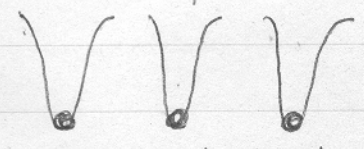


# Lattice Vibrations

- 1) Harmonic Theory.
  - a) Dynamical matrix. Normal modes
  - b) Acoustic and optical phonons
  - c) ~~Second~~ Quantization and energy spectrum.
  - d) Thermodynamic properties. Debye theory.
- 2) Phonon-phonon interactions <sup>effects of</sup> Anharmonicity. Phonon Green's functions. Feynman-Dyson expansion.
- 3) Phonon-photon interactions. One- and multi-phonon absorption. Raman & Brillouin scattering.
- [4] Electron-phonon interaction.

## Lattice Vibrations

So far, we have discussed the properties of the electrons in a static lattice. ~~La~~ The ions  $\alpha_i$  of course, are not stationary. They vibrate about their equilibrium positions. These vibrations were first studied by Einstein. He assumed that each ion vibrates ~~also~~ independently about its equilibrium position.



This is an <sup>an</sup> oversimplified picture because the potential wells are created by ion-ion interaction. So we have to consider the collective motion of the ions. [Debye, Born & others] => Theory of phonons.

We'll start with an equilibrium configuration, and consider small vibrations of the ions about this equilibrium configuration. It is very difficult to do a first-principle determination of the equilibrium configuration, given the interaction among the ions. We'll assume that we are given a configuration which is at least a local minimum of the total potential energy of the ions. We'll also neglect, for the time being, the presence of the electrons. The electrons are important in determining the forces between two ions (screening). We'll assume that the forces are given. More details of the effects of the electrons will be considered later.

One atom/unit cell.  $\vec{R}_1, \vec{R}_2, \vec{R}_3$

Equilibrium positions  $\vec{L} = l_1 \vec{R}_1 + l_2 \vec{R}_2 + l_3 \vec{R}_3$

Actual position of lth. ion:  $\vec{R}_e$

Displacement  $\vec{u}_e = \vec{R}_e - \vec{L}$

Total potential energy:  $\Phi(\vec{R}_1, \dots, \vec{R}_N)$

is a minimum when  $\vec{R}_e = \vec{L}$  for all  $l$ .

We can expand  $\Phi$  about this minimum.

$$\Phi = \Phi_0 + \sum_e \sum_\alpha \phi_\alpha(\vec{L}) u_e^\alpha + \frac{1}{2} \sum_{ee'} \sum_{\alpha\beta} \phi_{\alpha\beta}(\vec{L}, \vec{L}') u_e^\alpha u_{e'}^\beta$$

$$\Phi_0 = \Phi(\vec{R}_e = \vec{L}) \quad \alpha, \beta \rightarrow x, y, z$$

$$\phi_\alpha(\vec{L}) \equiv \left. \frac{\partial \Phi}{\partial R_e^\alpha} \right|_{\{\vec{R}_e \rightarrow \vec{L}\}} = \left( \frac{\partial \Phi}{\partial u_e^\alpha} \right)_0$$

$$\phi_{\alpha\beta}(\vec{L}, \vec{L}') = \left. \frac{\partial^2 \Phi}{\partial R_e^\alpha \partial R_{e'}^\beta} \right|_{\{\vec{R}_e \rightarrow \vec{L}\}} = \left( \frac{\partial^2 \Phi}{\partial u_e^\alpha \partial u_{e'}^\beta} \right)_0$$

$( )_0$  means that the derivatives are to be evaluated at the equilibrium position configuration.

Energy minimum  $\rightarrow \phi_\alpha = 0$ ,  $\hat{\phi}_{\alpha\beta}(\vec{L}, \vec{L}') \neq 0$ .  
 Eigenvalues associated with the third term positive.

Harmonic theory: neglect higher derivatives of  $\Phi$ . This is a good approximation at low temperatures where the displacements  $\vec{U}_e$  are small. At higher temperatures, one has to take into account higher order terms. This is called harmonic theory because in this approximation, the problem reduces to a set of harmonic oscillators.

Properties of  $\phi_{\alpha\beta}(\vec{L}, \vec{L}')$ :

$$\phi_{\beta\alpha}(\vec{L}', \vec{L}) = \phi_{\alpha\beta}(\vec{L}, \vec{L}')$$

Translational invariance:  $\phi_{\alpha\beta}(\vec{L}, \vec{L}') = \phi_{\alpha\beta}(\vec{L} - \vec{L}')$

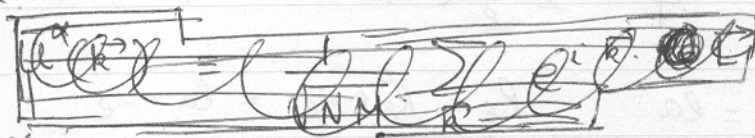
$$\sum_{\vec{L}'} \phi_{\alpha\beta}(\vec{L}, \vec{L}') = 0$$

$\vec{U}$  independent of  $e \Rightarrow$  no change in energy because this corresponds to uniform displacement of all the atoms.

Potential energy:  $\frac{1}{2} \sum_{ee'} \sum_{\alpha\beta} \phi_{\alpha\beta}(\vec{L}, \vec{L}') U_e^\alpha U_{e'}^\beta$

Kinetic energy:  $\frac{1}{2} M \sum_{e,\alpha} (\dot{U}_e^\alpha)^2$

We now have to find the normal modes of this system. It is convenient to go to Fourier space. We define



$$U_e^\alpha = \frac{1}{\sqrt{NM}} \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{L}} U^\alpha(\vec{k})$$

$$U^\alpha(\vec{k}) = \frac{\sqrt{M}}{\sqrt{N}} \sum_e e^{-i\vec{k} \cdot \vec{L}} U_e^\alpha$$

$\vec{k} \rightarrow \vec{k} + \vec{K}$   
does not  
change  $U^\alpha(\vec{k})$

⇒ Restrict  $\vec{k}$  to the first Brillouin zone.

Classical equation of motion:

$$M \ddot{U}_e^\alpha = - \sum_{e',\beta} \phi_{\alpha\beta}(\vec{L}, \vec{L}') U_{e'}^\beta$$

$$\Rightarrow \ddot{U}^\alpha(\vec{k}) = - \sum_{\beta} D_{\alpha\beta}(\vec{k}) U^\beta(\vec{k})$$

where

$$D_{\alpha\beta}(\vec{k}) \equiv \frac{1}{M} \sum_{(\vec{L}-\vec{L}')} \phi_{\alpha\beta}(\vec{L}, \vec{L}') e^{-i\vec{k} \cdot (\vec{L}-\vec{L}')}$$

Dynamical Matrix Hermitian ⇒ Real eigenvalues.  
 $D(\vec{k}) = D(\vec{k} + \vec{K})$

Eigenvalues give the frequencies associated with the normal modes.

Three eigenvectors:  $E_\sigma^\alpha(\vec{k})$   $d \Rightarrow$  component  
 $\sigma \Rightarrow$  eigenvector.

$$D_{\alpha\beta}(\vec{k}) = \frac{1}{M} \sum_{(\vec{l}, \vec{l}')} \Phi_{\alpha\beta}(\vec{l}, \vec{l}') e^{-i\vec{k} \cdot (\vec{l} - \vec{l}')} \quad (5)$$

$$\sum_{\sigma} \epsilon_{\sigma}^{\alpha*} \epsilon_{\sigma}^{\alpha} = \delta_{\alpha\alpha} \quad , \quad \sum_{\sigma} \epsilon_{\sigma}^{\alpha*} \epsilon_{\sigma}^{\beta} = \delta_{\alpha\beta}$$

$$\sum_{\beta} D_{\alpha\beta} \epsilon_{\sigma}^{\beta}(\vec{k}) = \omega^2(\vec{k}, \sigma) \epsilon_{\sigma}^{\alpha}(\vec{k})$$

Eigenvalues have to be positive, otherwise the lattice would be unstable.

The  $\vec{\epsilon}_{\sigma}(\vec{k})$  are the polarization vectors. For a given  $\vec{k}$ , we have three different eigenfrequencies.  $\sigma = 1, 2, 3$ .

Write the vectors  $U^{\alpha}(\vec{k})$  in terms of the eigenvectors of the dynamical matrix:

$$U^{\alpha}(\vec{k}) = \sum_{\sigma} Q_{\sigma}(\vec{k}) \epsilon_{\sigma}^{\alpha}(\vec{k})$$

$$Q_{\sigma}(\vec{k}) = \sum_{\alpha} U^{\alpha}(\vec{k}) \epsilon_{\sigma}^{\alpha*}(\vec{k}) \Rightarrow \text{amplitude component of the vibrations along the polarization direction } \sigma.$$

$$\ddot{Q}_{\sigma}(\vec{k}) = \sum_{\alpha, \beta} \epsilon_{\sigma}^{\alpha*}(\vec{k}) [-D_{\alpha\beta}(\vec{k})] \times \sum_{\sigma'} Q_{\sigma'}(\vec{k}) \epsilon_{\sigma'}^{\beta}(\vec{k})$$

$$= - \sum_{\alpha, \sigma'} \epsilon_{\sigma}^{\alpha*}(\vec{k}) \epsilon_{\sigma'}^{\alpha}(\vec{k}) Q_{\sigma'}(\vec{k}) \omega^2(\vec{k}, \sigma')$$

$$= - \omega^2(\vec{k}, \sigma) Q_{\sigma}(\vec{k})$$

$\Rightarrow$  Hamiltonian

$$H = \frac{1}{2} \sum_{\vec{k}, \sigma} \left[ \dot{Q}_{\sigma}^*(\vec{k}) \dot{Q}_{\sigma}(\vec{k}) + \omega^2(\vec{k}, \sigma) Q_{\sigma}^*(\vec{k}) Q_{\sigma}(\vec{k}) \right]$$

We'll later use this form to second quantize the Hamiltonian.

Frequency  $\omega(\vec{k}, \sigma)$ : phonon dispersion relation.

$\omega(\vec{k}, \sigma) \rightarrow 0$  as  $k \rightarrow 0$ . (Acoustic phonons)

$D_{\alpha\beta}(\vec{k}) \rightarrow 0$  as  $k \rightarrow 0$ .

Another way of seeing this:  $U_e^\alpha$  independent of  $l$   
 $\Rightarrow$  uniform displacement  $\Rightarrow$  zero energy.  
 "Goldstone modes"

Small  $\vec{k}$   $\omega \propto k$ .

$$D_{\alpha\beta}(\vec{k}) = \frac{1}{M} \sum_{(\vec{L}-\vec{L}')} e^{-i\vec{k} \cdot (\vec{L}-\vec{L}')} \phi_{\alpha\beta}(\vec{L}-\vec{L}')$$

$$= \frac{1}{M} \sum_{L, \mu} (-i k_\mu) L_\mu \phi_{\alpha\beta}(\vec{L})$$

$$= \frac{1}{2M} \sum_{L, \mu, \nu} k_\mu k_\nu L_\mu L_\nu \phi_{\alpha\beta}(\vec{L})$$

First term: zero if the interactions are invariant under inversion.

$$\Phi(\vec{R}_1, \dots, \vec{R}_N) = \Phi(-\vec{R}_1, \dots, -\vec{R}_N)$$

$$\Rightarrow \phi_{\alpha\beta}(\vec{L}-\vec{L}') = \phi_{\alpha\beta}(-\vec{L}+\vec{L}') \text{ or } \phi_{\alpha\beta}(\vec{L}) = \phi_{\alpha\beta}(-\vec{L})$$

$$\Rightarrow D_{\alpha\beta}(\vec{k}) = k^2 C_{\alpha\beta}(\hat{k})$$

$$C_{\alpha\beta}(\hat{k}) = -\frac{1}{2M} \sum_{L, \mu, \nu} \hat{k}_\mu \hat{k}_\nu L_\mu L_\nu \phi_{\alpha\beta}(\vec{L})$$

Eigenvalues:  $C^2(\hat{k}, \sigma)$

$$\Rightarrow \omega(\vec{k}, \sigma) = C(\hat{k}, \sigma) k.$$

$\uparrow$  Velocity of sound.

$$* H = \frac{1}{2} \sum_{\vec{r}, \sigma} \left[ \dot{Q}_\sigma^*(\vec{r}) \dot{Q}_\sigma(\vec{r}) + \omega^2(\vec{r}, \sigma) Q_\sigma^*(\vec{r}) Q_\sigma(\vec{r}) \right] \quad (7)$$

## Recap

1 atom/unit cell.

Dynamical matrix  $D_{\alpha\beta}(\vec{k}) = \frac{1}{M} \sum_{\vec{l}} e^{-i\vec{k} \cdot \vec{l}} \phi_{\alpha\beta}(\vec{l}, 0)$

The "force coefficients"  $\phi_{\alpha\beta}$  don't have to be individually positive. Stability requires that the eigenvalues of  $D$  are positive for all  $\vec{k}$ .

Eigenvectors  $\vec{e}_\sigma^\alpha(\vec{k}) \Rightarrow$  unit vectors = Polarization vectors.

$$\sum_{\beta} D_{\alpha\beta}(\vec{k}) e_{\sigma}^{\beta}(\vec{k}) = \omega^2(\vec{k}, \sigma) e_{\sigma}^{\alpha}(\vec{k})$$

$$Q_{\sigma}(\vec{k}) = \sum_{\alpha} e_{\sigma}^{\alpha}(\vec{k}) U^{\alpha}(\vec{k}) \quad \uparrow \text{Phonon frequencies.}$$

Polarization vectors are neither  $\parallel$  nor  $\perp$  to  $\vec{k}$  for  $\vec{k}$  along a general direction in the BZ.

Their directions, of course, depend on the direction of  $\vec{k}$ , and for  $\vec{k}$  along certain symmetry directions, the polarization vectors are actually  $\parallel$  &  $\perp$  to  $\vec{k}$ . One can then speak about transverse

of longitudinal phonons.

Transverse: vibrations  $\perp$  to  $\vec{k}$ . } TA } branches.  
 Longitudinal: vibrations  $\parallel$  to  $\vec{k}$ . } LA }

Small  $k$ :  $D_{\alpha\beta}(\vec{k}) \approx k^2 C_{\alpha\beta}(\vec{k})$

$\omega(\vec{k}, \sigma) = C(\hat{k}, \sigma) k$

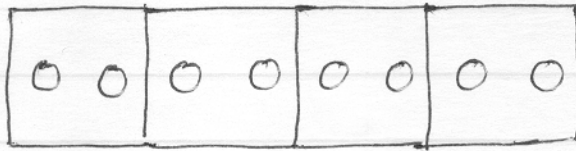
$\uparrow$  velocity of sound. (Related to

the elastic constants).

More than one atom/unit cell

Always 3 branches such that  $\omega(\vec{k}) \rightarrow 0$  as  $k \rightarrow 0$ .  
 (follows from symmetry)

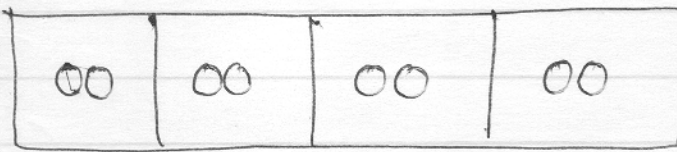
Extra branches such that  $\omega(\vec{k}) \neq 0$  as  $k \rightarrow 0$ .



These branches arise from the relative motion of the different atoms in the same unit cell.

(out of phase within a cell)

$k \rightarrow 0$  means that at every instant of time, the positions of the atoms are the same in each unit cell. But we can have a relative motion of the two atoms in the unit cell, of this motion may be in phase in all the cells. Such vibrations will have some energy, so that  $\omega \neq 0$ .



Frequencies are usually in the infrared range.

$\Rightarrow$  Optical ~~modes~~ phonons. ~~3 acoustic modes~~  
 $r$  atoms/unit cell : 3 : acoustic modes branches  
 3(r-1) : optical modes branches

Dynamical matrix

Displacements:  $\vec{u}_e \rightarrow \vec{u}(\vec{l}, s)$

$s$ : site in the unit cell.

$s = 1, 2 \dots r$

Equilibrium position of the  $s$ th. atom in the  $l$ th. unit cell :  $\vec{l} + \vec{s}$ .

$$D_{\alpha\beta}^{ss'}(\vec{k}) = \frac{1}{(M_s M_{s'})^{1/2}} \sum_{(\vec{l}-\vec{l}')} \phi_{\alpha\beta}(\vec{l} + \vec{s}, \vec{l}' + \vec{s}') e^{-i\vec{k} \cdot (\vec{l} - \vec{l}')}.$$



$$\phi_{\alpha\beta}(\vec{r}, \vec{s}; \vec{r}', \vec{s}') = \left( \frac{\partial^2 \Phi}{\partial U^\alpha(\vec{r}, \vec{s}) \partial U^\beta(\vec{r}', \vec{s}')} \right)_0$$

The dynamical matrix now is a  $(3r \times 3r)$  matrix  
 $\Rightarrow$   $3r$  eigenvalues.  $(D_{\alpha s', \beta s'}(\vec{k}))$

Polarization vectors:  $E_{\sigma}^{\alpha, s}(\vec{k})$        $\alpha: x, y, z$   
 $s: 1, 2, \dots, r$   
 $\sigma: 1, 2, \dots, 3r$

$$\sum_{\beta s'} D_{\alpha\beta}^{ss'}(\vec{k}) E_{\sigma}^{\beta s'}(\vec{k}) = \omega_{\sigma}^2(\vec{k}, \sigma) E_{\sigma}^{\alpha s}(\vec{k})$$

↑ Three of them  $\rightarrow 0$  as  $k \rightarrow 0$   
 $3(r-1)$  are optical branches.

Normal coordinates:

$$\left[ \begin{aligned} \sum_{\alpha, s} E_{\sigma}^{\alpha, s*}(\vec{k}) E_{\sigma'}^{\alpha, s}(\vec{k}) &= \delta_{\sigma\sigma'} \\ \sum_{\sigma} E_{\sigma}^{\alpha, s*}(\vec{k}) E_{\sigma}^{\beta, s'}(\vec{k}) &= \delta_{\alpha\beta} \delta_{ss'} \end{aligned} \right]$$

Normal coordinates

$$U^{\alpha}(\vec{k}, s) = \sum_{\sigma} Q_{\sigma}(\vec{k}) E_{\sigma}^{\alpha, s}(\vec{k})$$

$$\Rightarrow Q_{\sigma}(\vec{k}) = \sum_{\alpha, s} E_{\sigma}^{\alpha, s*}(\vec{k}) U^{\alpha}(\vec{k}, s)$$

$$\text{Hamiltonian: } H = \frac{1}{2} \sum_{\vec{k}, \sigma} \left[ \dot{Q}_{\sigma}(\vec{k}) \dot{Q}_{\sigma}(\vec{k}) + \omega^2(\vec{k}, \sigma) Q_{\sigma}(\vec{k}) Q_{\sigma}(\vec{k}) \right]$$

Calculate  $Q_{\sigma}(\vec{k})$

$$U^{\alpha}(\vec{r}, s) = \frac{1}{\sqrt{NM_s}} \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} U^{\alpha}(\vec{k}, s)$$

$$= \frac{1}{\sqrt{NM_s}} \sum_{\vec{k}, \sigma} Q_{\sigma}(\vec{k}) E_{\sigma}^{\alpha, s}(\vec{k}) e^{i\vec{k} \cdot \vec{r}}$$

Polarization vectors are in general complicated. Symmetry directions  $\Rightarrow$  Transverse of longitudinal TO, LO.

## Quantization

The Hamiltonian written in terms of the normal coordinates is just that of a set of non-interacting harmonic oscillators.

$$\mathcal{L} = T - V$$

Define canonically conjugate variable to  $Q_\sigma(\vec{k})$ :

$$P_\sigma(\vec{k}) = \frac{\partial \mathcal{L}}{\partial \dot{Q}_\sigma(\vec{k})} = \dot{Q}_\sigma^*(\vec{k})$$

$$\Rightarrow \left[ \underbrace{P_\sigma(\vec{k})}_{\sim \dot{Q}_\sigma^*(\vec{k})}, \underbrace{Q_{\sigma'}(\vec{k}')}_{\sim \dot{Q}_{\sigma'}(\vec{k}')} \right] = \frac{\hbar}{i} \delta_{\sigma\sigma'} \delta_{\vec{k}, \vec{k}'}$$

$[Q, Q] = [P, P] = 0.$

Define creation of annihilation operators.

$$a_\sigma(\vec{k}) = (2\omega\hbar)^{-1/2} \left[ \omega Q_\sigma(\vec{k}) + i P_\sigma^*(\vec{k}) \right]$$

$$\omega \leftrightarrow \omega(\vec{k}, \sigma)$$

$$a_\sigma^\dagger(\vec{k}) = (2\omega\hbar)^{-1/2} \left[ \omega Q_\sigma^*(\vec{k}) - i P_\sigma(\vec{k}) \right]$$

It follows that the creation of annihilation operators satisfy the commutation relations.

$$[a_\sigma(\vec{k}), a_{\sigma'}^\dagger(\vec{k}')] = \delta_{\sigma\sigma'} \delta_{\vec{k}, \vec{k}'}$$

$$[a, a] = 0 \quad [a^\dagger, a^\dagger] = 0.$$

$\Rightarrow$  Phonons are Bosons.

$$H = \sum_{\vec{k}, \sigma} \hbar \omega(\vec{k}, \sigma) \left[ a_\sigma^\dagger(\vec{k}) a_\sigma(\vec{k}) + \frac{1}{2} \right]$$

Ground state:  $|0\rangle$

Energy: Zero pt.

$$E_0 = \sum_{\vec{k}, \sigma} \frac{1}{2} \hbar \omega(\vec{k}, \sigma)$$

Excited states: In the harmonic approximation, the phonons ~~do not~~ do not interact with one another. Any ~~eigen~~ excited state can be written as

$$\left[ a_{\sigma_1}^+(\vec{k}_1) \right]^{n_1} \left[ a_{\sigma_2}^+(\vec{k}_2) \right]^{n_2} \dots |0\rangle$$

$$\text{Energy} = E_0 + \hbar \sum_i \left[ n_i \omega(\vec{k}_i, \sigma_i) \right]$$

Occupation number operator  $\hat{n}(\vec{k}_i, \sigma_i) \equiv a_{\sigma_i}^+(\vec{k}_i) a_{\sigma_i}(\vec{k}_i)$

$$\hat{n}(\vec{k}_i, \sigma_i) | \dots \rangle = n(\vec{k}_i, \sigma_i) | \dots \rangle$$

where  $| \dots \rangle$  is a product state of the form given above.

Write the displacements in terms of the phonon creation and destruction operators:

Use the phase convention that  $Q_{-\sigma}^*(\vec{k}) = Q_{\sigma}(\vec{k})$

$$\vec{U}(\vec{k}, s) = \sum_{\sigma} Q_{\sigma}(\vec{k}) \epsilon_{\sigma}^{d,s}(\vec{k})$$

~~Choose~~ above is correct.  $\uparrow$  choose the phase in such a way that the

$$\vec{U}^*(\vec{k}, s) = \vec{U}(-\vec{k}, s)$$

$$\left[ a_{\sigma}(\vec{k}) + a_{\sigma}^+(-\vec{k}) \right] = (2\omega\hbar)^{-1/2} 2\omega Q_{\sigma}(\vec{k})$$

$$\Rightarrow U^{\alpha}(\vec{k}, s) = \frac{1}{\sqrt{NM_s}} \sum_{\vec{k}', \sigma} \left[ \frac{\hbar}{2\omega(\vec{k}', \sigma)} \right]^{1/2} \epsilon_{\sigma}^{d,s}(\vec{k}') e^{i\vec{k}' \cdot \vec{L}} \left[ a_{\sigma}(\vec{k}') + a_{\sigma}^+(-\vec{k}') \right]$$

$$H = \sum_{\vec{k}, \sigma} \hbar \omega(\vec{k}, \sigma) \left[ a_{\vec{k}, \sigma}^{\dagger} a_{\vec{k}, \sigma} + \frac{1}{2} \right]$$

### Thermodynamics

Here, we are dealing with a system of non-interacting bosons. We can <sup>just</sup> write down the various thermodynamic quantities of interest.

Temperature  $T$ .

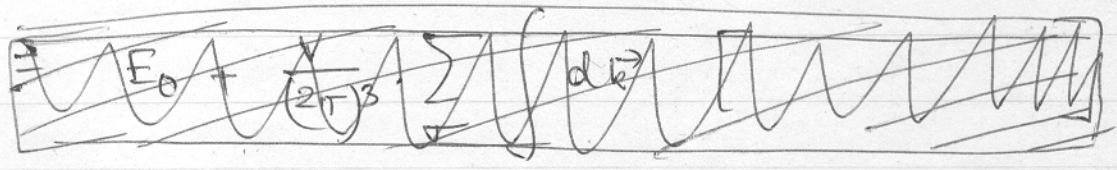
Av. energy  $\langle E \rangle = E_0 + \sum_{\vec{k}, \sigma} \langle n(\vec{k}, \sigma) \rangle \hbar \omega(\vec{k}, \sigma)$

$E_0 = \sum_{\vec{k}, \sigma} \frac{1}{2} \hbar \omega(\vec{k}, \sigma)$

$\langle n(\vec{k}, \sigma) \rangle$ : av. occupation number.

$$= \frac{1}{e^{\beta \hbar \omega(\vec{k}, \sigma)} - 1} \quad \beta = 1/k_B T$$

$$\Rightarrow \langle E \rangle = E_0 + \sum_{\vec{k}, \sigma} \frac{\hbar \omega(\vec{k}, \sigma)}{e^{\beta \hbar \omega(\vec{k}, \sigma)} - 1}$$



$$C_v = \left( \frac{\partial \langle E \rangle}{\partial T} \right)_v = 3N r k_B \int \left( \frac{\hbar \omega}{2 k_B T} \right)^2 \text{Coth}^2(\beta \hbar \omega / 2) g(\omega) d\omega$$

$$= \sum_{\vec{k}, \sigma} \left\{ \frac{1}{2} \hbar \omega(\vec{k}, \sigma) \text{Coth} \left[ \beta \hbar \omega(\vec{k}, \sigma) / 2 \right] \right\}$$

Density of states  $g(\omega) = \frac{1}{3Nr} \sum_{\vec{k}, \sigma} \delta[\omega - \omega(\vec{k}, \sigma)]$

$$= \frac{\hbar}{2} 3Nr \int d\omega \omega g(\omega) \text{Coth} \left[ \beta \hbar \omega / 2 \right]$$

Necessary to know  $g(\omega)$ .

$\omega_L$ : max frequency.

$$\int_0^{\omega_L} d\omega g(\omega) = 1$$

Density of state for the branch  $\sigma$

$$g_{\sigma}(\omega) = \sum_{\vec{k}, \sigma} g_{\sigma}(\omega) = \frac{1}{3Nr} \sum_{\vec{k}, \sigma} \delta(\omega - \omega(\vec{k}, \sigma))$$

$$\Rightarrow \int_{\omega_L^{\sigma}}^{\omega} g_{\sigma}(\omega) d\omega = \frac{1}{3Nr} \sum_{\vec{k}} \delta(\omega - \omega(\vec{k}, \sigma))$$

$$\int_0^{\omega} g_{\sigma}(\omega) d\omega = \frac{1}{3r}$$

General properties of the density of states:

Properties are similar to those obtained before for the density of states in the band theory.

In band theory, we had the <sup>energy</sup> dispersion <sup>spectrum</sup>  $E_n(\vec{k})$   
 $n$ : band index  $1, 2, \dots, \alpha$

Here also, we have the dispersion frequency spectrum  $\omega_{\sigma}(\vec{k})$   $\sigma = 1, 2, \dots, 3r$ .

Within each branch, the frequency is analytic in  $k$ , except at points of high symmetry, where different branches may touch. Density of states, however, has singularities. These are the van Hove singularities studied before.

$$g_{\sigma}(\omega) = \frac{1}{3Nr} \frac{V}{(2\pi)^3} \int d\vec{k} \delta(\omega - \omega(\vec{k}, \sigma))$$

$$= \frac{1}{3r} \frac{\Omega}{(2\pi)^3} \int \frac{dS}{|\nabla_{\vec{k}} \omega(\vec{k}, \sigma)|} \quad \Omega: \text{volume of unit cell.}$$

The surface integral is over the surface  $\omega(\vec{k}, \sigma) = \omega$ .

van Hove singularities ~~where~~ at those points in the BZ where  $\vec{\nabla}_{\vec{k}} \omega(\vec{k}, \sigma) = 0 \Rightarrow$  critical points. (maxima, minima, saddle pt.). Square root singularity.

Analytic critical points

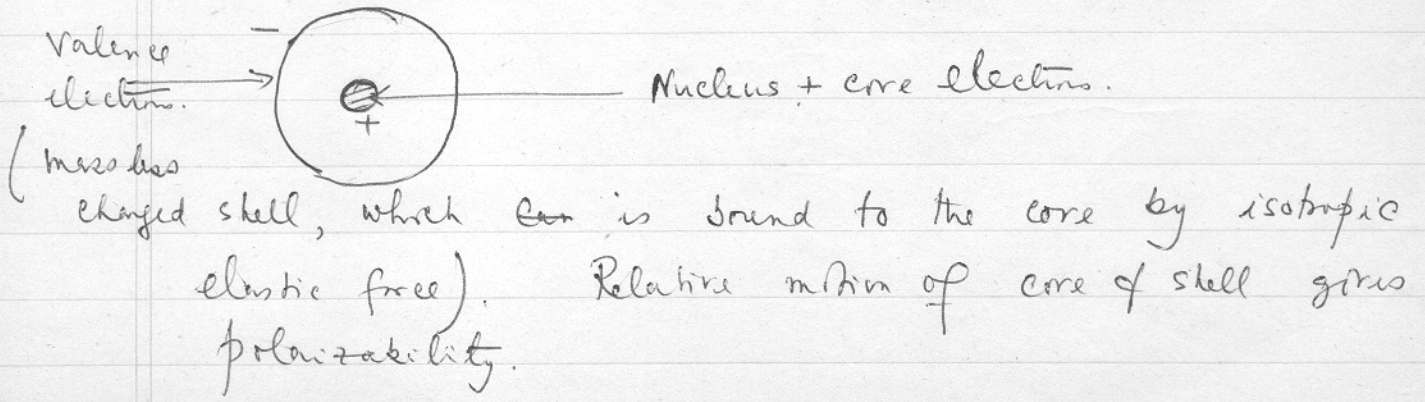
Non-analytic critical points occur at points of degeneracy.

Actual calculation of density of states

Numerical "root sampling method". Diagonalize the secular determinant (Dynamical matrix) at a large number of points in the BZ. Count the number of frequencies in a given interval. Represent the density of states by a histogram. Cannot reproduce the singularities. But the analytic form of the singularity is known in most cases.

The main problem is how to construct the dynamical matrix. This involves a knowledge of the force constants  $\phi_{\alpha\beta}^{ss'}(\vec{l}+\vec{s}; \vec{l}'+\vec{s}')$ . Forces are usually of long-range, non-central, and also, the atoms (ions) cannot usually be represented by rigid spheres. It is necessary to take into account the polarizability of the ions and their compressibility.

↓ Shell model. in which one considers the ion to be composed of two parts.

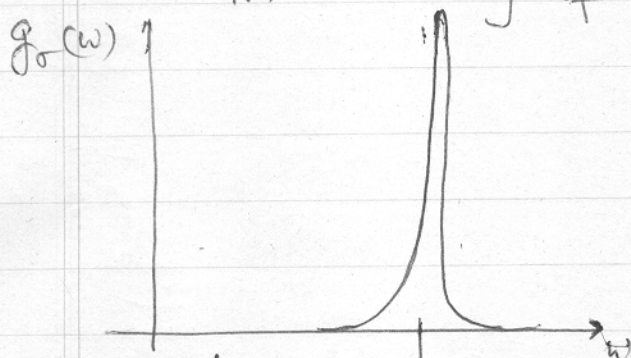


Compressibility is included by letting the ~~st~~ volume of the shell to vary.  $\Rightarrow$  Breathing shell model.

Parameters fixed by elastic constants, vibration spectrum of molecules etc.

Experimentally, we can determine the density of states dispersion relations by inelastic neutron scattering. Agreement is good for semiconductors. In metals, electron-phonon interactions have to be included.

The dispersion relation for optical phonons is usually rather flat.  $\omega$  does not depend strongly on  $\vec{k}$ . Density of states shows a sharp peak.



$\hbar\omega \sim$  infrared region.  
does not play an important role in the thermodynamics at low temperatures.

The acoustic phonons have density of states extending to  $\omega = 0$ , and they determine the thermodynamics at low temperatures. It is very useful to use the Debye approximation for the density of states for the acoustic modes.

### Debye Spectrum

Assumes isotropic continuum behavior throughout the frequency range. In other words, we assume that the frequencies of the 3 acoustic branches are given by

$$\textcircled{2} \quad \omega_t(\vec{k}) = C_t k, \quad \omega_e(\vec{k}) = C_e k.$$

This is not a bad approximation at low T (low k)

$$\omega_p(\vec{k}) = C(\vec{k}, \sigma) k$$

[C depends on the direction of  $\vec{k}$ , polarizations are not simply transverse & longitudinal. Also, this form is certainly not correct at large k.

→ (at long wavelengths, the lattice does look like a) continuum.

Introduce cutoff  $\omega_D$ : # of modes with frequency  $\omega < \omega_D = 3N$ .

Transverse mode:  $\omega < \omega_D$ :  $k < \omega_D/c_t$

Longitudinal mode:  $\omega < \omega_D$ :  $k < \omega_D/c_l$

$$\frac{4\pi}{3} \frac{V}{(2\pi)^3} \left[ 2 \left( \frac{\omega_D}{c_t} \right)^3 + \left( \frac{\omega_D}{c_l} \right)^3 \right] = 3N \Rightarrow \text{determines } \omega_D$$

~~N~~  $N(\omega) = \# \text{ of modes with freq } \leq \omega$

$$= 3N \left( \frac{\omega}{\omega_D} \right)^3 \quad \omega \leq \omega_D$$

$$g(\omega) = \frac{1}{3N} \frac{\partial N(\omega)}{\partial \omega} = \frac{3\omega^2}{\omega_D^3} \quad 0 \leq \omega \leq \omega_D$$

$\omega > \omega_D \Rightarrow$  Debye spectrum.

$\gamma=1$

Debye temperature:  $k_B \Theta_D = \hbar \omega_D$

$$C_V \approx (3Nk_B) \int_0^{\omega_D} \left( \frac{\hbar \omega}{2k_B T} \right)^2 \text{Cosech}^2 \left( \frac{\hbar \omega}{2k_B T} \right) \frac{3\omega^2}{\omega_D^3} d\omega$$

$$x = \frac{\hbar \omega}{k_B T}$$

$$\left( \frac{k_B T}{\hbar \omega_D} \right)^3 3x^2 dx$$

$$= 3Nk_B \int_0^{\Theta_D/T} \frac{x^2}{4} \text{Cosech}^2 \left( \frac{x}{2} \right) \left( \frac{T}{\Theta_D} \right)^3 3x^2 dx$$

$$= \frac{9Nk_B}{4} \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} x^4 \text{Cosech}^2 \left( \frac{x}{2} \right) dx$$

$$4x^2 \frac{4}{3}$$

↑ High T  $\sim \frac{2}{x}$

$C_V \approx 3Nk_B$  (equipartition)



Low T : upper limit  $\rightarrow \infty$

$$C_V = N k_B \frac{12\pi^4}{5} \left(\frac{T}{\Theta_D}\right)^3 \quad ; \quad \text{Debye } T^3 \text{ law.}$$

valid for  $T \ll \Theta_D$ .

Metal: El. sp. heat  $\sim T$   
(dominates at very low T)

Neutron scattering. Debye-Waller Factor

Scattering of slow neutrons provides us with a powerful method to experimentally measure the phonon dispersions. Here, we'll consider only potential scattering i.e. ignore the spin of the neutrons. Magnetic scattering will be considered later on.

Scattering can be either elastic (simple Bragg scattering) or inelastic in which phonons are emitted or absorbed. We consider only the coherent part of the scattering. Incoherent background comes from imperfections, disorder, and incoherent disordered distribution of atomic spins. Coherent part conserves energy and conserves the momentum modulo reciprocal lattice vector.

Differential Scattering cross section  $\frac{d^2\sigma}{d\Omega dE} \sim S(\vec{k}, \omega)$

$$\vec{k} : \text{momentum transfer} = \vec{k}_f - \vec{k}_i \quad \uparrow \frac{1}{2\pi\hbar} \frac{q^2 k_f}{k_i}$$

$$\hbar\omega : \text{energy transfer} = \frac{\hbar^2}{2m_N} (k_f^2 + k_i^2)$$

$S(\vec{k}, \omega)$ : Fourier transform of the density-density correlation fn. Dynamic structure Factor.  
(since we are considering only potential scattering here).

$$S(\vec{k}, \omega) = \int d\vec{r} \int d\vec{r}' \int dt S(\vec{r}, \vec{r}'; t, 0) e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} e^{i\omega t}$$

Scattering length approx:  

$$V(\vec{r}) = \frac{2\pi\hbar^2}{m_N} \sum_{\vec{R}_e} \delta(\vec{r} - \vec{R}_e)$$

## Coherent neutron scattering (spin-independent part).

Thermal neutron sees a potential  $V(\vec{r}) = \frac{2\pi a \hbar^2}{m_N} \times \sum_e \delta(\vec{r} - \vec{R}_e)$

$a$ : scattering length. (can be determined experimentally from the scattering cross-section of a single atom).

$\rho(\vec{r}) = \sum_e \delta(\vec{r} - \vec{R}_e)$  is the density operator.

Differential scattering cross section will involve the density-density correlation  $f_{\vec{r}}$ , or its FT, the dynamic structure factor.

Conservation of energy & momentum  $\Rightarrow$  two parameters

$\vec{k}$ : momentum transfer =  $\vec{k}_i - \vec{k}_f$

$\hbar\omega$ : energy transfer =  $E_i - E_f = \frac{\hbar^2}{2m_N} (-k_f^2 + k_i^2)$   
(non-relativistic)

Differential scattering cross-section

$$\left[ \begin{array}{l} \text{flux/unit solid angle,} \\ \text{with energy bet } E \text{ \& } E+dE. \end{array} \right] \frac{d^2\sigma}{dE d\Omega} = \frac{1}{2\pi\hbar} a^2 \frac{k_f}{k_i} S(\vec{k}, \omega)$$

$\vec{k}$  determines the angle,  $\hbar\omega$  determines the energy.

The  $S$  that comes in here is nearly the same as the dynamic structure factor defined earlier.

$$S(\vec{k}, \omega) = \int d\vec{r} \int d\vec{r}' \int_{-\infty}^{\infty} dt e^{-i\vec{k}\cdot(\vec{r}-\vec{r}')} e^{i\omega t} \times S(\vec{r}, \vec{r}'; t, 0)$$

$$S(\vec{r}, \vec{r}'; t, 0) \equiv \langle \rho(\vec{r}, t) \rho(\vec{r}', 0) \rangle$$

Previously, we had a  $\frac{1}{V}$  in front of the

integrals. Also, we had subtracted off the average value in defining the correlation function  $S(\mathbf{r}, \mathbf{r}'; t_0)$ . Here, we include the av. value, that gives the elastic part of the scattering (the part corresponding to  $\omega = 0$ ). Also, we want to look at finite temperature.  $\langle \dots \rangle$  represents an average w.r.t. a canonical density matrix. At  $T=0$ ,  $S(\mathbf{k}, \omega) = 0$  for  $\omega < 0$ . This means that  $E_f$  can't be greater than  $E_i$ . This makes sense because at  $T=0$ , there are no phonons present, so the neutron can't absorb a phonon & increase its energy.  $\omega > 0$  corresponds to emitting a phonon & this has non-zero weight. At  $T \neq 0$ , both emission & absorption are possible.  $S(\mathbf{k}, \omega)$  can be calculated exactly in the harmonic approximation.

$$S(\mathbf{k}, \omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{cc'} \left\langle e^{-i\mathbf{k} \cdot \vec{R}_c(t)} e^{i\mathbf{k} \cdot \vec{R}_c(0)} \right\rangle$$

↑ Heisenberg operator

Write  $\vec{R}_c(t) = \vec{L} + \vec{u}_c(t)$

We then write  $\vec{u}_c(t)$  in terms of the phonon creation & annihilation operators.

$$\vec{u}_c(t) \sim \left[ \dots \right] (a_{\vec{q}}(\vec{q}, t) + a_{\vec{q}}^{\dagger}(-\vec{q}, t))$$

In the harmonic approximation,

$$a_{\vec{q}}(\vec{q}, t) = e^{-i\omega(\vec{q}, t)t} a_{\vec{q}}(\vec{q})$$

\* Also  $\langle \dots \rangle = \frac{1}{Z} \sum_n e^{-\beta E_n} \langle n | \dots | n \rangle$

$$|n\rangle = \prod_i [a_{\vec{\sigma}_i}^{\dagger}(\vec{k}_i)]^{n(\vec{k}_i, \vec{\sigma}_i)} |0\rangle \rightarrow \frac{1}{\sqrt{n(\vec{k}_i, \vec{\sigma}_i)!}}$$

\*  $\hbar \vec{k} = \hbar \vec{k}_1 + \hbar \vec{k}_2$      $\hbar \omega = \hbar [\omega(\vec{k}_1, \sigma_1) + \omega(\vec{k}_2, \sigma_2)]$  (angle bet.  $\vec{k}_1, \vec{k}_2$  is not fixed) 20

The two operators  $\vec{u}_e(t)$  and  $\vec{u}_e(0)$  don't commute. So we can not write

$$e^{-i\vec{k} \cdot \vec{u}_e(t)} e^{i\vec{k} \cdot \vec{u}_e(0)} = e^{-i\vec{k} \cdot (\vec{u}_e(t) - \vec{u}_e(0))}$$

We have to take into account the commutator which turns out to be a c-number. So we have to calculate an average like

$$\left\langle e^{i \sum_{\vec{k}, \sigma} [\alpha(\vec{k}, \sigma) a_{\vec{k}}(\sigma) + \alpha^*(\vec{k}, \sigma) a_{\vec{k}}^\dagger(\sigma)]} \right\rangle$$

$a, a^\dagger$  with different  $\vec{k}, \sigma$  commute with each other. So, we can reduce the problem to calculating single-phonon averages (non-interacting limit). Algebra is complicated. (Worked out in Callaway).

Result: (only single phonon processes)

$\Omega$ : volume of unit cell.  
1 atom/unit cell  
 $\sigma = 1, 2, 3$

$$S(\vec{k}, \omega) = 2\pi N e^{-2W(\vec{k})} \left\{ \frac{(2\pi)^3}{\Omega} \delta(\omega) \sum_{\vec{k}_e} \delta(\vec{k} - \vec{k}_e) + \frac{k_\alpha k_\beta}{2M} \hbar \sum_{\sigma} \frac{1}{\omega(\vec{k}, \sigma)} \epsilon_{\sigma}^{\alpha}(\vec{k}) \epsilon_{\sigma}^{\beta}(\vec{k}) \right\}$$

Sum over  $\alpha, \beta$ .

$\epsilon$  are real

$$\times \left[ (\langle n(\vec{k}, \sigma) \rangle + 1) \delta(\omega - \omega(\vec{k}, \sigma)) + \langle n(\vec{k}, \sigma) \rangle \delta(\omega + \omega(\vec{k}, \sigma)) \right]$$

$W(\vec{k})$ : Debye-Waller Factor

First term: Elastic scattering Bragg reflections:  $\vec{k} = \vec{k}_e$

Second term: Emission of phonons  $\omega > 0$ .

Third term: Absorption of phonons (only at finite T).

In the harmonic theory, we get  $\delta$ -fn spikes. The effect of anharmonicity is to give a finite-lifetime to phonons  $\Rightarrow$  broadened peaks. Two phonon processes: no sharp peak \*

Phonon dispersion relation can be obtained.

$$* \langle \vec{u}^2 \rangle \neq 0$$

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## Debye-Waller Factor.

It contains some of the effects of the zero pt. and thermal motion of the atoms.  $W$  is positive, so that it has the effect of reducing the probability of coherent processes.  $*$  Its effect becomes clear if we consider the ~~coherent~~ <sup>elastic</sup> part.

$$S_{el}(\vec{k}, \omega) = [2\pi \delta(\omega)] N \frac{(2\pi)^3}{\Omega} \sum_e \delta(\vec{k} - \vec{k}_e) \times e^{-2W(\vec{k})}$$

$$\delta(\vec{k} - \vec{k}_e) \Rightarrow \frac{V}{(2\pi)^3} \delta_{\vec{k}, \vec{k}_e}$$

$$S_{el}(\vec{k}, \omega) = [2\pi \delta(\omega)] N \frac{(2\pi)^3}{\Omega} \frac{V N}{(2\pi)^3} e^{-2W} \\ \sim N^2 e^{-2W(\vec{k})}$$

If all the atoms were fixed at the lattice sites, then we'd get  $S_{el} = N^2 2\pi \delta(\omega)$

Debye-Waller factor thus reflects the effect of the motion of the atoms.

$$W(\vec{k}) = \frac{\Omega \hbar}{16\pi^3 M} k_x k_y \sum_{\sigma} \int_{\Omega} \frac{d\vec{q}}{\omega(\vec{q}, \sigma)} E_{\sigma}^{\alpha}(\vec{q}) E_{\sigma}^{\beta}(\vec{q}) \\ \times \left[ \langle n(\vec{q}, \sigma) \rangle + \frac{1}{2} \right]$$

$$2W(\vec{k}) \sim \langle |\vec{k} \cdot \vec{u}_e|^2 \rangle \quad (\text{independent of } e)$$

The factor  $\frac{1}{2}$  reflects the effect of the zero pt. motion.

$\langle n(\vec{q}, \sigma) \rangle$  represents the thermal motion.

For the acoustic modes,  $\omega(\vec{q}) \sim Cq$  for small  $q$ .

$$\langle n(\vec{q}, \sigma) \rangle = \frac{1}{e^{\beta \hbar \omega(\vec{q}, \sigma)} - 1} \sim \frac{1}{\beta \hbar \omega(\vec{q}, \sigma)} \sim \frac{\alpha k_B T}{q}$$

$$\Rightarrow \int \frac{d\vec{q}}{q} \left[ \frac{\alpha k_B T}{q} + \frac{1}{2} \right]$$

AdM  
appendix

In 3-d, this is finite.

In 2-d, the term coming from the zero pt. motion is finite, but the thermal term diverges as  $q \rightarrow 0$ .

$$\int_{q_0} \frac{q dq}{q^2} \sim \ln\left(\frac{1}{q_0}\right)$$

$$q_0 \sim \frac{1}{L} \Rightarrow W \sim \ln L \sim \ln N.$$

$e^{-2W} \sim N^{-\alpha(k^2)} \Rightarrow$  No crystal in two dimensions in the  $N \rightarrow \infty$  limit, if  $T \neq 0$ .

$S_{el}(k^2)$  still diverges @, but with a smaller power than 2. This means that, if we define an order parameter

$$\textcircled{\otimes} d(k^2) = \frac{1}{N} \sum_e e^{i \mathbf{k} \cdot \mathbf{R}_e},$$

then  $d(k^2) \sim N^{-\alpha(k^2)/2} \rightarrow 0$  as  $N \rightarrow \infty$ . In practice,  $N$  has to be really large for  $d(k^2)$  to vanish, and we do have 2-d crystals. Algebraic decay of <sup>order</sup> correlation in 2-D.

The absence of crystalline order can be proved more rigorously (without invoking the harmonic approximation). But the physics is the same. We have three ~~mass~~ soft acoustic phonons (Goldstone modes) whose energy  $\rightarrow 0$  as  $k \rightarrow 0$ . Because of their low energy, they can be excited rather easily if  $T \neq 0$ . In 2-d, the fluctuations coming from them destroy the order.

In 1-d, the zero pt. motion is enough to destroy LRO. So, we don't have a crystal even at  $T=0$ . Effect of dimensionality is contained in the amount of phase space available for these excitations.

$d$ -dimension  $\rightarrow k^{d-1} \rightarrow$  decreases as  $d$  is increased.

# Anharmonic Effects in Lattice Dynamics.

Harmonic theory works well at low T. At higher T, it is no longer adequate. We need to consider the higher order terms like

$$\left( \frac{\partial^3 \Phi}{\partial u_e^\alpha \partial u_{e'}^\beta \partial u_{e''}^\gamma} \right), \left( \frac{\partial^4 \Phi}{\partial u_e^\alpha \partial u_m^\beta \partial u_n^\gamma \partial u_p^\delta} \right) \text{ etc.}$$

$$\Phi = \Phi_0 + \Phi_2 + \Phi_3 + \Phi_4 + \dots$$

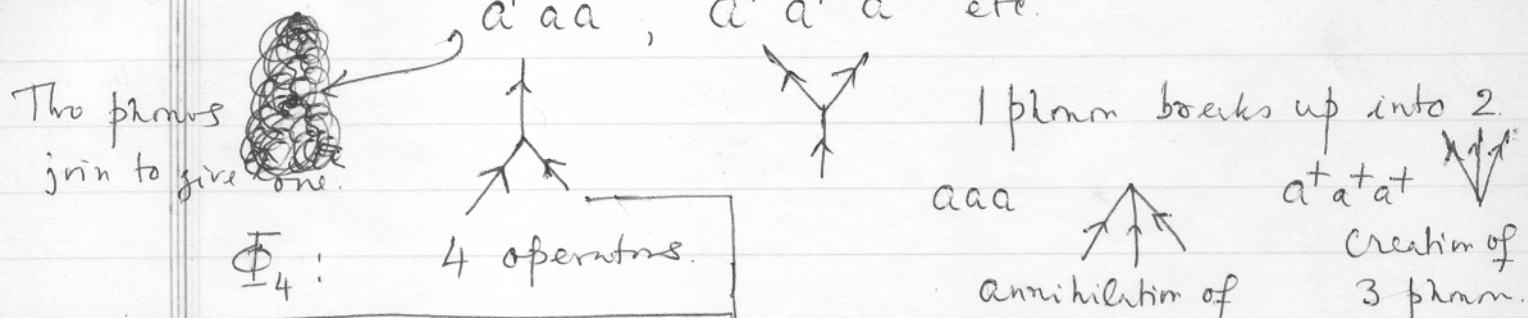
↑ contains 3 U's

The necessity to include these terms show up as a temperature dependence of the phonon frequency, finite-phonon lifetime etc. Also, thermal properties such as thermal expansion can not be explained in the harmonic approximation. (Also, thermal conductivity)

Basic approach: Write  $\Phi_3, \Phi_4$  etc. in terms of the phonon creation & annihilation operators  $a, a^\dagger$ .

$$\Phi_3: u u u \rightarrow u \sim a(k) + a^\dagger(-k)$$

$$a^\dagger a a, a^\dagger a^\dagger a \text{ etc.}$$



$\Phi_4$ : 4 operators.

$$H = H_0 + V_3 + V_4 + \dots \quad H_0 = \sum_{k, \sigma} \hbar \omega(k, \sigma) \times [a_{k, \sigma}^\dagger a_{k, \sigma} + \frac{1}{2}]$$

We'll treat these terms in perturbation theory. The formalism will be similar to that used for electrons. [There are, however, some important differences]. We'll define a one-phonon GF, calculate its self-energy, <sup>then see where the pole of the GF occurs</sup> The effect of the interaction will show up in ~~modifying the~~ <sup>both the real & imaginary parts of</sup> both the real & imaginary parts of the pole.

Also, phenomena like thermal expansion, which can't be explained in the harmonic theory, will be explained by including ~~real & imaginary parts of the self energy~~ anharmonicity. ~~the imaginary parts of the self energy.~~ The real part

Changing the ~~real part~~ real part of the pole (which means that the frequency will be changed) and adding an imaginary part to the pole, which means that the phonons will have a finite lifetime.\* The formalism is similar to that for electrons, but with some major differences.

- 1) Phonons are ~~fermi~~ bosons, so some of the rules have to be changed.
- 2) No. of phonons is not conserved. This will lead to certain diagrams not present in the electron case
- 3) Calculation has to be done at finite T.

# of phonons determined by thermal equilibrium.  $\Rightarrow$  chemical potential  $\mu=0$ .

Anharmonic terms

$$V_3 = \frac{1}{3!} \sum_{\ell, m, n} \phi_{\ell m n}(\vec{\ell}, \vec{m}, \vec{n}) u_{\ell}^{\alpha} u_{m}^{\beta} u_{n}^{\gamma} \quad \left. \begin{array}{l} 1 \text{ atm / cell.} \\ \phi_{\alpha\beta\gamma} = \frac{\partial^3 \Phi}{\partial R_{\ell}^{\alpha} \partial R_m^{\beta} \partial R_n^{\gamma}} \Big|_{R_{\ell}^{\alpha} = R_m^{\beta} = R_n^{\gamma}} \end{array} \right\}$$

$$u_{\ell}^{\alpha} = \frac{1}{\sqrt{NM}} \sum_{\vec{k}, \sigma} e^{i\vec{k} \cdot \vec{\ell}} \epsilon_{+}^{\alpha}(\vec{k}) \left[ \frac{\hbar}{2W(\vec{k}, \sigma)} \right]^{1/2} (q_{\sigma}(\vec{k}))$$

$$q_{\sigma}(\vec{k}) = a_{\sigma}(\vec{k}) + a_{\sigma}^{\dagger}(-\vec{k})$$

$$\Rightarrow V_3 = \sum_{\substack{\vec{k}_1, \vec{k}_2, \vec{k}_3 \\ \sigma_1, \sigma_2, \sigma_3}} V^{(3)}(\vec{k}_1, \vec{k}_2, \vec{k}_3; \sigma_1, \sigma_2, \sigma_3) q_{\sigma_1}(\vec{k}_1) q_{\sigma_2}(\vec{k}_2) q_{\sigma_3}(\vec{k}_3)$$

$$V^{(3)} \sim \sum_{\ell, m, n} \phi(\vec{\ell}, \vec{m}, \vec{n}) e^{i(\vec{k}_1 \cdot \vec{\ell} + \vec{k}_2 \cdot \vec{m} + \vec{k}_3 \cdot \vec{n})}$$

$\left. \begin{array}{l} \vec{\ell} \rightarrow \vec{\ell} + \vec{p} \\ \vec{m} \rightarrow \vec{m} + \vec{p} \\ \vec{n} \rightarrow \vec{n} + \vec{p} \end{array} \right\}$  does not change  $\phi$ , but picks up a factor  $e^{i(\vec{k}_1 + \vec{k}_2 + \vec{k}_3) \cdot \vec{p}}$   
 Sum over  $\vec{p} \Rightarrow \vec{k}_1 + \vec{k}_2 + \vec{k}_3 = \vec{K}$



⇒ crystal momentum is conserved modulo reciprocal lattice vectors.

$\vec{K} = 0$ : normal process.

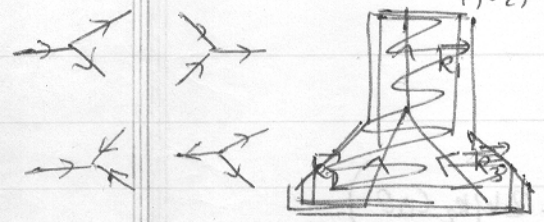
$\vec{K} \neq 0$ : Umklapp processes. (Normal scattering + Bragg reflection)

From the definition of  ~~$V_3$~~   $q_{\sigma}(\vec{k})$ , we see that

$$q_{\sigma}^+(\vec{k}) = a_{\sigma}^+(\vec{k}) + a_{\sigma}(-\vec{k}) = q_{\sigma}(-\vec{k})$$

$$V_3 = \sum_{\substack{k_1, k_2, k_3 \\ \sigma_1, \sigma_2, \sigma_3}} V^{(3)}(-\vec{k}_1, \vec{k}_2, \vec{k}_3; \sigma_1, \sigma_2, \sigma_3) q_{\sigma_1}^+(\vec{k}_1) q_{\sigma_2}(\vec{k}_2) q_{\sigma_3}(\vec{k}_3)$$

$\vec{k}_2 + \vec{k}_3 - \vec{k}_1 = \vec{K}$



Writing  $V_3$  &  $V_4$  in terms of the  $q$ 's is just a matter of convention.

$$V_4 = \sum_{\substack{k_1, k_2, k_3, k_4 \\ \sigma_1, \dots, \sigma_4}} V^{(4)}(\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4; \sigma_1, \sigma_2, \sigma_3, \sigma_4) q_{\sigma_1}(\vec{k}_1) q_{\sigma_2}(\vec{k}_2) q_{\sigma_3}(\vec{k}_3) q_{\sigma_4}(\vec{k}_4)$$

$$\vec{k}_1 + \vec{k}_2 + \vec{k}_3 + \vec{k}_4 = \vec{K}$$

Here, we have assumed that the crystal is under no external stress, such as pressure or stretching. This assumption is necessary because here, we have calculated the anharmonic terms by from the derivatives of the potential, evaluated at the "free" equilibrium configuration. In other words, we have assumed that the lattice vectors  $\vec{L}, \vec{M}, \vec{N}$  etc. are those corresponding to the free crystal under no stress. If the crystal is under stress, then

the equilibrium positions of the atoms change. This does not change the phonon Hamiltonian in the harmonic approximation. But it does change the anharmonic terms. These terms are the so-called strain stress Hamiltonian. We'll consider them later on when we talk about thermal expansion. But for now, we assume that there is no external stress.

One-phonon Green's function

Since the anharmonic terms involve the operators  $q_\sigma(\vec{k})$ , rather than  $a_\sigma(\vec{k})$ , it is convenient to define the phonon GF in terms of these operators.

$$q_\sigma(\vec{k}) = a_\sigma(\vec{k}) + a_\sigma^\dagger(-\vec{k}) = \sqrt{\frac{2M}{\hbar}} Q_\sigma(\vec{k})$$

↑  
"Normal co-ordinates"

↓  
Particular mode, not phonons.

Bosons, Finite Temperature

$$G(\vec{k}, \sigma; \vec{k}', \sigma'; t) = \langle P [q_\sigma(\vec{k}, t), q_{\sigma'}^\dagger(\vec{k}', 0)] \rangle$$

P: Dyson chronological operator. ↑ Heisenberg operators.

$$P [q_\sigma(\vec{k}, t), q_{\sigma'}^\dagger(\vec{k}', 0)] = \begin{cases} q_\sigma(\vec{k}, t) q_{\sigma'}^\dagger(\vec{k}', 0) & t > 0 \\ q_{\sigma'}^\dagger(\vec{k}', 0) q_\sigma(\vec{k}, t) & t < 0 \end{cases}$$

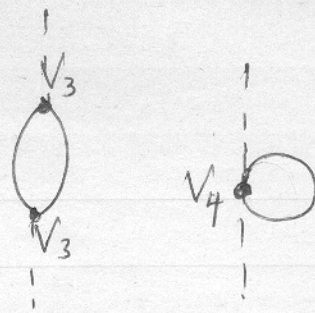
$$q_\sigma(\vec{k}, t) = e^{+i\hbar t/\hbar} q_\sigma(\vec{k}, 0) e^{-i\hbar t/\hbar}$$

$$\langle \dots \rangle = \frac{1}{Z} \sum_n e^{-\beta E_n} \langle n | \dots | n \rangle$$

$$Z = \sum_n \langle n | e^{-\beta H} | n \rangle = \sum_n e^{-\beta E_n}$$

|n>: eigenstates of the system

Lowest order diagrams:



Results can be compared with neutron scattering expt. This is one way of estimating the anharmonic contribution.

Alternative method: Molecular Dynamics

Thermal Expansion

Coefficient of thermal expansion is zero in the harmonic theory. It is necessary to include anharmonic effects in order to obtain a temperature dependence of the lattice constant. The reason is straightforward. We know that if we change the lattice constant by a factor  $\lambda$  ( $a \rightarrow \lambda a$ ,  $\lambda = 1 + \epsilon$ ,  $\epsilon \ll 1$ ), then the phonon frequencies don't change in the harmonic approximation. Thus, the dynamic part of the free energy does not depend upon  $\epsilon$ . The equilibrium value of  $\epsilon$  is determined by

$$\frac{\partial F}{\partial \epsilon} = 0.$$

The static strain energy  $\sim \epsilon^2$

$\Rightarrow \epsilon = 0$  at all  $T$ . If we include anharmonic terms, the phonon frequencies change as  $\epsilon$  is changed. This gives an  $\epsilon$  which depends upon the temperature, and thus gives a finite coefficient of thermal expansion.