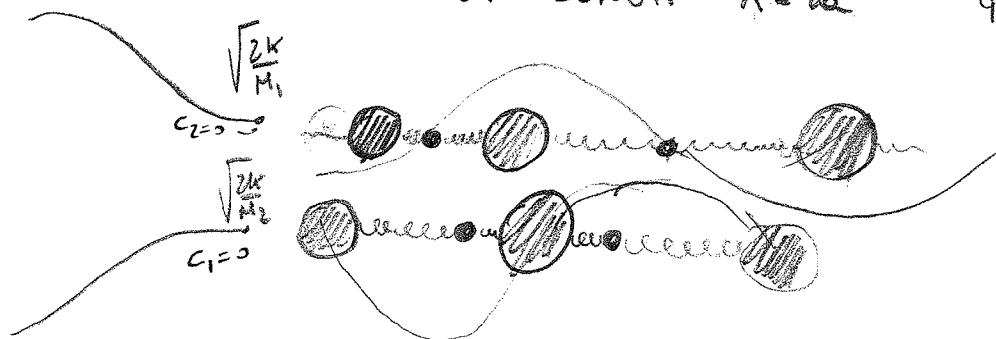
$$q = \frac{\pi}{a} \quad \omega = \omega_+ = \sqrt{\frac{2K}{M_2}} \quad \rightarrow \quad c_2/c_1 = 0$$

$c_1 = 0 \rightarrow \omega = \sqrt{\frac{2K}{M_2}}$
 $c_2 = 0 \rightarrow \omega = \sqrt{\frac{2K}{M_1}}$

for $q = \pm \frac{\pi}{2}$ (Bragg, c_1 OR $c_2 = 0$)

\Rightarrow atoms are NODES OF VIBRATION OF LENGTH $\lambda = 2a$

$$q = \frac{2\pi}{\lambda} = \frac{\pi}{a} \Rightarrow \lambda = 2a$$



CAN BE TRANSVERSAL OR LONGITUDINAL (theory is same, K changes) PCH

DISCUSSION

longitudinal \longleftrightarrow
 transverse \updownarrow δ \nearrow } small amplitude same theory

generic Basis r

\Rightarrow d acoustic $d(r-1)$ optical
 BRANCHES

\uparrow
 DIM
 1D, 2D, 3D

\uparrow
 usually, but not always
 excited by photons
 (no excitation if
 charge of (1) & (2)
 is same)

degenerate @ $q=0$ (Γ)
 α in directions/points
 of high symmetry in B.Z.

Lattice vibrations
 are longitudinal
 and transverse only
 along lines of
 high symmetry.

QUANTUM

Remember $\Delta_{m\alpha i}(q, t) = \frac{1}{\sqrt{M\alpha}} e_{\alpha i}^{(j)}(\bar{q}) e^{i(q \cdot \bar{R}_m - \omega_j(\bar{q})t)}$

Annotations:
 - (j) : eigenvalue label
 - (\bar{q}) : eigen values
 - $\Delta_{m\alpha i}$: all basis
 - $\omega_j(\bar{q})$: can be imaginary
 - $c_{\alpha i} \forall q$: (PAGE 107)

Real solution = $\sum_q \text{vibrations}(q) \sum_j \text{eigenvalues}(q_j)$

$\Delta_{m\alpha i}(t) = \frac{1}{\sqrt{M\alpha}} \sum_{qj} e_{\alpha i}^{(j)}(q) e^{-i\omega_j(q)t} e^{i\bar{q} \cdot \bar{R}_m}$

Annotations:
 - $e^{-i\omega_j(q)t}$: $\Phi_j(q, t) = \sqrt{N} e^{-i\omega_j(q)t} [\text{coeff}(q)]$
 - \rightarrow all TIME evolution

$\Delta_{m\alpha i}(t) = \frac{1}{\sqrt{NM\alpha}} \sum_{qj} \Phi_j(q, t) e_{\alpha i}^{(j)}(q) e^{i\bar{q} \cdot \bar{R}_m}$

\rightarrow MUST BE REAL

Hamiltonian Harmonic

$$H = \sum_{m\alpha i} \frac{M\alpha}{2} (\dot{\Delta}_{m\alpha i})^2 + \frac{1}{2} \sum_{\substack{m\alpha i \\ m'\alpha'i'}} \Phi_{m\alpha i}^{m'\alpha'i'} \Delta_{m\alpha i} \Delta_{m'\alpha'i'}$$

Remember $\frac{1}{N} \sum_n e^{i\bar{q} \cdot \bar{R}_n} = \delta_{\bar{q}, \bar{k}_m}$

set 1 $\forall q \in R.L. \ni k_m$

if $\bar{q} \notin R.L.$
 then the numbers are random and cancel out!
 \forall value \neq opposite - values

$\Rightarrow \sum_n e^{i(\bar{q}-\bar{q}') \cdot \bar{R}_n} = N \delta_{\bar{q}-\bar{q}', \bar{k}_m}$

①

$\Delta_{n,2i}(t)$ real $\Rightarrow \phi^* = \phi \Rightarrow$

$$\phi^* \phi_j(\vec{r}) = \sum_{q,j} \phi_j^*(q,t) e_{2i}^{*(j)}(q) e^{-i\vec{q} \cdot \vec{R}_m}$$

\downarrow
with $q \rightarrow -q$

$$= \sum_{q,j} \phi_j^*(-q,t) e_{2i}^{*(j)}(-q) e^{i\vec{q} \cdot \vec{R}_m}$$

$$\Rightarrow \phi_j(q,t) e_{2i}^{(j)}(q) = \phi_j^*(-q,t) e_{2i}^{*(j)}(-q) \quad \forall q$$

$$\Rightarrow \phi_j(q,t) = \phi_j^*(-q,t) \quad (2)$$

complex $\leftarrow e_{2i}^{(j)}(q) = e_{2i}^{*(j)}(-q) \quad (3)$

but

$e_{2i}^{(j)}(q)$ are the eigenvectors
so we pick them \perp

there might be eigenvalues not distinct!
so \perp might be necessary

$$\sum_j e_{2i}^{*(j)}(q) e_{2i}^{(j)}(q) = \delta_{jj} \quad (4)$$

combining (1), (2), (3), (4) we get

$$H = \frac{1}{2} \sum_{j,q} \left[\underbrace{\dot{\phi}_j^*(q,t) \dot{\phi}_j(q,t)}_T + \omega_j^2(q) \underbrace{\phi_j^*(q,t) \phi_j(q,t)}_V \right]$$

Hamiltonian

$L = T - V$ Lagrange eq

$$P = \frac{\partial L}{\partial \dot{Q}} \Rightarrow P_j(q,t) = \dot{\phi}_j(q,t) \quad \text{PCA}$$

$$H = \frac{1}{2} \sum_{j,q} \left[P_j^*(q,t) P_j(q,t) + \omega_j^2(q) \phi_j^*(q,t) \phi_j(q,t) \right]$$

gas of phonons

HAMILTON
 $\dot{p} = -\frac{\partial H}{\partial q}$
 $\dot{q} = \frac{\partial H}{\partial p}$

$$\dot{P}_j(q,t) = -\omega_j^2(q) Q_j(q,t)$$

$$\ddot{Q}_j(q,t) + \omega_j^2(q) Q_j(q,t) = 0$$

freq harmon

each contribution
is a harmonic oscillator
of freq $\omega_j(q)$

QUANTUM MECHANICS of oscillator $\forall q, j \text{ eng } (1 \dots 3r)$

commutator

$$[Q_j(q,t), P_{j'}(q',t)] = i\hbar \delta_{qq'} \delta_{jj'}$$

$$[q,t] = i\hbar$$

\uparrow same phonon
same branch

death
 \downarrow
in $a_j^+(q) a_j(q)$
OPERATOR

\uparrow construction excitations $q, \omega_j(q)$

$$\Rightarrow \hat{H} = \frac{1}{2} \sum_{j,q} \hbar \omega_j(q) \left(\underbrace{\hat{a}_j^+(q) \hat{a}_j(q)}_{n_j(q)} + \frac{1}{2} \right)$$

each state
 (q,j) is
occupied by
 $n_j(q)$ phonons
with energy $\hbar \omega_j(q)$

$$E = \frac{1}{2} \sum_{j,q} \hbar \omega_j(q) \left[n_j(q) + \frac{1}{2} \right]$$

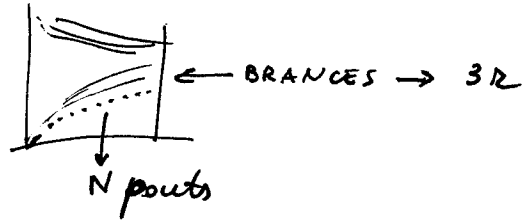
NON INTERACTING
gas of PHONONS
(but phonons = BOSONS
electron = Fermions).

$T=0 \Rightarrow$ NO PHONONS excited
only zero point motion

\swarrow
DIFFERENT STATISTICS

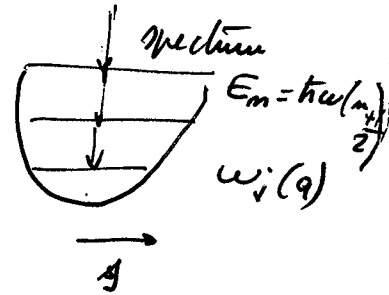
COUNTING

how many oscillators



$3RN$ oscillators

with energy $\omega_j(q)$ \Rightarrow each oscillator



\Rightarrow each oscillator has energy

$$E_m = h\omega\left(m + \frac{1}{2}\right) \propto \exp(-E_m/kT)$$

$$\Rightarrow P_m = \frac{e^{-\beta E_m}}{\sum_n e^{-\beta E_n}} = \frac{e^{-\beta h\omega m}}{\sum_n e^{-\beta h\omega m}}$$

$\frac{h\omega}{2}$ goes away

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

$$\frac{1}{1 - e^{-\beta h\omega}}$$

$$\Rightarrow P_m = e^{-\beta h\omega m} (1 - e^{-\beta h\omega})$$

$$E_0 = h\omega/2$$

$$\langle E \rangle = \sum_m E_m P_m = \frac{\sum_m h\omega\left(m + \frac{1}{2}\right) e^{-\beta h\omega m}}{\sum_m e^{-\beta h\omega m}}$$

$$= \frac{h\omega}{2} \frac{\sum_0^{\infty} 1}{\sum_0^{\infty} 1} + \frac{\sum_0^{\infty} m h\omega e^{-\beta h\omega m}}{\sum_0^{\infty} e^{-\beta h\omega m}} \rightarrow \frac{-\frac{\partial}{\partial \beta} \sum_0^{\infty} e^{-\beta h\omega m}}{\sum_0^{\infty} e^{-\beta h\omega m}} \Rightarrow$$

$$\frac{\partial}{\partial x} \log f(x) = \frac{f'(x)}{f(x)} \frac{\partial f(x)}{\partial x}$$

$$-\frac{\partial}{\partial \beta} \log \sum_m e^{-\beta h\omega m}$$

$$= \frac{h\omega}{2} + \frac{\partial}{\partial \beta} \log(1 - e^{-\beta h\omega}) = \frac{h\omega}{2} + \frac{h\omega e^{-\beta h\omega}}{1 - e^{-\beta h\omega}} = \frac{h\omega}{2} + \frac{h\omega}{e^{\beta h\omega} - 1}$$

$$\frac{1}{1 - e^{-\beta h\omega}}$$

PC19

$$\bar{n}(h\omega) = \frac{1}{e^{\beta h\omega} - 1} \Rightarrow \langle E \rangle = E_0 + h\omega_j(q) \bar{n}_j(h\omega_j(q)) \leftarrow \text{BOSE-EINSTEIN PIST}$$

gas of phonons each with $\bar{E} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} + 1}$
 average energy

TOTAL ENERGY + SPECIFIC HEATS

$$E = \sum_{j,q} \hbar\omega_j(q) \left[\frac{1}{2} + n_j(q) \right]$$

\downarrow
 all phonons
 \downarrow
 B.E.

EO

$\hbar\omega \ll kT$ high temp
 $\beta\hbar\omega$ small

$$= \sum_{j,q} \hbar\omega_j(q) \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_j(q)} - 1} \right]$$

$$e^{\beta\hbar\omega} - 1 \sim \frac{\hbar\omega}{kT} + \frac{1}{2}(\beta\hbar\omega)^2 + \frac{1}{6}(\beta\hbar\omega)^3 + \dots$$

$$= \sum_{j,q} \hbar\omega_j \left[\frac{1}{2} + \frac{1}{\beta\hbar\omega + \frac{(\beta\hbar\omega)^2}{2}} \right]$$

$$\beta\hbar\omega \left(1 + \frac{\beta\hbar\omega}{2} + \frac{1}{6}(\beta\hbar\omega)^2 \right)$$

\downarrow
small

$$= \sum_{j,q} \hbar\omega_j \left[\frac{1}{2} + \frac{1}{\beta\hbar\omega} \left(1 - \frac{\beta\hbar\omega}{2} - \frac{(\beta\hbar\omega)^2}{6} \right) \right]$$

$$= \sum \hbar\omega \left[\frac{1}{2} + \frac{1}{\beta\hbar\omega} - \frac{1}{2} - \frac{\beta\hbar\omega}{6} + \dots \right]$$

$$= \sum \frac{1}{\beta} \left[1 - \frac{\beta^2(\hbar\omega)^2}{6} + \dots \right] \Rightarrow \underbrace{KT \sum_{j,q}}_{3Nk} \left[1 - \frac{1}{6} \left(\frac{\hbar\omega}{kT} \right)^2 + \dots \right]$$

book $\frac{1}{12} \left(\frac{\hbar\omega}{kT} \right)^2$?
 how?

$E = 3NkT$ Dulong-Petit Law

HIGH TEMP $C_V = 3Nk$!

LOW TEMP

KT small but \sum over all ω , but $\hbar\omega \gg kT$ here
 no hope to be populated

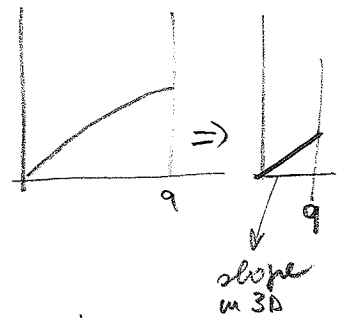
\Rightarrow LIMIT SUMMATION
 at low spectrum
 (ACOUSTIC BRANCHES)

$$E = \sum_{j,q} \hbar \omega_j(q) \left[\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega_j(q)} - 1} \right]$$

Zero point energy

Does not depend on T

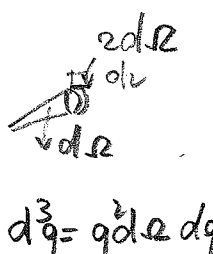
$$= E_0 + \sum_{j,q} \frac{\hbar s_j q}{e^{\beta \hbar s_j q} - 1}$$



$$\omega_j(q) = s_j(\theta, \varphi) q$$

$$\Delta q \rightarrow \sum_{j,q} \rightarrow \int \frac{d^3q}{(2\pi)^3} \xrightarrow{\Delta q \rightarrow V_{solid}} \frac{V}{(2\pi)^3} \int d^3q$$

$$\Rightarrow E - E_0 = \frac{V}{(2\pi)^3} \sum_j \int \frac{\hbar s_j q}{e^{\beta \hbar s_j q} - 1} d^3q$$



$$x = \hbar s_j q \beta \rightarrow (dq)^3 = \left(\frac{dx}{\hbar s_j \beta} \right)^3$$

$$\frac{x^3 d\Omega dx}{\hbar^3 s_j^3 \beta^4 (e^x - 1)}$$

$BZ \rightarrow \infty$
 because e^x in denominator

$$\frac{x}{\beta} \frac{1}{e^x - 1} \frac{(dx)^3}{(\hbar s_j \beta)^3}$$

$$\rightarrow E - E_0 = \frac{V}{(2\pi)^3} \frac{(kT)^4}{\hbar^3} \sum_j \int \frac{d\Omega}{s_j^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

$$\frac{1}{\hbar^3 s_j^3 \beta^4} \frac{x dx^3}{e^x - 1}$$



$$dx^3 = x^2 dx d\Omega$$

$$E = E_0 + \frac{V}{(2\pi)^3} \frac{(kT)^4}{h^3} \sum_j \int \frac{d\Omega}{S_j^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

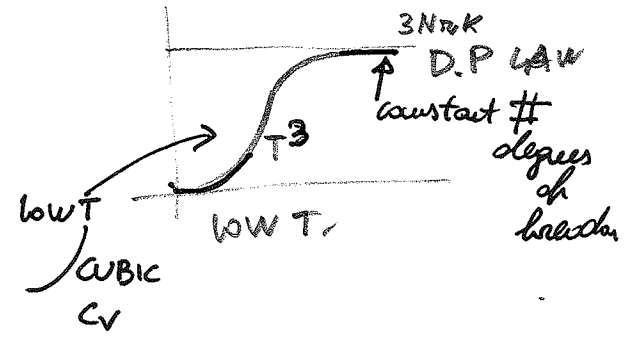
$\frac{4\pi}{S_j^3}$
 $\frac{3}{S_j^3}$
 S_j^3 average over directions of slope of ACOUSTIC BRANCH!

$\int \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$ wikipedia "tables of integrals"

$E = E_0 + \frac{V}{(2\pi)^3} \frac{(kT)^4}{h^3} \frac{4\pi}{S_j^3} \frac{\pi^4}{15} = E_0 + V \Rightarrow$
 (with annotations: $\frac{4\pi}{S_j^3} \frac{\pi^4}{15} = \frac{4\pi^5}{15 S_j^3}$, $\frac{4\pi^5}{15} = \frac{16\pi^5}{3 \cdot 5}$, $\frac{16\pi^5}{3 \cdot 5}$ Bravais)

$E = E_0 + \frac{h^2}{10} \frac{V_g}{h^3} \frac{(kT)^4}{S_j^3}$
 (with annotation: $\frac{h^2}{10} \frac{V_g}{h^3} = \frac{h^2}{10} \frac{1}{h^3} = \frac{1}{10 h}$)

$\Rightarrow C_V = \frac{1}{V} \frac{\partial E}{\partial T} = \frac{4k}{10} \frac{(kT)^3}{h^3 S_j^3}$



$E = E_0 + \frac{h^2}{10} \frac{V_g}{h^3} \frac{(kT)^4}{S_j^3}$ low T

$\frac{1}{S_j^3} = \frac{1}{3} \frac{1}{4\pi} \sum \int \frac{d\Omega}{S_j^3}$ AVERAGE

MUST CORRECT

INTERMEDIATE

Density of states number to all electrons, $\epsilon \leftrightarrow \omega$
 $n \leftrightarrow$ band j branch $1, \dots, r$

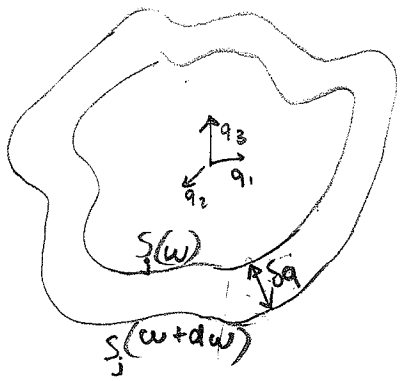
here

$$g_j(\omega) d\omega = \left\{ \begin{array}{l} \# \text{ of phonons of } j\text{-branch} \\ \text{with } \omega \text{ in } [\omega, \omega + d\omega[\end{array} \right\}$$

$$\Rightarrow g_j(\omega) d\omega = \sum_{\vec{q}} \left\{ \begin{array}{l} 1 \text{ if } \omega_j(\vec{q}) \text{ in } [\omega, \omega + d\omega[\\ 0 \text{ otherwise} \end{array} \right\}$$

$$= \int \frac{d^3 q}{(\Delta q)^3 = \left(\frac{2\pi}{V_j}\right)^3} \left\{ \begin{array}{l} 1 \text{ if } \omega_j(\vec{q}) \\ \text{in } [\omega, \omega + d\omega[\end{array} \right\} = \frac{V_j}{(2\pi)^3} \int d^3 q \left\{ \begin{array}{l} 1 \text{ if } \omega_j(\vec{q}) \\ \text{in } [\omega, \omega + d\omega[\end{array} \right\}$$

in \vec{q} -space, contour surfaces of constant ω for branch $j \Rightarrow S_j(\omega)$ Volume surface between $[\omega + d\omega]$

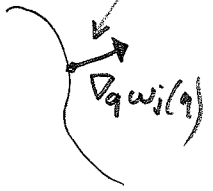


$$g_j(\omega) d\omega = \frac{V_j}{(2\pi)^3} \int \text{Volume between } S_j(\omega) \text{ \& } S_j(\omega + d\omega)$$

$$= \frac{V_j}{(2\pi)^3} \int_{S_j(\omega)} d\vec{S} \cdot \delta \vec{q}$$

look $\omega_j(\vec{q}) = \mathbb{R}^3 \rightarrow \mathbb{R}$
 $\vec{q} \rightarrow \omega$ scalar function

so $\vec{\nabla}_{\vec{q}} \omega_j(\vec{q}) = \text{grad} \Rightarrow$ vector \perp at surface at const ω_j
 with magnitude, the rate of change of ω



$$\Rightarrow \omega + d\omega = \omega + \nabla \omega \cdot \delta \vec{q} \Rightarrow \text{change in } \delta q$$

\uparrow distance \Rightarrow
 \downarrow
 to the $\delta \vec{q} \perp S_{\text{surf}}$
 δq

$$d\omega = |\nabla \omega| \delta q \quad \delta q = \frac{d\omega}{|\nabla_{\vec{q}} \omega_j(\vec{q})|} \quad \text{PC23}$$

$$\Rightarrow g_j(\omega) d\omega = \frac{Vg}{(2\pi)^3} \int_{S_j(\omega)=\omega} \frac{ds d\omega}{|\nabla_{\mathbf{q}} \omega_j(\mathbf{q})|}$$

\nwarrow directly \perp \mathbf{q} space b_i
 \swarrow number
 $S_j(\omega)=\omega \leftarrow$ surface @ ω const

$$g_j(\omega) d\omega = \frac{Vg}{(2\pi)^3} \int_{\omega \text{ const}} \frac{ds d\omega}{|\nabla_{\mathbf{q}} \omega_j(\mathbf{q})|}$$

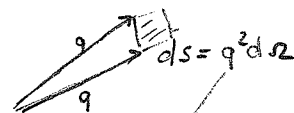
$$\Rightarrow \sum_{\substack{\mathbf{q} \\ \text{in branch } j \\ \text{the function depends only on } \omega}} \text{function}(\omega) \rightarrow \frac{Vg}{(2\pi)^3} \int_{BZ} F(\mathbf{q}(\omega)) d^3\mathbf{q} = \int_0^\infty g_j(\omega) F(\omega) d\omega$$

LINEAR ACOUSTIC BRANCH APPROX

$$\omega_j(\bar{\mathbf{q}}) = s_j(\bar{\mathbf{v}}, \varphi) |\mathbf{q}| \stackrel{\langle \rangle}{=} \bar{s}_j \mathbf{q} \quad \text{d}\Omega \text{ average}$$

$$|\nabla_{\mathbf{q}} \omega_j(\mathbf{q})| = \bar{s}_j$$

$$g_j(\omega_j) d\omega = \frac{Vg}{(2\pi)^3} \int_{\omega \text{ const}} \frac{ds d\omega}{|\nabla_{\mathbf{q}} \omega_j(\mathbf{q})|} = \frac{Vg}{(2\pi)^3} d\omega \int \frac{ds}{\bar{s}_j}$$



$$ds = q^2 d\Omega$$

$$\Leftarrow \omega_j = \bar{s}_j q \Rightarrow q = \frac{\omega_j}{\bar{s}_j}$$

$$ds = \frac{\omega_j^2}{\bar{s}_j^2} d\Omega$$

$$= \frac{Vg}{(2\pi)^3} \int_{\omega \text{ const}} \frac{\omega_j^2}{\bar{s}_j^3} d\Omega d\omega = \frac{Vg}{8\pi^3} \frac{\omega_j^2}{\bar{s}_j^3} 4\pi d\omega$$

LINEAR APPROX

$$\omega_j(\mathbf{q}) = \bar{s}_j q \Rightarrow g_j(\omega_j) d\omega = \left(\frac{Vg}{2\pi^2} \frac{\omega_j^2}{\bar{s}_j^3} \right) d\omega$$

$g_j(\omega_j)$

Energy

$$B.E. = \frac{1}{e^{\beta \hbar \omega_j(q)} - 1}$$

$$E_{qj} = \hbar \omega_j(q) \left[n_j(q) + \frac{1}{2} \right]$$

↘ disp w

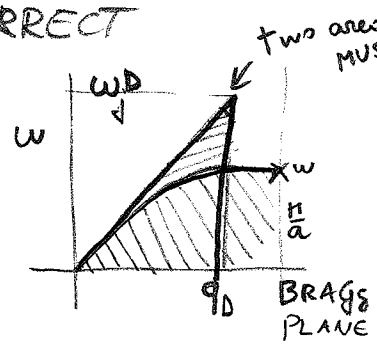
$$E_0 = \sum_{qj} \frac{\hbar \omega_j(q)}{2} \quad \text{NUMBER}$$

$$E = \sum_{qj} E_{qj} = \sum_j \sum_q E[\omega_j(q)] \Rightarrow \sum_j \int_0^\infty E(\omega_j) g(\omega_j) d\omega_j$$

$$E - E_0 = \frac{Vg}{2\hbar^2} \int_0^\infty \frac{\hbar \omega_j}{e^{\beta \hbar \omega_j} - 1} \frac{\omega_j^2 d\omega_j}{s_j^3} = \sum_j \frac{Vg}{2\hbar^2} \frac{(kT)^4}{\hbar^3 s_j^3} \int_0^\infty \frac{x^3}{e^x - 1} dx$$

SAME AS LOW TEM.

BUT WE MUST CORRECT
(we over count!)



$$\int_0^\infty d\omega \Rightarrow \int_0^{\text{cutoff}} d\omega$$

See

per branch

$$N_q = \sum_q 1(\omega)$$

↓
3N per branch
N ← unit cells

$$= \int_0^{\omega_D} g(\omega) d\omega$$

$$= \frac{Vg}{2\hbar^2} \frac{1}{s_j^3} \int_0^{\omega_D} \omega^2 d\omega$$

$$\frac{d}{d\omega} \frac{1}{3} \omega^3 = \omega^2 d\omega$$

$$\frac{Vg}{2\hbar^2} \frac{1}{s_j^3} \frac{\omega_{jD}^3}{3} = N$$

DEBYE FREQ

$$q_D = \sqrt[3]{\frac{6\hbar^2 N}{Vg}} = (6\hbar^2 m)^{1/3}$$

DEBYE MOM
ω_j = q s_j
⇒
RADIUS SPHERE OF VOL = VOL BZ

SIMILAR IDEA THAN FERMION (E_F, k_F)

density of unit cell / volume

Vol Solid

$$\frac{Vg}{N} = v_g \leftarrow \text{vel } \perp \text{ UNIT cell}$$

WIGNER SETTE ⇒

Unit cell

$$\frac{1}{v_g} = \frac{\text{Volume B.Z.}}{(2\pi)^3} \Rightarrow \frac{1}{v_g} = \frac{1}{(2\pi)^3} \frac{4\pi}{3} (6\hbar^2 m)^{1/3} \frac{V_{BZ}}{8\pi^3}$$

$$q_D = \text{radius sphere of volume BZ}$$

$$\frac{4}{3} \pi q_D^3 = V_{BZ}$$

PC25

DEBYE

$$\int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15} \Rightarrow$$

$$\frac{15}{\pi^4} \int_0^{\hbar\omega_D/kT} \frac{x^3}{e^x - 1} dx = f\left(\frac{\hbar\omega_D}{kT}\right)$$

$$f(x \rightarrow \infty) \rightarrow 1$$

$$\omega_D \rightarrow \theta_D \Rightarrow k\theta_D = \hbar\omega_D$$

↳ DEBYE TEMP.

$$\Rightarrow E = E_0 + \frac{\hbar^2}{10} \frac{V_0}{\hbar^3} \frac{(kT)^4}{5^3} f\left(\frac{\theta_D}{T}\right)$$

$f\left(\frac{\theta_D}{T}\right)$ FROM TABLES

DEBYE MODEL

DEBYE MODEL

LOW T $f \rightarrow 1$

$$\frac{1}{5^3} \equiv \frac{1}{3.4 \dots} \sum_j \int \frac{d\omega}{5_j^3}$$

good for ACOUSTIC BRANCH

EINSTEIN MODEL

(good for OPTICAL) 1 oscillator

1 only phonon existing

$$\omega_j(q) = \omega_E$$

$$g(\omega_j) d\omega = N \delta_j(\omega_j - \omega_E) d\omega$$

$$\Rightarrow E = E_0 + \frac{N\hbar\omega_E}{\exp(\hbar\omega_E/kT) - 1}$$

$\exp(\hbar\omega_E/kT) \rightarrow 1$ R 1 only phonon

IF calculate C_V ($C_P = C_V$ in harmonic solid no thermal ex $C_P - C_V \sim \exp - 0$)

HIGH $C^{DP} = 3Nk$

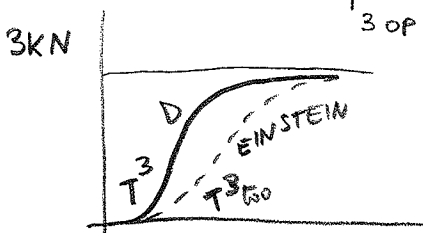
LOW \rightarrow only 1 branch $\Rightarrow \nu = 1$ $C^{DP} \sim 3Nk$

$$\Rightarrow C^{DEBYE}(T) = 3Nk f_D\left(\frac{\theta_D}{T}\right) \quad T^3 \text{ low T} \quad f_D(x) = \frac{3}{x^3} \int_0^x \frac{y^4 e^y}{(e^y - 1)^2} dy$$

$$C^{EINSTEIN}(T) = 3Nk f_E\left(\frac{\theta_E}{T}\right) \quad \uparrow \text{3 OP BRANCH}$$

$T \downarrow x \rightarrow \infty$ $f_D \sim \frac{4\pi^4}{15x^3} \rightarrow T^3$

$$f_E(x) = \frac{x^2 e^x}{(e^x - 1)^2}$$



These operators create or annihilate excitons with quasi-momentum \mathbf{K} and electron-hole separation β . The transformation means the transition from individual excitations with defined \mathbf{k} or \mathbf{R} to collective excitations in which only \mathbf{K} and β are given. Corresponding to (3.76), we then construct general *exciton operators* from linear combinations of these operators

$$b_{\nu\mathbf{K}}^{(+)} = \sum_{\beta} U_{\nu\mathbf{K}}(\beta) b_{\beta\mathbf{K}}^{(+)} \quad (3.92)$$

By considering the commutation relations of these $b_{\nu\mathbf{K}}^{(+)}$, one can show that the excitons have boson character. The proof is simpler if carried out for the limiting case of Frenkel excitons. We shall restrict ourselves to this. As in the previous section we put $\beta = 0$. We have then just one term left in (3.92). If we further put $m = 0$ and $n = 1$ then, since the operators for $\mathbf{K} \neq \mathbf{K}'$ clearly commute,

$$\begin{aligned} [b_{\mathbf{K}}, b_{\mathbf{K}'}^{+}] &= \delta_{\mathbf{K}\mathbf{K}'} [b_{\mathbf{K}}, b_{\mathbf{K}'}^{+}] \\ &= \frac{1}{N} \sum_{\mathbf{R}} [c_{0\mathbf{R}}^{+} c_{0\mathbf{R}} (1 - c_{1\mathbf{R}}^{+} c_{1\mathbf{R}}) - c_{1\mathbf{R}}^{+} c_{1\mathbf{R}} (1 - c_{0\mathbf{R}}^{+} c_{0\mathbf{R}})] \delta_{\mathbf{K}\mathbf{K}'} \end{aligned} \quad (3.93)$$

The product operators appearing in the last line are the particle number operators $N_{1\mathbf{R}}$ and $N_{0\mathbf{R}}$. They have the eigenvalues 1 or 0 depending on whether an electron at \mathbf{R} is in an excited state or the ground state. The sum of the operators $N_{1\mathbf{R}} + N_{0\mathbf{R}}$ is correspondingly equal to the unit operator. (In our model there is an electron in either excited or ground state of the atom at every lattice position). On the other hand, the product of the two operators is clearly zero. Eq. (3.93) then becomes

$$[b_{\mathbf{K}}, b_{\mathbf{K}'}^{+}] = \delta_{\mathbf{K}\mathbf{K}'} \frac{1}{N} \sum_{\mathbf{R}} (1 - 2N_{1\mathbf{R}}) = \delta_{\mathbf{K}\mathbf{K}'} \left(1 - \sum_{\mathbf{R}} \frac{2N_{1\mathbf{R}}}{N} \right) \quad (3.94)$$

The last term is of the order of "the number of excitons divided by the number of unexcited lattice atoms". When one is concerned with the lowest excitations of the insulator, this term can be neglected as small by comparison with 1. In this approximation excitons are therefore bosons.

High exciton excitations has recently become an area of particular interest (Bose-Einstein condensation of excitons, exciton molecules, electron-hole drops). For further reading on this we refer the reader to the review article by *Haken* and *Nikitine* [11d.73].

3.3 Ion-Ion Interaction: Phonons

3.3.1 Introduction

Having so far taken an interest only in electron motion, we want to turn now to the motion of the ion lattice itself.

Lattice dynamics is important in many areas of solid-state physics. As a result of their thermal motion, the lattice ions vibrate about their equilibrium positions. The forces which oppose this motion are those of the chemical bond. All the elastic properties, compressibility, the propagation of acoustic waves are related to it. These features are mostly described in the context of a continuum theory by disregarding the atomic structure of the lattice.

The continuum approximation is a limiting case of the microscopic theory which looks at the dynamics of the lattice ions themselves. To discuss this theory we shall first of all set up equations of motion for the lattice ions within the framework of classical mechanics and derive from these the energy and frequency of the "normal modes of oscillations" of the lattice. In describing the dispersion relations of these normal modes, we shall again meet up with the reciprocal lattice, the Brillouin zone concept, and other mathematical aids already introduced in the previous chapter. We shall be able to draw many parallels with earlier results which will allow us to limit the discussion necessary in this chapter. Section 3.3.2 is dedicated to a classical description of lattice vibrations.

If we supply thermal energy to a lattice ion, it will rapidly be distributed throughout the entire lattice by the mutual interaction between the ions. Local excitations will therefore lead to *collective vibrations* of the whole ion system. It is therefore appropriate to use collective coordinates (normal coordinates) for the mathematical description. The lattice vibrations can be readily quantized in this new representation. The associated quanta are elementary excitations called *phonons*. Phonons are bosons and thus call for the application of a different sort of statistics to electrons. Section 3.3.3 is devoted to the phonon concept.

We come to grips with our first application of this concept in Section 3.3.4 when we consider the energy content of lattice vibrations and specific heat. Section 3.3.5 then presents an overview of the calculation of phonon dispersion relations.

The phonon dispersion spectrum allows us to determine the associated density of states in a way similar to that in which the density of one-electron states followed from the band model. The close similarity means that the treatment of this question in Section 3.3.6 can be kept short.

In the last two sections of this chapter we examine the limiting case of lattice vibrations of very long wavelength. If the wavelength is large compared with the atomic separation, the microscopic structure of the solid can be neglected. This gives us, therefore, a link to the classical continuum theory.

In the approximation used throughout, the potential energy of a lattice ion is expanded in powers of the instantaneous deviation from its equilibrium position and only the first nonvanishing (harmonic) term is taken. This is the *harmonic approximation*. With it the Hamiltonian can be resolved into a sum of independent terms with the form of Hamiltonians of harmonic oscillators. This is the basis of the quantization and with it the description of lattice vibrations as a noninteracting phonon gas. The inclusion of higher anharmonic terms in the expansion means an *interaction between the phonons*. This forms the content of a later chapter (Chap. 7).

The topic of lattice vibrations and the harmonic approximation is treated in many publications. Special attention is given to lattice dynamics in the books by *Maradudin, Montroll*, and *Weiss* [102.3]; *Wallis* [120]; *Stevenson* [121]; *Enns* and *Haering* [133.II]; *Bak* [66]; and *Born* and *Huang* [67]. An excellent overview is also given by *Cochran* and *Cowley* [106, XXV/20], by *Leibfried* in [113a] and *Parrott* in [117]. The book series [101] contains numerous special articles. Phonon dispersion relations are collected in a book by *Bilz* and *Kress* [107.10].

3.3.2 The Classical Equations of Motion

We shall now consider ion-ion interaction and in doing so we shall ignore electron motion. The model is therefore that of (1.8): the lattice ions vibrate about their equilibrium positions. Between them forces are present which correlate the individual motions. The electron system is replaced by a spatially uniform negative space charge (inverse jellium model). Again we consider the ion lattice within a volume V_g with cyclic boundary conditions. Let the number of Wigner-Seitz cells in this volume be N . Let the equilibrium positions of the ions be $\mathbf{R}_{n\alpha} = \mathbf{R}_n + \mathbf{R}_\alpha$. Here \mathbf{R}_n is a suitable reference point inside the Wigner-Seitz cell and the \mathbf{R}_α are the vectors from this point to the α th basis atom. The index α will run from 1 to r for a basis made up of r ions. Let the instantaneous displacement of the n th ion from its equilibrium position be given by the time-dependent vector $s_{n\alpha}(t)$.

In this section we consider the classical problem. The classical Hamiltonian is made up of the kinetic energy of all the ions and of their interaction energy. The *kinetic energy* is

$$T = \sum_{n\alpha} \frac{M_\alpha}{2} \dot{s}_{n\alpha}^2 \quad n = 1, \dots, N, \quad \alpha = 1, \dots, r, \quad i = 1, 2, 3. \quad (3.95)$$

M_α here is the mass of the α th basis atom. The index i distinguishes the three cartesian coordinates of the vector $s_{n\alpha}$.

We expand the *potential energy* in increasing powers of the displacement $s_{n\alpha}$. The first (constant) term in this expansion is the potential energy of the ion lattice in equilibrium. We shall omit this component along with the negative background since it does not contribute to the dynamics of lattice vibrations which is our sole interest here.

The second term in the expansion is linear in the $s_{n\alpha i}$. Since we are expanding about an equilibrium position, this term must disappear. The third term is quadratic in the displacement and has the form

$$\frac{1}{2} \sum_{n'\alpha' i'} \frac{\partial^2 V}{\partial R_{n\alpha i} \partial R_{n'\alpha' i'}} s_{n\alpha i} s_{n'\alpha' i'} = \frac{1}{2} \sum_{n'\alpha' i'} \Phi_{n\alpha i}^{n'\alpha' i'} s_{n\alpha i} s_{n'\alpha' i'}. \quad (3.96)$$

The matrix $\Phi_{n\alpha i}^{n'\alpha' i'}$ appearing here has $3rN$ rows and columns. We terminate the expansion at this first nonvanishing term (*harmonic approximation*). We shall not look at corrections to this approximation until Chapter 7. We recognize the meaning of the $\Phi_{n\alpha i}^{n'\alpha' i'}$ from the equations of motion

$$M_\alpha \ddot{s}_{n\alpha i} = - \frac{\partial V}{\partial s_{n\alpha i}} = - \sum_{n'\alpha' i'} \Phi_{n\alpha i}^{n'\alpha' i'} s_{n'\alpha' i'}. \quad (3.97)$$

$\Phi_{n\alpha i}^{n'\alpha' i'}$ is hereafter the force in the i -direction on the α th ion in the n th elementary cell when the α' th ion in the n' th cell is displaced by unit distance in the i' -direction.

The $\Phi_{n\alpha i}^{n'\alpha' i'}$ are called atomic force constants. They are linked by a large number of symmetry relations. First we recognize from (3.96) that the force constants are symmetric

$$\Phi_{n\alpha i}^{n'\alpha' i'} = \Phi_{n'\alpha' i'}^{n\alpha i}. \quad (3.98)$$

Furthermore they are clearly real. We obtain further relations when we use the fact that the potential energy must be invariant to an (infinitesimal) translation or rotation of the crystal. Let the translation be given by $s_{n\alpha i} = \delta s_i$ for all n, α, i and the rotation by $s_{n\alpha i} = \sum_k \delta \omega_{ik} R_{n\alpha k} (\delta \omega_{ik} = -\delta \omega_{ki})$. These operations are not allowed to result in any forces on the lattice ions, so the right-hand side in (3.97) must disappear. This leads to

$$\sum_{i'} \delta s_{i'} \sum_{n'\alpha'} \Phi_{n\alpha i}^{n'\alpha' i'} = 0 \quad \text{and} \quad \sum_{i'k'} \delta \omega_{i'k'} \sum_{n'\alpha'} \Phi_{n\alpha i}^{n'\alpha' i'} R_{n'\alpha' k'} = 0 \quad (3.99)$$

for translation and rotation, respectively, and hence to the symmetry relations

$$\sum_{n\alpha} \Phi_{n\alpha i}^{n\alpha i} = 0 \quad (3.100)$$

and

$$\sum_{n\alpha} \Phi_{n\alpha i}^{n\alpha i} R_{n\alpha k} = \sum_{n\alpha} \Phi_{n\alpha i}^{n\alpha k} R_{n\alpha i}. \quad (3.101)$$

Along with these general relations, many others can be derived by use of lattice symmetry. We want to go into these later, but for the moment we shall

leave lattice symmetry out of our treatment. We shall then be in a better position later to distinguish between general statements and those which spring from lattice symmetry.

We are looking for solutions of the equations of motion which are periodic in time. To do this we put

$$s_{nai}(t) = \frac{1}{\sqrt{M_\alpha}} u_{nai} \exp(-i\omega t) \quad \text{with time-independent } u_{nai}. \quad (3.102)$$

Here we have drawn out a factor $M_\alpha^{-1/2}$. Using this expression, the equations of motion become

$$\omega^2 u_{nai} = \sum_{n'\alpha'i'} D_{nai}^{n'\alpha'i'} u_{n'\alpha'i'} \quad \left(D \equiv \frac{\Phi}{\sqrt{M_\alpha M_{\alpha'}}} \right). \quad (3.103)$$

This is an eigenvalue equation for the real symmetric matrix $D_{nai}^{n'\alpha'i'}$ with $3rN$ real eigenvalues ω_j^2 . The ω_j can only be either real or purely imaginary. The latter possibility can be eliminated since (3.102) would then lead to s_{nai} which increase or decrease continuously with time.

The eigenvectors u_{nai} of (3.103) are correspondingly characterized by the index j : $u_{nai}^{(j)}$, i.e., for each ω_j there are $3rN$ $u_{nai}^{(j)}$. They are called *normal modes*. We now take account of the translation symmetry of the lattice. This requires that the $\Phi_{nai}^{n'\alpha'i'}$ (or $D_{nai}^{n'\alpha'i'}$) can depend not on the cell indices n' and n separately, but only on their difference $n' - n$: $\Phi_{nai}^{n'\alpha'i'} = \Phi_{ai}^{\alpha'i'}(n' - n)$.

With this condition and the expression

$$u_{nai} = c_{ai} \exp(i\mathbf{q} \cdot \mathbf{R}_n) \quad (3.104)$$

(3.103) becomes

$$\omega^2 c_{ai} = \sum_{\alpha'i'} \left\{ \sum_n \frac{1}{\sqrt{M_\alpha M_{\alpha'}}} \Phi_{ai}^{\alpha'i'}(n' - n) \exp[i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_{n'})] \right\} c_{\alpha'i'}. \quad (3.105)$$

or since the summation over n' can be changed into a summation over $n' - n$

$$\omega^2 c_{ai} = \sum_{\alpha'i'} D_{ai}^{\alpha'i'}(\mathbf{q}) c_{\alpha'i'}, \quad (3.106)$$

with $D_{ai}^{\alpha'i'}(\mathbf{q})$ defined by (3.105).

Lattice periodicity has thus reduced the system of $3rN$ equations (3.103) to a system of $3r$ equations. This system then has only $3r$ eigenvalues, that is, $3r$ ω_j . However these are functions of the vector \mathbf{q}

$$\omega = \omega_j(\mathbf{q}) \quad j = 1, \dots, 3r. \quad (3.107)$$

For each ω_j (3.106) has a solution $c_{\alpha'i} = e_{\alpha'i}^{(j)}(\mathbf{q})$. These solutions can be combined to vectors. They are defined except for a common factor which can be chosen such that the $e_{\alpha'i}^{(j)}(\mathbf{q})$ are normalized (and orthogonal to each other).

For the displacements $s_{na}(t)$ we then have, as special solutions of the equations of motion (3.97),

$$s_{na}^{(j)}(\mathbf{q}, t) = \frac{1}{\sqrt{M_\alpha}} e_{\alpha}^{(j)}(\mathbf{q}) \exp(i[\mathbf{q} \cdot \mathbf{R}_n - \omega_j(\mathbf{q})t]), \quad (3.108)$$

from which we can construct the general solutions.

Before looking more closely at (3.108) we want to examine the dispersion relations (3.107). $\hbar\omega_j$ is an energy, \mathbf{q} is a vector in reciprocal space. The function $\omega_j(\mathbf{q})$ therefore has the same significance for lattice vibrations as the function $E_n(\mathbf{k})$ has for the motion of the electrons in the periodic lattice. We can adopt all the important results concerning qualitative properties from Section 2.2.

1) The function $\omega_j(\mathbf{q})$ is periodic in \mathbf{q} -space. So we need only consider one Brillouin zone, the form of which is given by the point group of the crystal.

2) The set of \mathbf{q} -values is finite as a result of the cyclic boundary conditions imposed on the crystal. If V_g contains N elementary cells, then there are N values of \mathbf{q} in the Brillouin zone. Since j can take $3r$ values, there are $3rN$ different $\omega_j(\mathbf{q})$, that is, as many as the crystal has internal degrees of freedom.

3) $\omega_j(\mathbf{q})$ is an analytic function of \mathbf{q} in the Brillouin zone in the same sense as $E_n(\mathbf{k})$ is analytic. However, whereas the index n in $E_n(\mathbf{k})$ can take any number of integer values, j has only $3r$ different values; $\omega_j(\mathbf{q})$ has $3r$ branches.

4) In the Brillouin zone $\omega_j(\mathbf{q})$ has the same symmetries as the band structure $E_n(\mathbf{k})$. In addition to the symmetries resulting from the space group of the crystal, we have by time reversal symmetry $\omega_j(\mathbf{q}) = \omega_j(-\mathbf{q})$.

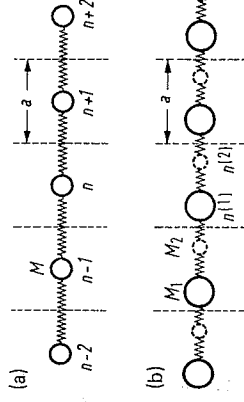


Fig. 3.6a and b. The linear chain (a) without and (b) with a basis.

The behaviour of $\omega_j(\mathbf{q})$ as $\mathbf{q} \rightarrow 0$ is important. We shall take the simple example of an oscillating linear chain to look at the most important aspects. Let us assume a chain of identical spheres linked together by springs of force constant f (Fig. 3.6a). Let a further be the separation between the spheres in equilibrium and let s_n be the displacement of the n th sphere from its equilibrium position. Eq. (3.97) then becomes

$$M \ddot{s}_n = -f(s_n - s_{n+1}) + f(s_{n-1} - s_n). \quad (3.109)$$

In accordance with (3.102) and (3.104) we put

$$s_n = \frac{1}{\sqrt{M}} c \exp [i(qan - \omega t)]. \tag{3.110}$$

We then find

$$\omega^2 M = f[2 - \exp(-iga) - \exp(iga)] \tag{3.111}$$

and

$$\omega = 2 \sqrt{\frac{f}{M} \left| \sin \frac{qa}{2} \right|} \tag{3.112}$$

so that ω is a periodic function of q . The first period (Brillouin zone) lies between $-\pi/a$ and $+\pi/a$ (Fig. 3.7).

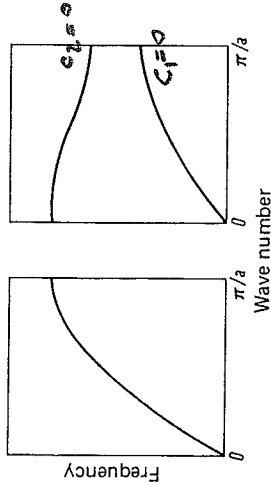


Fig. 3.7. Dispersion relations $\omega(q)$ for the linear chain without and with a basis (left and right, respectively).

If there are two atoms in the elementary cell, instead of (3.109) we have the equations (see Fig. 3.6b for the notation)

$$\begin{aligned} M_1 s_n^{(1)} &= -f(2s_n^{(1)} - s_n^{(2)} - s_{n-1}^{(2)}), \\ M_2 s_n^{(2)} &= -f(2s_n^{(2)} - s_{n+1}^{(1)} - s_n^{(1)}). \end{aligned} \tag{3.113}$$

Using the following expressions

$$\begin{aligned} s_n^{(1)} &= \frac{1}{\sqrt{M_1}} c_1 \exp \left(i \left[q \left(n - \frac{1}{4} \right) a - \omega t \right] \right) \\ s_n^{(2)} &= \frac{1}{\sqrt{M_2}} c_2 \exp \left(i \left[q \left(n + \frac{1}{4} \right) a - \omega t \right] \right) = \exp \left(i \frac{qa}{2} \right) \frac{c_2}{c_1} \frac{s_n^{(1)}}{\sqrt{M_2}} \end{aligned} \tag{3.114}$$

we find

$$\begin{aligned} -\omega^2 \sqrt{M_1} c_1 &= -\frac{2f}{\sqrt{M_1}} c_1 + \frac{2f}{\sqrt{M_2}} c_2 \cos \frac{qa}{2}, \\ -\omega^2 \sqrt{M_2} c_2 &= -\frac{2f}{\sqrt{M_2}} c_2 + \frac{2f}{\sqrt{M_1}} c_1 \cos \frac{qa}{2}. \end{aligned} \tag{3.115}$$

and as the solutions of the determinant

$$\begin{vmatrix} \frac{2f}{\sqrt{M_1}} - \omega^2 \sqrt{M_1} & -\frac{2f}{\sqrt{M_2}} \cos \frac{qa}{2} \\ -\frac{2f}{\sqrt{M_1}} \cos \frac{qa}{2} & \frac{2f}{\sqrt{M_2}} - \omega^2 \sqrt{M_2} \end{vmatrix} = 0, \tag{3.116}$$

we finally arrive at

$$\omega_{\pm}^2 = f \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm f \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4}{M_1 M_2} \sin^2 \frac{qa}{2}}. \tag{3.117}$$

ω has therefore two branches, $\omega_+(q)$ and $\omega_-(q)$, which take the values $[2f(1/M_1 + 1/M_2)]^{1/2}$ and 0, respectively, at $q = 0$, and the values $(2f/M_1)^{1/2}$ and $(2f/M_2)^{1/2}$, respectively, at $q = \pm\pi/a$ (Fig. 3.7).

For the two limits $q = 0$ and $\pm\pi/a$, the ratio of the amplitudes c_2/c_1 follows from (3.115) as

$$\begin{aligned} c_2/c_1 &= +(M_2/M_1)^{1/2} \text{ for } q = 0 \text{ and } \omega = \omega_- \\ &= -(M_1/M_2)^{1/2} \text{ for } q = 0 \text{ and } \omega = \omega_+ \end{aligned} \tag{3.118}$$

$$\begin{aligned} &= \infty \text{ for } q = \pm\pi/a \text{ and } \omega = \omega_- \\ &= 0 \text{ for } q = \pm\pi/a \text{ and } \omega = \omega_+. \end{aligned} \tag{3.119}$$

These limiting cases correspond to typical modes of oscillation. Since $|q| = 2\pi/\lambda$, $q = 0$ means oscillations of infinite wavelength. All elementary cells move in the same sense. For $\omega = \omega_-$ the displacements of the two basis atoms in the cell are in the same direction, for $\omega = \omega_+$ they are in opposite directions.

The first case is the limiting case of an acoustic wave. The branch disappearing at $q = 0$ is correspondingly called the *acoustic branch*. The second type of vibration is readily excited optically in ionic crystals. The associated branch is therefore called the *optical branch*.

For $q = \pm\pi/a$ the basis atoms of one sort (M_1 or M_2) are at the nodes of the vibrations of wavelength $2a$. If each elementary cell has r basis atoms, then in addition to the acoustic branch there are $r - 1$ optical branches.

We have said nothing in (3.109) about whether these equations are meant to describe *transverse* vibrations (displacements perpendicular to the chain) or *longitudinal* vibrations (displacements along the chain). Eq. (3.109) applies to both situations as long as the vibration amplitudes are small. The meaning of the force constant f is different though for the two cases. For small amplitudes, each three-dimensional vibration of the chain can be resolved into three independent components, one longitudinal and two transverse. The two transverse

vibrations take place in two perpendicular planes whose line of intersection is the equilibrium position of the chain.

Thus we see that in the general case the function $\omega_j(\mathbf{q})$ for the oscillating chain has three acoustic and $3(r-1)$ optical branches.

If we now go from this example to a crystal with r atoms per elementary cell, we find that qualitatively the picture is the same. $\omega_j(\mathbf{q})$ is made up of three acoustic branches (degenerate at $\mathbf{q} = 0$) and $3(r-1)$ optical branches. These branches are now functions of a vector \mathbf{q} . The degeneracy of the pair of transverse branches in the one-dimensional case only remains at points or along lines of high symmetry in the Brillouin zone. At a general point \mathbf{q} all $3r$ branches are separated.

The expression "optical branch" cannot always be taken literally. Optical vibrations can in some cases not be excited optically, e.g., if the two basis atoms have the same effective charge. Again, away from $\mathbf{q} = 0$ the vibrations of an optical branch are not always out of phase and those of an acoustic branch not always in phase. Complicated mixed modes of the two limiting cases (3.118) can arise here. Likewise, the lattice vibrations are only strictly longitudinal or transverse at points or along lines of high symmetry.

3.3.3 Normal Coordinates, Phonons

According to (3.95) and (3.96), the Hamiltonian function for lattice vibrations has the form

$$H = \sum_{n\alpha i} \frac{M_\alpha}{2} \dot{s}_{n\alpha i}^2 + \frac{1}{2} \sum_{\substack{n\alpha i \\ n'\alpha' i'}} \Phi_{n\alpha i, n'\alpha' i'}^{\alpha' i'} s_{n\alpha i} s_{n'\alpha' i'} \quad (3.120)$$

The $s_{n\alpha i}(t)$ are linear combinations of the particular solutions (3.108)

$$s_{n\alpha i}(t) = \frac{1}{\sqrt{NM_\alpha}} \sum_{j\mathbf{q}} Q_j(\mathbf{q}, t) e_{\alpha i}^{(j)}(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{R}_n) \quad (3.121)$$

where the time-dependent exponential factor in (3.108) has been included in the $Q_j(\mathbf{q}, t)$ and a factor $1/\sqrt{N}$ has been separated out.

By putting (3.121) into (3.120), the Hamiltonian can be expressed in terms of the *normal coordinates* Q_j . For the conversion we use

$$\sum_n \exp [i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}_n] = N \delta_{\mathbf{q} - \mathbf{q}', \mathbf{K}_m} \quad (3.122)$$

where $\delta_{\mathbf{q}, \mathbf{K}_m}$ is equal to unity, when \mathbf{q} equals zero or a reciprocal lattice vector, and otherwise disappears.

Since the $s_{n\alpha i}(t)$ must be real, we have

$$e_{\alpha i}^{(j)*}(\mathbf{q}) Q_j^*(\mathbf{q}, t) = e_{\alpha i}^{(j)}(-\mathbf{q}) Q_j(-\mathbf{q}, t). \quad (3.123)$$

We satisfy this by the requirements

$$e_{\alpha i}^{*(j)}(\mathbf{q}) = e_{\alpha i}^{(j)}(-\mathbf{q}) \quad \text{and} \quad Q_j^*(\mathbf{q}, t) = Q_j(-\mathbf{q}, t). \quad (3.124)$$

Here we have complex $e_{\alpha i}$. Following (3.106), the e_α can be chosen mutually orthogonal. We must then have further for the $e_{\alpha i}$

$$\sum_{\alpha i} e_{\alpha i}^{*(j)}(\mathbf{q}) e_{\alpha i}^{(j')}(\mathbf{q}) = \delta_{jj'}. \quad (3.125)$$

After much calculation, (3.122–125) yield

$$H = \frac{1}{2} \sum_{j\mathbf{q}} [\dot{Q}_j^*(\mathbf{q}, t) \dot{Q}_j(\mathbf{q}, t) + \omega_j^2(\mathbf{q}) Q_j^*(\mathbf{q}, t) Q_j(\mathbf{q}, t)]. \quad (3.126)$$

By introducing normal coordinates, the Hamiltonian resolves into a sum of $3rN$ individual terms. The coupled individual oscillations of the ions are formally replaced by decoupled collective oscillations. The normal coordinates used here are complex. One can also choose real normal coordinates instead.

One finds the conjugate momentum P to the Q^* from the Lagrange function $L = T - V$ according to

$$P_j(\mathbf{q}, t) = \frac{\partial L}{\partial \dot{Q}_j^*(\mathbf{q}, t)} = \dot{Q}_j(\mathbf{q}, t). \quad (3.127)$$

We then find that

$$H = \frac{1}{2} \sum_{j\mathbf{q}} [P_j^*(\mathbf{q}, t) P_j(\mathbf{q}, t) + \omega_j^2(\mathbf{q}) Q_j^*(\mathbf{q}, t) Q_j(\mathbf{q}, t)]. \quad (3.128)$$

The Hamilton equations yield ($\dot{P} = -\partial H/\partial Q^*$)

$$\dot{P}_j(\mathbf{q}, t) = \dot{Q}_j(\mathbf{q}, t) = -\omega_j^2(\mathbf{q}) Q_j(\mathbf{q}, t). \quad (3.129)$$

The equation of motion in normal coordinates is then

$$\ddot{Q}_j(\mathbf{q}, t) + \omega_j^2(\mathbf{q}) Q_j(\mathbf{q}, t) = 0 \quad (3.130)$$

which is formally identical with the equation of motion of a harmonic oscillator of frequency $\omega_j(\mathbf{q})$.

The transition to a quantum mechanical description is now easy to execute. We have only to interpret the P and Q as operators which have been subjected to the commutation relations

$$[Q_j(\mathbf{q}), P_{j'}(\mathbf{q}')] = i\hbar \delta_{\mathbf{q}\mathbf{q}'} \delta_{jj'}. \quad (3.131)$$

The Hamiltonian operator (3.128) together with the commutation relations (3.131) corresponds exactly to (A.1) and (A.2) of the Appendix. We can therefore interpret the quantized collective oscillations as elementary excitations. They are called *phonons*. The introduction of creation and annihilation operators leads to a Hamiltonian of the form

$$H = \sum_{j\mathbf{q}} \hbar\omega_j(\mathbf{q}) \left[a_j^\dagger(\mathbf{q})a_j(\mathbf{q}) + \frac{1}{2} \right]. \quad (3.132)$$

Each of the states defined by a pair (\mathbf{q}, j) is occupied by $n_j(\mathbf{q})$ phonons of energy $\hbar\omega_j(\mathbf{q})$, where the $n_j(\mathbf{q})$ are the eigenvalues of the operator $a_j^\dagger(\mathbf{q})a_j(\mathbf{q})$ appearing in (3.132). The contribution which such a state (a normal mode) makes to the total energy is $n_j(\mathbf{q})\hbar\omega_j(\mathbf{q})$ and the total energy (including the zero point energy) is

$$E = \sum_{j\mathbf{q}} \hbar\omega_j(\mathbf{q}) \left[n_j(\mathbf{q}) + \frac{1}{2} \right]. \quad (3.133)$$

In the harmonic approximation used here, the phonon gas described by (3.132) consists of noninteracting phonons. It is therefore appropriate to make a comparison with the noninteracting electron gas of Section 2.1. The basic difference between the two cases lies in the fact that electrons are *fermions* and phonons are *bosons*. Each state in the lattice vibration spectrum can therefore be occupied by any number of (indistinguishable) phonons. In addition, the number of phonons depends on the energy content of the lattice vibrations, i.e., on the temperature. At $T = 0$, no phonons are excited and the lattice has its zero point energy only.

Consequently the statistics are different. We are not interested, as in Section 2.1.4, in the distribution of N indistinguishable fermions among given energy states at a given temperature, but in the number of excited bosons in the oscillator states as a function of temperature. The probability P_n that a particular oscillator has the excitation energy $E_n = \hbar\omega(n + \frac{1}{2})$ is proportional to $\exp(-E_n/k_B T)$. Since $\sum_n P_n = 1$, this probability is given explicitly by

$$P_n = \frac{\exp(-E_n/k_B T)}{\sum_n \exp(-E_n/k_B T)} = \frac{\exp(-n\hbar\omega/k_B T)}{\sum_n \exp(-n\hbar\omega/k_B T)}. \quad (3.134)$$

Since $\sum_n x^n = (1-x)^{-1}$ (all summations run from $n = 0$ to $n = \infty$), it follows that

$$P_n = \exp(-n\hbar\omega/k_B T) \{1 - \exp[-\hbar\omega/k_B T]\}^{-1}. \quad (3.135)$$

We then find for the mean energy of the oscillator

$$\bar{E} = \sum_n E_n P_n = E_0 + \sum_n n\hbar\omega P_n. \quad (3.136)$$

Since $\sum_n n x^n = x/(1-x)^2$, we finally have

$$\bar{E} = \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} + \frac{\hbar\omega}{2}. \quad (3.137)$$

The mean occupation probability of an oscillator, i.e., the mean number of phonons in state j, \mathbf{q} is then given by

$$\bar{n}_j(\mathbf{q}) = \frac{1}{\exp[\hbar\omega_j(\mathbf{q})/k_B T] - 1} \quad (\text{Bose distribution}). \quad (3.138)$$

Following Section 3.3.2, the spectrum of the lattice vibrations resolves into $3r$ branches (index j), each of which can be represented as a function in \mathbf{q} -space. Since there is a state associated with each (quasi-discrete) point \mathbf{q} of each branch, we have to distinguish between phonons of the different branches. Depending of the behaviour of a branch at $\mathbf{q} = 0$ and the polarization of the normal mode, we distinguish between *acoustic* and *optical*, *longitudinal* and *transverse phonons*. Since they show different properties when interacting with other quasi-particles and collective excitations, we shall note the different types, as far as necessary: TA-, TO-, LA-, LO-phonons.

We close this section with two fundamental remarks. The transition to normal coordinates, and the decoupling of the Hamiltonian into independent normal modes thereby achieved, was made possible by the fact that the Hamiltonian (3.120) is a positive definite quadratic form. Such a form can be diagonalized. We could therefore have already made the transition to quantum mechanics and introduced phonons by following on from (3.103), and before the explicit consideration of lattice periodicity. The appearance of elementary excitations at this point is not therefore linked to the properties of the lattice. The division of all ω_j into branches which can be presented in one Brillouin zone of \mathbf{q} -space, on the other hand, is a consequence of the periodicity of the lattice.

If one had not terminated the expansion (3.96) at the second term, it would not have been possible to diagonalize. The consideration of higher, anharmonic terms therefore brings *phonon-phonon interaction* into the picture (Chap. 7).

3.3.4 The Energy Content of the Lattice Vibrations, Specific Heat

The total energy of the lattice vibrations at a temperature T is given from (3.133) and (3.138) by

$$E = \sum_{j\mathbf{q}} \left[\frac{1}{\exp(\hbar\omega_j/k_B T) - 1} + \frac{1}{2} \right] \hbar\omega_j(\mathbf{q}). \quad (3.139)$$

The summation over all \mathbf{q} and over all branches j can be readily evaluated in two limiting cases.

1) *High temperature.* When $k_B T$ is large compared with $\hbar\omega_j$, the exponential function in the denominator can be expanded and it follows that

$$E = \sum_{j\mathbf{q}} k_B T \left[1 + \frac{1}{12} \left(\frac{\hbar\omega_j(\mathbf{q})}{k_B T} \right)^2 + \dots \right] \approx 3rNk_B T. \quad (3.140)$$

To a first approximation each of the $3rN$ oscillators makes a contribution $k_B T$ to the total energy (Dulong-Petit law). This is the classical result. Quantum effects do not appear.

2) *Low temperature.* In this case we cannot put $k_B T$ small in comparison with $\hbar\omega_j$ since all values of frequency from zero up to $\hbar\omega_j \gg k_B T$ appear. On the other hand, (3.139) allows us to conclude that frequencies for which $\hbar\omega_j \gg k_B T$ make no contribution. We can therefore limit the summation to the three acoustic branches. Here too only the lowest frequencies will be important. For these the dispersion relation $\omega_j = \omega_j(\mathbf{q})$ can be approximated by the linear expression $\omega_j(\mathbf{q}) = s_j(\theta, \varphi)q$. We then have

$$E = \sum_{j\mathbf{q}} \frac{\hbar s_j q}{\exp(\hbar s_j q / k_B T) - 1} + \text{zero point energy } E_0. \quad (3.141)$$

For sufficiently large V_g we can replace the summation over discrete \mathbf{q} -points by an integration in \mathbf{q} -space: $\sum_{\mathbf{q}} = [V_g / (2\pi)^3] \int d\tau_{\mathbf{q}}$. Eq. (3.141) then becomes

$$\begin{aligned} E - E_0 &= \frac{V_g}{(2\pi)^3} \sum_j \int \frac{\hbar s_j q}{\exp(\hbar s_j q / k_B T) - 1} d\tau_{\mathbf{q}} \\ &= \frac{V_g}{(2\pi)^3} \frac{(k_B T)^4}{\hbar^3} \sum_j \int \frac{d\Omega}{s_j^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}. \end{aligned} \quad (3.142)$$

The upper integration limit can be made infinity since large values of x make no contribution to the integrand. If we now average s_j^{-3} over all directions and branches we find

$$E = \frac{\pi^2}{10} \frac{V_g}{\hbar^3} \frac{(k_B T)^4}{s^3} + \text{zero point energy} \quad (3.143)$$

in which the value $\pi^4/15$ has been inserted for the integral over all x .

These approximations are insufficient for the intermediate temperature range. We note first of all that a function of $\omega_j(\mathbf{q})$ is involved in the sum over \mathbf{q} in (3.139). By replacing the summation with an integration one can immediately rearrange it as an integration over ω_j . To do this we introduce, as in Section

2.2.10, a *density of states* $g(\omega)$. Thus

$$g(\omega)d\omega = \frac{V_g}{(2\pi)^3} \int_{\omega=\text{const}} \frac{df_{\mathbf{q}}}{|V_{\mathbf{q}} \omega_j(\mathbf{q})|} d\omega. \quad (3.144)$$

In contrast to Section 2.2.10, we have not normalized $g(\omega)$ here to V_g . With (3.144), we have for any function $F(\omega)$

$$\sum_{\mathbf{q}} F(\omega) = \frac{V_g}{(2\pi)^3} \int_0^\infty F(\omega) d\tau_{\mathbf{q}} = \int_0^\infty F(\omega) g(\omega) d\omega. \quad (3.145)$$

For the approximation $\omega_j(\mathbf{q}) = s_j q$ (with s_j already averaged over all angles) we have for example

$$g_j(\omega_j) d\omega_j = \frac{V_g}{2\pi^2} \frac{\omega_j^2 d\omega_j}{s_j^3} \quad (3.146)$$

and

$$\begin{aligned} E - E_0 &= \sum_j \int_0^\infty \frac{\hbar\omega_j}{\exp(\hbar\omega_j/k_B T) - 1} g_j(\omega_j) d\omega_j \\ &= \sum_j \frac{V_g}{2\pi^2} \frac{(k_B T)^4}{\hbar^3} \frac{1}{s_j^3} \int_0^\infty \frac{x^3}{e^x - 1} dx. \end{aligned} \quad (3.147)$$

But this is exactly the result we have just obtained above for the low temperature limit. In this formulation we can at least correct it in one respect. The integration of the density of states (3.144) over all ω has to give exactly N \mathbf{q} -values for a branch [(3.145) with $F = 1$].

In the linear approximation we must therefore terminate the spectrum $\omega_j(\mathbf{q})$ at a frequency ω_D (*Debye frequency*) in order that this condition be met. This leads to the equation

$$\frac{V_g}{2\pi^2} \frac{1}{s_j^3} \omega_{jD}^3 = N, \quad (3.148)$$

or with $q_{jD} = \omega_{jD}/s_j$ independent of j

$$q_{jD} = \left(\frac{6\pi^2 N}{V_g} \right)^{1/3} = (6\pi^2 n)^{1/3}. \quad (3.149)$$

Now N/V_g is the reciprocal volume of a Wigner-Seitz cell and is therefore equal to the volume of a Brillouin zone divided by $(2\pi)^3$. If we insert this into (3.149) it follows immediately that q_D is the radius of a sphere with volume

equivalent to that of the Brillouin zone. The Debye approximation used here therefore consists of three approximations to the spectrum $\omega_j(\mathbf{q})$: 1) neglect of optical branches, 2) linear approximation of acoustic branches, and 3) replacement of the Brillouin zone by a sphere of equivalent volume and assumption of directional-independence of the linear approximation in this sphere.

In our approximation the Debye correction means replacing the upper limit ∞ in the integral (3.142) by $\hbar\omega_D/k_B T$, and hence the multiplication of (3.143) with a temperature-dependent factor

$$\frac{1.5}{\pi^4} \int_0^{\hbar\omega_D/k_B T} \frac{x^3}{e^x - 1} dx = f\left(\frac{\hbar\omega_D}{k_B T}\right) = f\left(\frac{\theta_D}{T}\right). \quad (3.150)$$

Here we have also introduced the *Debye temperature* θ_D through $k_B\theta_D = \hbar\omega_D$.

We want to touch here on a model introduced by Einstein, in preparation for its application later. In this it is assumed that only one oscillation frequency occurs: $\omega_j(\mathbf{q}) = \omega_E$. Then for the density of states

$$g(\omega_j)d\omega_j = N\delta(\omega_j - \omega_E)d\omega_j, \quad (3.151)$$

and from (3.147) follows that

$$E - E_0 = \frac{N\hbar\omega_E}{\exp(\hbar\omega_E/k_B T) - 1}. \quad (3.152)$$

Coarse as this approximation appears to be, it is nevertheless important for extending the Debye approximation. From Fig. 3.7 we see that, for the linear chain with a basis, the Debye approximation gives a very good description for the acoustic branch. For the optical branch, however, it is clear that an assumption of constant frequency for all optical phonons will be more accurate than a linear approximation of the Debye type.

In making a comparison between theory and experiment, the change of total energy with temperature, i.e., the *specific heat*, will prove to be more important than the total energy itself.

We do not have to distinguish between c_p and c_v in the harmonic approximation since this approximation does not include thermal expansion of the lattice. We obtain the specific heat from the Debye approximation by differentiating (3.147), (3.150) with respect to the temperature.

$$c_D(T) = 3Nk_B f_D\left(\frac{\theta_D}{T}\right) \quad \text{with} \quad f_D(x) = \frac{3}{x^3} \int_0^x \frac{y^4 e^y dy}{(e^y - 1)^2}. \quad (3.153)$$

For large θ_D/T (low temperatures), $f_D(x)$ is approximately given by $4\pi^4/5x^3$. In this approximation the specific heat is then proportional to T^3 (Debye's T^3 -law).

If we further introduce the Einstein temperature θ_E corresponding to the Debye temperature and a factor 3 for the three optical branches, we then find in the Einstein approximation that

$$c_E(T) = 3Nk_B f_E\left(\frac{\theta_E}{T}\right) \quad \text{with} \quad f_E(x) = \frac{x^2 e^x}{(e^x - 1)^2}. \quad (3.154)$$

The temperature dependence of both approximations is given in Fig. 3.8.

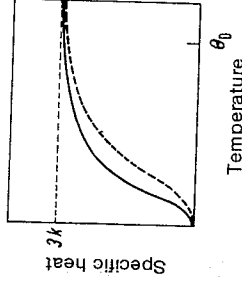


Fig. 3.8. Specific heat according to the Debye (upper curve) and Einstein (lower curve) approximations.

3.3.5 Calculation of Phonon Dispersion Relations

As already pointed out in Section 3.3.2, the function $\omega_j(\mathbf{q})$ can be represented in a Brillouin zone of \mathbf{q} -space in a way corresponding to that in which a band structure $E_n(\mathbf{k})$ is represented in a Brillouin zone of \mathbf{k} -space. In particular the same symmetry requirements apply.

Before we consider the calculation of such dispersion curves, let us draw attention to a few important points by taking the simple case of a two-dimensional square lattice.

The function $\omega_j(\mathbf{q})$ follows from (3.106) when the $3r \times 3r$ matrix $D_{\alpha i}^{\alpha' i'}(\mathbf{q})$ is known. The latter in turn is found from the force constants according to the equation

$$D_{\alpha i}^{\alpha' i'}(\mathbf{q}) = \sum_n \frac{1}{\sqrt{M_\alpha M_{\alpha'}}} \Phi_{\alpha \alpha' i i'}^{n \alpha' i'} \exp[i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_i)]. \quad (3.155)$$

In our model we assume elastic (spring) forces between neighbouring atoms, as in the one-dimensional case in Section 3.3.2. In accordance with the assumption that the forces are strongest between nearest neighbours and diminish with increasing distance to the next-nearest neighbour, third-nearest neighbour, etc., we limit ourselves to consideration of the nearest and next-nearest (Fig. 3.9). It would not be realistic to restrict our consideration to nearest neighbours only, if only because a square lattice (just like a cubic lattice in space) would not be stable against shear forces if elastic forces only exist between directly adjacent neighbours.

We consider now a particular atom $n = 0$. If the n' th atom is moved from its equilibrium position by a vector distance $s_{n'}$, the i th component of force acting