But: Suppose we consider the conduction electrons as frozen and uniform, 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 $\vec{q} \to 0$, at the plasma frequency. For ions of mass M and density n_{ion}, this would be

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

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

Why? Because if interaction between ions is bare Coulomb, then the sum $\sum_{R_i} (\hat{q}\cdot\vec{R}_i)^2 \overleftrightarrow{D}(\vec{R}_i)$ 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 $\omega_\ell = c_\ell q$ linear dispersion relation! What is the resolution of this paradox?

also called Born-Oppenheimer approx

The answer is screening! We make the <u>adiabatic approximation</u> 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 $\sum_i (\hat{q}\cdot\vec{R}_i)^2 \overleftrightarrow{\mathbb{D}}(R_i)$ now converges and we get the longitudinal elastic modes with $\omega_\ell = c_\ell q$. 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

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

If we let $\overleftrightarrow{\mathbb{D}}^0(q)$ be the dynamical matrix due to bare Coulombic ion-ion interactions, the we expect for the longitudinal mode that $\omega_\ell = \Omega_p$, ie

$$\Omega_p^2 M \vec{\epsilon}_\ell = \overleftrightarrow{\mathbb{D}}^0(q)\cdot\vec{\epsilon}_\ell$$

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 $\frac{1}{\varepsilon(q)}$ where $\varepsilon(q)$ is the electron dielectric function.

Since $\overleftrightarrow{D}(q)$, 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 $\overleftrightarrow{D}$ is related to the bare $\overleftrightarrow{D}^{\circ}$ by

$$\overleftrightarrow{D}(\vec{q}) = \frac{\overleftrightarrow{D}^{\circ}(\vec{q})}{\varepsilon(\vec{q})}$$

Hence we expect that

$$\Omega_p^2 M \vec{\epsilon}_\ell = \overleftrightarrow{D}^{\circ}(\vec{q})\cdot\vec{\epsilon}_\ell \Rightarrow \frac{\Omega_p^2}{\varepsilon(q)} M \vec{\epsilon}_\ell = \frac{\overleftrightarrow{D}^{\circ}(q)}{\varepsilon(q)}\cdot\vec{\epsilon}_\ell$$

$$\Rightarrow \frac{\Omega_p^2}{\varepsilon(q)} M \vec{\epsilon}_\ell = \overleftrightarrow{D}(q)\cdot\vec{\epsilon}_\ell$$

so the freq of oscillation is now

$$\boxed{\omega_\ell^2(\vec{q}) = \frac{\Omega_p^2}{\varepsilon(q)}}$$

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

$$\varepsilon(q) \simeq 1 + k_0^2/q^2 \quad \text{where } k_0^2 = 4\pi e^2 g(\varepsilon_F)$$

So

$$\omega_\ell^2(q) = \frac{\Omega_p^2}{1+k_0^2/q^2} = \frac{\Omega_p^2 q^2}{k_0^2+q^2} \simeq \frac{\Omega_p^2}{k_0^2} q^2$$

for small $q \ll k_0$

$$\omega_\ell(q) = \left(\frac{\Omega_p}{k_0}\right) q \Rightarrow \text{speed of sound is } \boxed{c_\ell = \frac{\Omega_p}{k_0}}$$

$$\Rightarrow c_\ell^2 = \frac{4\pi n_{ion} Q_{ion}^2}{M} \frac{1}{4\pi e^2 g(\varepsilon_F)}$$

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

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

$$\boxed{c_\ell^2 = \frac{nZ}{M\, g(\varepsilon_F)}}$$

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

So $$c_\ell^2 = \frac{nZ}{M\left(\frac{3}{2}\frac{n}{\varepsilon_F}\right)} = \frac{2Z\varepsilon_F}{3M} = \frac{2Z}{3M}\frac{1}{2}mv_F^2$$

$$c_\ell^2 = \frac{Zm}{3M} v_F^2 \qquad \boxed{c_\ell = \sqrt{\frac{Z}{3}\frac{m}{M}}\, v_F}$$

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

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

Our result that $c_e \simeq 0.01 v_F$ 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

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

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

Electron-Phonon interaction potential

Elastic displacement of ions gives ~~effective~~ perturbed potential energy to electrons

$$\delta U_{ion} = U_{ion}(\vec{r}; \{\vec{R}_i^0 + \vec{u}\}) - U_{ion}(\vec{r}; \{\vec{R}_i^0\})$$

$$= \sum_i V(\vec{r} - \vec{R}_i) - \sum_i V(\vec{r} - \vec{R}_i^0)$$

$$= \sum_i V(\vec{r} - \vec{R}_i^0 - \vec{u}_i) - \sum_i V(\vec{r} - \vec{R}_i^0)$$

$$\boxed{\delta U_{ion}(\vec{r}) = -\sum_i \vec{\nabla} V(\vec{r} - \vec{R}_i^0) \cdot \vec{u}_i}$$

$V(\vec{r})$ is potential from ion centered at origin

Now $\vec{u}_i(t) = \int_{BZ} d^3q \, e^{i\vec{q}\cdot\vec{R}_i^0} \vec{u}_q(t)$

$$V(\vec{r}) = \int_{-\infty}^{\infty} d^3k \, e^{i\vec{k}\cdot\vec{r}} V_k$$

So

$$\delta U_{ion}(\vec{r}) = -\int_{BZ} d^3q \int_{-\infty}^{\infty} d^3k \, V_k \, i\vec{k}\cdot\vec{u}_q \sum_i e^{i\vec{k}\cdot(\vec{r}-\vec{R}_i^0)} e^{i\vec{q}\cdot\vec{R}_i^0}$$

$$= -\int_{BZ} d^3q \int_{-\infty}^{\infty} d^3k \, V_k \, i\vec{k}\cdot\vec{u}_q \, e^{i\vec{k}\cdot\vec{r}} \underbrace{\sum_i e^{i(\vec{q}-\vec{k})\cdot\vec{R}_i^0}}_{\sum_K \delta(\vec{q}-\vec{k}+\vec{K})}$$

K in RL

$$\boxed{\delta U_{ion}(\vec{r}) = -\sum_K \int_{BZ} d^3q \, V_{\vec{q}+\vec{K}} \, i(\vec{q}+\vec{K})\cdot\vec{u}_q \, e^{i(\vec{q}+\vec{K})\cdot\vec{r}}}$$

For a single normal mode wave vector q, polarization s

$$\vec{u}_i(t) = u_0 \vec{\epsilon}_s \left[e^{i(\vec{q}\cdot\vec{R}_i^0 - \omega_{qs} t)} + e^{-i(\vec{q}\cdot\vec{R}_i^0 - \omega_{qs} t)} \right]$$

$$\cancel{\delta U_{ion}(\vec{r}) = -\sum_K i(\vec{q}+\vec{K})\cdot\vec{\epsilon}_s u_0 V_{q+K}}$$

$$u_q = u_0 \vec{\epsilon}_s e^{-i\omega_{qs} t}$$
$$u_{-q} = u_0 \vec{\epsilon}_s e^{i\omega_{qs} t}$$

$$\delta U_{ion}(\vec{r},t) = -iu_0 \sum_K \Big[V_{q+K} (q+K)\cdot\vec{\epsilon}_s e^{i[(\vec{q}+\vec{K})\cdot\vec{r} - \omega_{qs} t]} + V_{-q+K} (-q+K)\cdot\vec{\epsilon}_s e^{i[(-\vec{q}+\vec{K})\cdot\vec{r} + \omega_{qs} t]} \Big]$$

Take $K \to -K$ in 2nd term, use $V_{-k} = V_k$ for ~~radial~~ potential with $V(\vec{r}) = V(-\vec{r})$

$$\delta U_{ion}(\vec{r},t) = -iu_0 \sum_K V_{q+K} (\vec{q}+\vec{K})\cdot\vec{\epsilon}_s \left[e^{i[(\vec{q}+\vec{K})\cdot\vec{r} - \omega_{qs} t]} - e^{i[(-\vec{q}-\vec{K})\cdot\vec{r} + \omega_{qs} t]} \right]$$

From time dependent perturbation theory applied to $\delta U_{ion}(\vec{r},t)$ the probability amplitude for an electron in initial Bloch state $\psi_{k_i n}(\vec{r})$ to have transition to final Bloch state $\psi_{k_f n'}(\vec{r})$ is,

$$A = \frac{-i}{\hbar} \int_{-\infty}^{\infty} dt \, \langle \psi_{k_f n'} | \delta U_{ion}(t) | \psi_{k_i n} \rangle \, e^{-i(\varepsilon_n(k_i) - \varepsilon_{n'}(k_f))t/\hbar}$$

scattering rate $\propto |A|^2$

$$\psi_{k_i n}(\vec{r}) = \sum_{K} c_{k_i+K}\, e^{i(\vec{k}_i+\vec{K})\cdot\vec{r}}$$

$$\psi_{k_f n'}(\vec{r}) = \sum_{K} c'_{k_f+K}\, e^{i(\vec{k}_f+\vec{K})\cdot\vec{r}}$$

$$A = \frac{-u_0}{\hbar}\sum_{K,K',K''} V_{q+K}\,(\vec{q}+\vec{K})\cdot\vec{\epsilon}_s\, c'^{*}_{k_f+K'}\, c_{k_i+K''}$$

$$\times \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} d^3r \left[e^{-i(\vec{k}_f+\vec{K}')\cdot\vec{r}}\, e^{i(\vec{k}_i+\vec{K}'')\cdot\vec{r}} \right]$$

$$\times \left[e^{i(q+K)\cdot\vec{r}}\, e^{-i\omega_{qs}t} - e^{-i(q+K)\cdot\vec{r}}\, e^{i\omega_{qs}t} \right]$$

$$\times\, e^{-i(\varepsilon_n(k_i)-\varepsilon_{n'}(k_f))t/\hbar}$$

$$= \frac{-u_0}{\hbar}\sum_{K,K',K''} V_{q+K}\,(\vec{q}+\vec{K})\cdot\vec{\epsilon}_s\, c'^{*}_{k_f+K'}\, c_{k_i+K''}$$

$$\times \Bigg\{ \int_{-\infty}^{\infty} d^3r\, e^{-i(k_f+K'-k_i-K''-q-K)\cdot\vec{r}} \int_{-\infty}^{\infty} dt\, e^{-i\left(\frac{\varepsilon_n(k_i)-\varepsilon_{n'}(k_f)}{\hbar}+\omega_{qs}\right)t}$$

$$- \int_{-\infty}^{\infty} d^3r\, e^{-i(k_f+K'-k_i-K''+q+K)\cdot\vec{r}} \int_{-\infty}^{\infty} dt\, e^{-i\left(\frac{\varepsilon_n(k_i)-\varepsilon_{n'}(k_f)}{\hbar}-\omega_{qs}\right)t} \Bigg\}$$

$$= -u_0 \sum_{K,K',K''} V_{q+K}\,(\vec{q}+\vec{K})\cdot\vec{\epsilon}_s\, c'^{*}_{k_f+K'}\, c_{k_i+K''}$$

$$\times \Big[\delta(\vec{k}_f-\vec{k}_i-\vec{q}+K'-K''-K)\,\delta\big(\varepsilon_n(k_i)-\varepsilon_{n'}(k_f)+\omega_{qs}\hbar\big)$$

$$- \delta(\vec{k}_f-\vec{k}_i+\vec{q}+K'-K''+K)\,\delta\big(\varepsilon_n(k_i)-\varepsilon_{n'}(k_f)-\omega_{qs}\hbar\big) \Big]$$

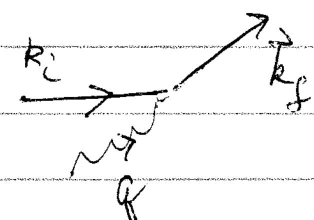
1st term:

$$\left\{\begin{aligned} \varepsilon_{n'}(\vec{k}_f) &= \varepsilon_n(\vec{k}_i) + \hbar\omega_{qs} \\ \vec{k}_f &= \vec{k}_i + \vec{q} \underbrace{- \vec{K}' + \vec{K}'' + \vec{K}}_{\vec{K}_0 \in RL} \end{aligned}\right\} \text{ electron absorbs phonon}$$

2nd term:

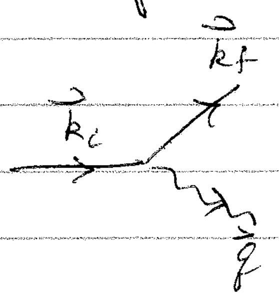
$$\left\{\begin{aligned} \varepsilon_{n'}(\vec{k}_f) &= \varepsilon_n(\vec{k}_i) - \hbar\omega_{qs} \\ \vec{k}_f &= \vec{k}_i - \vec{q} \underbrace{- \vec{K}' + \vec{K}'' - \vec{K}}_{\vec{K}_1 \in RL} \end{aligned}\right\} \text{ electron emitts phonon}$$

1



absorb

2



emitt

in both processes, energy is conserved <u>and</u> crystal momentum is conserved

ie wave vector is conserved within a RL vector