

# Lattice vibrations, phonons, and the speed of sound

Assume Hamiltonian of ionic degrees of freedom looks like

$$H = \sum_{R_i} \frac{\vec{P}_i^2}{2M} + U_{\text{ion}}(\{\vec{R}_i\})$$

kinetic                      potential due to ion-ion interactions

ions at positions  $\vec{R}_i$ , momentum  $\vec{P}_i$ , mass  $M$

$$\text{Write } \vec{R}_i = \vec{R}_i^0 + \vec{u}_i$$

↑                      ↖

position in periodic BL                      small displacement due to elastic distortions

If  $\vec{u}_i$  is small, expand  $U_{\text{ion}}$  about the BL positions  $\vec{R}_i^0$ . Since the positions  $\vec{R}_i^0$  are assumed to be positions of mechanical equilibrium, the linear term in the expansion must vanish, and the quadratic term is the leading order term.

$$U_{\text{ion}}(\{\vec{u}_i\}) = U_{\text{ion}}^0 + \frac{1}{2} \sum_{i\alpha} \sum_{j\beta} u_{i\alpha} D_{ij}^{\alpha\beta} u_{j\beta}$$

$i, j$  label BL sites

$\alpha, \beta$  label components  $x, y, z$  of the displacement

$$D_{ij}^{\alpha\beta} = \left. \frac{\partial^2 U_{\text{ion}}}{\partial u_{i\alpha} \partial u_{j\beta}} \right|_{\{\vec{R}_i^0\}}$$

is the dynamical matrix

The classical equations of motion for the ions are then

$$M \ddot{\vec{u}}_i = - \frac{\partial U_{ion}}{\partial \vec{u}_i} \Rightarrow M \ddot{u}_{i\alpha} = - \sum_{j\beta} D_{ij}^{\alpha\beta} u_{j\beta}$$

Now by translational invariance of the Bravais lattice  $D_{ij}^{\alpha\beta}$  depends only on  $\vec{R}_i - \vec{R}_j$ .

We can define the Fourier transforms

$$\vec{u}_i(t) = \int_{\vec{q} \in 1^{st} BZ} d^3q \int_{-\infty}^{\infty} d\omega e^{i\vec{q} \cdot \vec{R}_i} e^{-i\omega t} \vec{u}(\vec{q}, \omega)$$

$$D_{ij}^{\alpha\beta} = \int_{\vec{q} \in 1^{st} BZ} d^3q e^{i\vec{q} \cdot (\vec{R}_i - \vec{R}_j)} D^{\alpha\beta}(\vec{q})$$

Note: in defining Fourier transform of a function that exists only on the discrete sites of a B.L., the only wave vectors we need to consider of those  $\vec{q}$  in the 1<sup>st</sup> BZ. This is because any wave vector  $\vec{k}$  can always be written as  $\vec{k} = \vec{q} + \vec{K}$  with  $\vec{K}$  a unique R.L. vector and  $\vec{q}$  in the 1<sup>st</sup> BZ. Then the plane wave factor would be

$$e^{i\vec{k} \cdot \vec{R}_i} = e^{i(\vec{q} + \vec{K}) \cdot \vec{R}_i} = e^{i\vec{q} \cdot \vec{R}_i} \quad \text{since } e^{i\vec{K} \cdot \vec{R}_i} = 1$$

so we still only get oscillations at  $\vec{q}$  in 1<sup>st</sup> BZ

substitute these into the equation of motion

$$\int_{\vec{q} \in 1^{st} BZ} d^3q \int_{-\infty}^{\infty} d\omega e^{i\vec{q} \cdot \vec{R}_i} e^{-i\omega t} (-\omega^2) M \vec{u}(\vec{q}, \omega)$$

$$= - \int_{\vec{q} \in 1^{st} BZ} d^3q \int_{\vec{q}' \in 1^{st} BZ} d^3q' \int_{-\infty}^{\infty} d\omega \sum_j e^{i\vec{q} \cdot (\vec{R}_i - \vec{R}_j)} e^{i\vec{q}' \cdot \vec{R}_j} e^{-i\omega t} \overleftrightarrow{D}(\vec{q}) \cdot \vec{u}(\vec{q}, \omega)$$

$\uparrow$   
 matrix product  
 over coordinates

Do the ~~integral~~ summation

$$\sum_j e^{i(\vec{q}' - \vec{q}) \cdot \vec{R}_j} = \delta(\vec{q} - \vec{q}')$$

Follows since  $\{\vec{R}_j + \vec{R}_0\} = \{\vec{R}_j\}$  since BL is closed under translation by any BL vector  $\vec{R}_0$

$$\Rightarrow \sum_{\vec{R}_j} e^{i(\vec{q}' - \vec{q}) \cdot \vec{R}_j} = \sum_{\vec{R}_j} e^{i(\vec{q}' - \vec{q}) \cdot (\vec{R}_j + \vec{R}_0)}$$

$$= e^{i(\vec{q}' - \vec{q}) \cdot \vec{R}_0} \sum_{\vec{R}_j} e^{i(\vec{q}' - \vec{q}) \cdot \vec{R}_j}$$

$$\Rightarrow e^{i(\vec{q}' - \vec{q}) \cdot \vec{R}_0} = 1 \text{ for any } \vec{R}_0 \text{ in BL}$$

$$\Rightarrow \vec{q}' - \vec{q} = \vec{K} \text{ in R.L.}$$

But since  $\vec{q}, \vec{q}'$  both in 1<sup>st</sup> BZ  $\Rightarrow \vec{K} = 0$   
 and

$$\vec{q} = \vec{q}' \text{ or the sum must vanish}$$

$$\int_{1st\ BZ} d^3q \int d\omega e^{i(\vec{q} \cdot \vec{R}_i - \omega t)} (-\omega^2) M \vec{u}(\vec{q}, \omega)$$

$$= - \int_{1st\ BZ} d^3q d\omega e^{i(\vec{q} \cdot \vec{R}_i - \omega t)} \overleftrightarrow{D}(\vec{q}) \cdot \vec{u}(\vec{q}, \omega)$$

equating Fourier amplitudes to get

$$+\omega^2 M \vec{u}(\vec{q}, \omega) = \overleftrightarrow{D}(\vec{q}) \cdot \vec{u}(\vec{q}, \omega)$$

If the eigenvectors and eigenvalues of  $\overleftrightarrow{D}(\vec{q})$  are  $\vec{E}_1(\vec{q}), \vec{E}_2(\vec{q}), \vec{E}_3(\vec{q})$  and  $\lambda_1(\vec{q}), \lambda_2(\vec{q}), \lambda_3(\vec{q})$

Then

$$+\omega^2 M_s = \lambda_s(\vec{q}) \quad s=1, 2, 3$$

$$\omega_s = \sqrt{\frac{\lambda_s(\vec{q})}{M}}$$

dispersion relation for elastic vibrations at wave vector  $\vec{q}$ , polarization  $\vec{E}_s(\vec{q})$

We expect that in the long wave length limit we can expand

$$\overleftrightarrow{D}(\vec{q}) = \sum_i e^{-i\vec{q} \cdot \vec{R}_i} \overleftrightarrow{D}(\vec{R}_i)$$

$$\approx \sum_i \left\{ 1 - i\vec{q} \cdot \vec{R}_i - \frac{1}{2}(\vec{q} \cdot \vec{R}_i)^2 \overleftrightarrow{D}(\vec{R}) \right\}$$

$\sum_i \vec{D}(\vec{R}_i) = 0$  because if all  $\vec{u}_i = \vec{u}_0$   
 a uniform displacement, then  
 net force on con.  $\vec{z}$  must vanish

$\sum_i \vec{R}_i \vec{D}(\vec{R}_i) = 0$  by inversion symmetry  $\vec{R}_i \rightarrow -\vec{R}_i$   
 $\vec{D}(\vec{R}_i) = \vec{D}(-\vec{R}_i)$

so

$$\vec{D}(\vec{q}) \approx -\frac{q^2}{2} \sum_{\vec{R}_i} (\hat{q} \cdot \vec{R}_i)^2 \vec{D}(\vec{R}_i)$$

$\Rightarrow \vec{D}(\vec{q}) \propto q^2$  ↑ we assume this  
sum converges

so  $\lambda_s(\vec{q}) \propto q^2$  or  $\lambda_s(\vec{q}) = \overset{A_s}{\cancel{A_s}} q^2$   
 for small  $\vec{q}$

$\Rightarrow \omega_s = \sqrt{\frac{A_s}{M}} |\vec{q}|$  with

$c_s = \sqrt{A_s/M}$  the speed of sound  
~~for~~ for polarization  $s$ .

$\omega_s = c_s q$  for small  $\vec{q}$

Also at small  $\vec{q}$  we expect the spatial orientation  
 of the B.L. to get "averaged over" and so the  
 only directions of  $\vec{E}$  and  $\perp$  to  $\vec{q}$ . We then  
 expect the polarization vectors to become as  $q \rightarrow 0$

$\vec{E}_1(\vec{q}) = \hat{q}$  longitudinal sound mode, speed  $c_l$   
 $\left. \begin{matrix} \vec{E}_2(\vec{q}) \\ \vec{E}_3(\vec{q}) \end{matrix} \right\} \perp \hat{q}$  transverse sound modes, speed  $c_{t1}, c_{t2}$

When we treat the elastic vibrations of the solid quantum mechanically, these "normal modes" of elastic vibration, i.e. the independent modes of harmonic oscillation, get quantized just like harmonic oscillators. Each degree of excitation of a given mode of oscillation is called a "phonon".

For example, if the vibration at wave vector  $\vec{q}$ , polarization  $s$  has energy

$$\hbar \omega_s(\vec{q}) \left( n + \frac{1}{2} \right)$$

We say there are  $n$  phonons of wave vector  $\vec{q}$  polarization  $s$ .

As with excitations of any harmonic oscillator, phonons behave as bosons, and ~~are not~~ their number is not conserved (chemical potential  $\mu_{\text{phonon}} = 0$ ).

Electrons can scatter by absorbing or emitting phonons, while conserving energy and crystal momentum, i.e. for absorption

$$E(\vec{k}_f) = E(\vec{k}_i) + \hbar \omega_s(\vec{q})$$

$$\vec{k}_f = \vec{k}_i + \vec{q} + \vec{K}$$

$\vec{k}_f$   $\uparrow$  final electron crystal momentum  
 $\vec{k}_i$   $\uparrow$  initial electron crystal momentum  
 $\vec{q}$   $\uparrow$  phonon crystal momentum  
 $\vec{K}$   $\uparrow$  Br. vector

But: Suppose we consider the conduction electrons as frozen, <sup>and uniform</sup> and the ion-ion interaction therefore is Coulomb.

In our discussion of plasma oscillations we saw that the only longitudinal mode of oscillation of a Coulomb interacting set of charges is, as  $q \rightarrow 0$ , at the plasma frequency. For ions of mass  $M$  and density  $n_{ion}$ , this would be

$$\Omega_p = \sqrt{\frac{4\pi n_{ion} Q_{ion}^2}{M}} \quad Q_{ion} = \text{charge of ion}$$

This does not agree with the expectation above that the frequency of oscillation for a longitudinally polarized elastic vibration should be,  $\omega_s = c_s q$ , vanishing as  $q \rightarrow 0$ !

Why? Because if interaction between ions is pure Coulomb, then the sum  $\sum_{R_i} (\hat{q} \cdot \vec{R}_i)^2 \frac{1}{R_i}$  does not converge, as we had assumed in the previous discussion!

But we know from experiment and experience that longitudinal (acoustic) sound modes do exist with  $\omega_s = c_s q$  linear dispersion relation! What is the resolution of this paradox?

The answer is screening! We make the adiabatic approximation and assume that conduction electrons move so much faster than ions that they always relax to their minimum energy configuration corresponding to the instantaneous positions of the ions, as the ions move. The electrons will then screen the Coulombic ion-ion interaction and make it short ranged. The sum  $\sum_i (\hat{q} \cdot \vec{R}_i)^2 \vec{D}(\vec{R}_i)$  now converges and we get the longitudinal elastic modes with  $\omega_q = c_l q$ . Moreover we can use this argument to estimate the speed of sound  $c_l$ .

The phonon freq for polarization  $s$ , wavevector  $\vec{q}$  was determined by

$$\omega^2 M \vec{E}_s = \overleftrightarrow{D}(\vec{q}) \cdot \vec{E}_s$$

If we let  $\overleftrightarrow{D}^0(q)$  be the dynamical matrix due to bare Coulombic ion-ion interactions, then we expect for the longitudinal mode that  $\omega_q = \Omega_p$ , i.e.

$$\Omega_p^2 M \vec{E}_l = \overleftrightarrow{D}^0(q) \cdot \vec{E}_l$$

Now a longitudinal ionic vibration of wave vector  $\vec{q}$  sets up a charge density of wave vector  $\vec{q}$ , which sets up an electric field of wave vector  $\vec{q}$ . The electrons screen this field by a factor  $\frac{1}{\epsilon(\vec{q})}$  where  $\epsilon(\vec{q})$  is the electron dielectric function.

Since  $\vec{D}(\vec{q})$ , the dynamical matrix, is  $\propto$  to the ion-ion forces (effective ion-ion spring constant in the harmonic approx) we expect that these forces will get screened by the electrons and so the screened dynamical matrix  $\vec{D}$  is related to the bare  $\vec{D}^0$  by

$$\vec{D}(\vec{q}) = \frac{\vec{D}^0(\vec{q})}{\epsilon(\vec{q})}$$

Hence we expect that

$$\Omega_p^2 M \vec{E}_e = \vec{D}^0(\vec{q}) \cdot \vec{E}_e \Rightarrow \frac{\Omega_p^2}{\epsilon(\vec{q})} M \vec{E}_e = \frac{\vec{D}^0(\vec{q})}{\epsilon(\vec{q})} \cdot \vec{E}_e$$

$$\Rightarrow \frac{\Omega_p^2}{\epsilon(\vec{q})} M \vec{E}_e = \vec{D}(\vec{q}) \cdot \vec{E}_e$$

so the freq of oscillation is now

$$\omega_e^2(\vec{q}) = \frac{\Omega_p^2}{\epsilon(\vec{q})}$$

For small  $\vec{q}$  we can use the Thomas-Fermi approx

$$\epsilon(q) \approx 1 + k_0^2/q^2 \quad \text{where } k_0^2 = 4\pi e^2 g(\epsilon_F)$$

So

$$\omega_e^2(q) = \frac{\Omega_p^2}{1 + k_0^2/q^2} = \frac{\Omega_p^2 q^2}{k_0^2 + q^2} \approx \frac{\Omega_p^2}{k_0^2} q^2$$

for small  $q \ll k_0$

$$\omega_e(q) = \left( \frac{\Omega_p}{k_0} \right) q \Rightarrow \text{speed of sound is}$$

$$c_s = \frac{\Omega_p}{k_0}$$

$$\Rightarrow c_s^2 = \frac{4\pi n_{\text{ion}} Q_{\text{ion}}^2}{M} \frac{1}{4\pi e^2 g(\epsilon_F)}$$

if  $n$  is conduction electron density and  $Z$  the valence number of conduction electrons, then

$$n_{\text{ion}} = \frac{n}{Z}, \quad Q_{\text{ion}} = Ze$$

$$c_s^2 = \frac{n Z}{M g(\epsilon_F)}$$

In the free electron approx,  $g(\epsilon_F) = \frac{3}{2} \frac{M}{\epsilon_F}$

$$\text{So } c_s^2 = \frac{n Z}{M \left( \frac{3}{2} \frac{M}{\epsilon_F} \right)} = \frac{2 Z \epsilon_F}{3 M} = \frac{2 Z}{3 M} \frac{1}{2} m v_F^2$$

$$c_s^2 = \frac{Z m}{3 M} v_F^2$$

$$c_s = \sqrt{\frac{Z m}{3 M}} v_F$$

For ions ( $\frac{m_{elec}}{m_{proton}} \sim \frac{1}{2000}$ ) we expect

$$\frac{c_e}{v_F} = \sqrt{\frac{Z}{3} \frac{m}{M}} \sim 0.01$$

Our result that  $c_e \approx 0.01 v_F$  is consistent with the adiabatic approx that electrons move with speeds ( $v_F$ ) much greater than the ions ( $c_e$ )

The above result is known as the Bohm-Staver relation

It gives results in correct order of magnitude agreement with experiment. For typical metals

$$v_F \sim 10^8 \text{ cm/sec}$$

$$c_e \sim 10^6 \text{ cm/sec}$$