Quantization of Ionic Vibrations

So far we have treated ionic vibrations classically. When we quantize these vibrations, each classical normal mode of oscillation can be treated as a quantum harmonic oscillator. Instead of allowing the amplitude of oscillation at a mode $\vec{q}, s$ ($\vec{q}$ is wave vector in 1st BZ, s is polarization) to have any value, and hence the energy of the mode to have any value, the energy of the mode is now <u>quantized</u> to the discrete values

$$\hbar \omega_s(\vec{q}) \left(n + 1/2\right) \qquad n = 0, 1, 2, \ldots$$

For an oscillator excited to level n, we say that there are n "phonons" of wave vector $\vec{q}$, polarization s.

The displacement amplitude $\vec{u}_{qs}$ of this mode becomes a quantum mechanical operator, which can be expressed in terms of the usual "raising" and "lowering" operators of the quantum harmonic oscillator

(see A+M Appendix L)

$$\vec{u}_{qs} = \sqrt{\frac{\hbar}{2M\omega_s(\vec{q})}} \left(\underset{\text{destroy phonon}}{a_{qs}} + \underset{\text{create phonon}}{a^{+}_{-qs}}\right) \vec{\epsilon}_s(\vec{q})$$

Because n can be any integer, ie we can have any number phonons in a given mode $\vec{q}, s$, we conclude that phonons are bosons.

Like any harmonic oscillator, the excitation level is not a conserved quantity → we can create and destroy phonons; phonon number is not conserved → chemical potential for phonons is equal to zero,

In equilibrium, the average number of phonons in any given mode is given by the Bose distribution function

$$\langle n_{qs} \rangle = \frac{1}{e^{\beta\hbar\omega_s(q)} - 1} \qquad \beta = 1/k_BT$$

$$\sim \frac{k_BT}{\hbar\omega_s(q)} \qquad \text{when } \beta\hbar\omega_s(q) \ll 1$$

ie large T

$$\sim e^{-\hbar\omega_q(s)/k_BT} \qquad \text{when } \beta\hbar\omega_s(q) \gg 1$$

ie small T.

Specific Heat due to ionic vibrations

Classically we have $\langle E \rangle = \left(\frac{1}{2}k_B T\right)(6N) = 3Nk_BT$

energy per quadratic degree of freedom

number quadratic degrees of freedom (3 position and 3 momentum per ion)

$$\langle E \rangle = 3Nk_BT$$

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = 3Nk_B \quad \text{constant}$$

Law of Dulong + Petit

But this is observed to fail even at room temp. C_V is not indep of T.

Quantum mechanically

$$\langle E \rangle = \sum_{q s} \hbar\omega_s(\vec{q}) \left[\langle n_{qs} \rangle + \tfrac{1}{2} \right]$$

with $\langle n_{qs} \rangle = \dfrac{1}{e^{\beta\hbar\omega_s(\vec{q})} - 1}$

$$C_V = \frac{\partial \langle E \rangle}{\partial T}$$

To evaluate we use the Debye model and assume a phonon dispersion relation

$$\omega_s(\vec{q}) = c_s |\vec{q}|$$

where speed of sound c_s is same for all polarizations s.

Define density of phonon states
$g(\omega)\, d\omega$ is the number of phonon modes per unit volume with frequency between ω and $\omega + d\omega$

We know that since there are N ions, there are $3N$ phonon modes. In the Debye model where $\omega_s(\vec{q})$ depends only on $|\vec{q}|$, we define a maximum phonon frequency ω_D, the Debye freq, by

$$\frac{3N}{V} = \int_0^{\omega_D} d\omega\, g(\omega)$$

Since n_{qs} depends on $\vec{q}$ only via $\omega_s(\vec{q})$, we can then write

$$\frac{\langle E\rangle}{V} = \int_0^{\omega_D} d\omega\, g(\omega)\, \hbar\omega \left[\langle n(\omega)\rangle + 1/2 \right]$$

$$= \int_0^{\omega_D} d\omega\, g(\omega)\, \hbar\omega \left[\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2} \right]$$

Now we need to find $g(\omega)$. We have

$$\frac{1}{V}\sum_s \sum_q = \frac{3}{V}\sum_q \overset{\text{continuum approx}}{\simeq} \frac{3}{V}\frac{1}{(\Delta q)^3}\int d^3 q = \frac{3}{(2\pi)^3}\int dq\, q^2\, 4\pi$$

since all polarizations have same $\omega_s(\vec{q})$ in Debye model

since quantities depend only on $q = |\vec{q}|$

also used $\Delta q = \frac{2\pi}{L}$, $V = L^3$

So

$$\int d\omega\, g(\omega) = \frac{3}{2\pi^2}\int dq\, q^2$$

$\Rightarrow \quad g(\omega)\,d\omega = \frac{3}{2\pi^2} q^2\,dq$ use $q = \frac{\omega}{c_s}$

$$\Rightarrow \quad \boxed{g(\omega) = \frac{3}{2\pi^2}\frac{\omega^2}{c_s^3}}$$

Debye freq

$$\frac{3N}{V} = \int_0^{\omega_D} d\omega\, g(\omega) = \int_0^{\omega_D} d\omega\, \frac{3}{2\pi^2}\frac{\omega^2}{c_s^3} = \frac{\omega_D^3}{2\pi^2 c_s^3}$$

$$\Rightarrow \quad \underset{\uparrow}{n} = \frac{N}{V} = \frac{\omega_D^3}{6\pi^2 c_s^3} \quad \Rightarrow \quad \omega_D = \left[6\pi^2 c_s^3 n\right]^{1/3}$$

ion density

If put in numbers for n and c_s of typical metals, we find

Debye temperature: $\Theta_D \equiv \frac{\hbar\omega_D}{k_B} \simeq 100°K - 300°K \ll T_F$ Fermi temperature

or $\hbar\omega_D \ll \mathcal{E}_F$ Fermi energy

Now

$$\frac{\langle E\rangle}{V} = \int_0^{\omega_D} d\omega\, g(\omega)\,\hbar\omega \left[\frac{1}{e^{\beta\hbar\omega}-1} + \frac{1}{2}\right]$$

$$\frac{C_V}{V} = \frac{\partial \langle E\rangle/V}{\partial T} = \int_0^{\omega_D} d\omega\, g(\omega)\,\hbar\omega\, \frac{\left(\frac{\hbar\omega}{k_B T^2}\right) e^{\beta\hbar\omega}}{\left[e^{\beta\hbar\omega}-1\right]^2}$$

substitute in $g(\omega)$ to get

$$\frac{C_V}{V} = \frac{3}{2\pi^2 c_s^3}\int_0^{\omega_D} d\omega\, \omega^2 k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\beta\hbar\omega}}{\left[e^{\beta\hbar\omega}-1\right]^2}$$

let $x = \frac{\hbar\omega}{k_B T} = \beta\hbar\omega$ $\qquad x_D \equiv \beta\hbar\omega_D$

$$\frac{C_V}{V} = \frac{3k_B}{2\pi^2 c_s^3}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{x_D} dx\, \frac{x^4 e^x}{\left[e^x-1\right]^2}$$

$$= 9 k_B n \left(\frac{k_B T}{\hbar\omega_D}\right)^3 \int_0^{x_D} dx\, \frac{x^4 e^x}{\left[e^x-1\right]^2}$$

where we used

$\omega_D = c_s\left[6\pi^2 n\right]^{1/3}$

$$\frac{C_V}{V} = 9 n k_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} dx\, \frac{x^4 e^x}{\left[e^x-1\right]^2}$$

Consider integral as $T \to \infty$, $\beta \to 0$ and $x_D \to 0$

for small x, $\frac{x^4 e^x}{\left[e^x-1\right]^2} \simeq \frac{x^4}{x^2} = x^2$

$$\int_0^{x_D} dx\, \frac{x^4 e^x}{\left[e^x-1\right]^2} \simeq \int_0^{x_D} dx\, x^2 = \frac{x_D^3}{3} = \frac{(\beta\hbar\omega_D)^3}{3} = \left(\frac{\Theta_D}{T}\right)^3 \frac{1}{3}$$

Gives $\frac{C_V}{V} = 9 n k_B \left(\frac{T}{\Theta_D}\right)^3 \left(\frac{\Theta_D}{T}\right)^3 \frac{1}{3} = 3 n k_B$

this is classical result of Dulong & Petit!

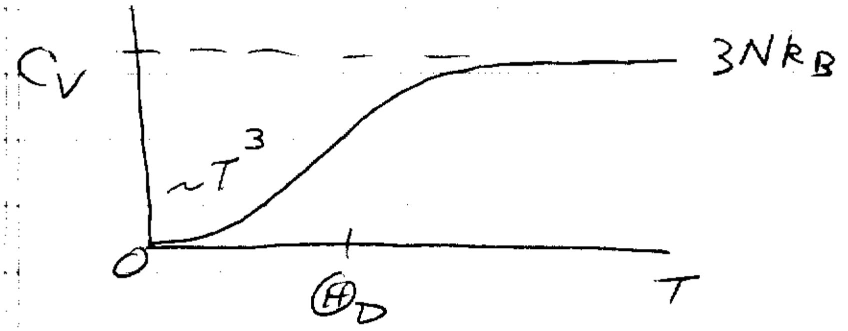
Holds for $T \gg \Theta_D$, ie $x_D \ll 1$

for small $T \to 0$, $\beta \to \infty$, $x_D \to \infty$

approx $\int_0^{x_D} dx \, \frac{x^4 e^x}{[e^x - 1]^2} \simeq \int_0^{\infty} dx \, \frac{x^4 e^x}{[e^x - 1]^2} = \frac{4}{15}\pi^4$

$$\frac{C_V}{V} = \frac{4}{15}\pi^4 \, 9 n k_B \left(\frac{T}{\Theta_D}\right)^3 = \frac{12}{5}\pi^4 n k_B \left(\frac{T}{\Theta_D}\right)^3$$

holds for $T \ll \Theta_D$ ie $x_D \gg 1$



Since $\Theta_D \sim 100 - 300$ K, quantum effects on specific heat of solid can be seen in macroscopic samples at room temperature!

Electron - Phonon Scattering and Resistivity of Metals

We want to understand the temperature dependence of metallic resistivity at low T.

Bloch law $\rho \sim T^5$

$$\delta U_{ion} = -\sum_{sK} \int_{BZ} d^3q \; V_{q+K} \, i(\vec{q}+\vec{K})\cdot \vec{u}_{qs} \, e^{i(\vec{q}+\vec{K})\cdot\vec{r}}$$

where operator for displacement is

$$\vec{u}_{qs} = \sqrt{\frac{\hbar}{2M\omega_s(\vec{q})}} \left(a_{qs} + a^{+}_{-qs} \right) \vec{\epsilon}_s(\vec{q})$$

In Heisenberg picture we will use $a_{qs}(t) = a_{qs}(0)\, e^{-i\omega_{qs}t}$

$$a^{+}_{-qs}(t) = a^{+}_{-qs}(0)\, e^{i\omega_{qs}t}$$

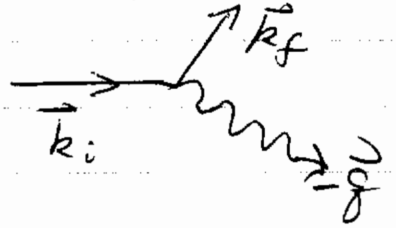
Transition amplitude for electron scattering

$\vec{k}_i, n \longrightarrow \vec{k}_f, n'$

$$A = \frac{-i}{\hbar} \int_{-\infty}^{\infty} dt \left\langle \psi_{k_f,n'} + \text{phonons} \right| \delta U_{ion}(t) \left| \psi_{k_i,n} + \text{phonons} \right\rangle \times e^{-i(\mathcal{E}_n(\vec{k}_i) - \mathcal{E}_n(\vec{k}_f))t/\hbar}$$

When we insert the operator for $\vec{u}_{qs}$ into δU_{ion} in the above we again will get conservation of energy and crystal momentum.

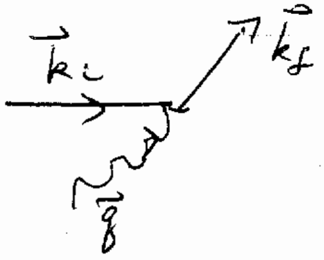
In each mode $\vec{q}, s$ the a^{+}_{-qs} term corresponds to the process



$$\vec{k}_i = \vec{k}_f - \vec{q} + \vec{K}$$
$$\varepsilon_n(\vec{k}_i) = \varepsilon_{n'}(\vec{k}_f) + \hbar\omega_s(-\vec{q})$$

emission of phonon with $-\vec{q}$

The a_{qs} term corresponds to



$$\vec{k}_i + \vec{q} = \vec{k}_f + \vec{K}$$
$$\varepsilon_n(k_i) + \hbar\omega_s(\vec{q}) = \vec{k}_f + \vec{K}$$

absorption of phonon with $\vec{q}$.

The amplitude for such scattering events is

$$A \propto \underbrace{\sqrt{\frac{\hbar}{2M\omega_s(q)}}}_{\text{from } \vec{U}_{qs} \text{ operator}} V_{q+K} \,(\vec{q}+\vec{K})\cdot\vec{\epsilon}_s(\vec{q})$$

For understanding resistivity in metals, we are only concerned with scattering of electrons near the Fermi surface (FS) since these are the only occupied electron states that are near to unoccupied electron states that can be scattered into.

Since $\hbar\omega \lesssim \hbar\omega_D \ll \varepsilon_F$ both initial and final states must lie very close to (within $\hbar\omega_D$ of) the FS.

In the following discussion we will have in mind the case where the FS does not lie very close to the boundary of the 1st BZ. In this case, for

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

we will have nearly free electron states with $C_{k_i} \sim 1$ and $C_{k_i+K''} \sim$ very small for $\vec{K}'' \neq 0$

Similarly

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

will have $C'_{k_f} \sim 1$ and $C_{k_f+K'} \sim$ very small

So we will approx $\psi_{k_i,n} \sim e^{i\vec{k}_i\cdot\vec{r}}$

$$\psi_{k_f,n'} \sim e^{i\vec{k}_f\cdot\vec{r}}$$

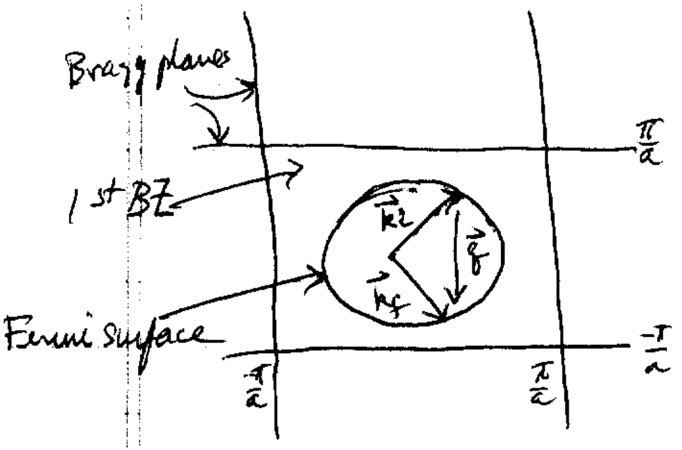
where n and n' label the BZ that $\vec{k}_i$ and $\vec{k}_f$ lie in

Next we will consider only the case $n=n'$, ie scattering within the same band. This is reasonable ~~if~~ the energy gap between E_F and the bottom of the next higher band is $\gg \hbar\omega_D$.

When $\hbar\omega_D \ll k_B T$, all phonon modes are thermally excited and can give rise to scattering. The wave vectors $\vec{q}$ of such phonons can be as large as the size of the 1st BZ ie $q \sim \frac{\pi}{a}$ with a the lattice constat. One can scatter from any point on the FS to any other point on the FS because such large phonon $\vec{q}$'s are present in equilibrium. In this case there are two types of processes to consider.

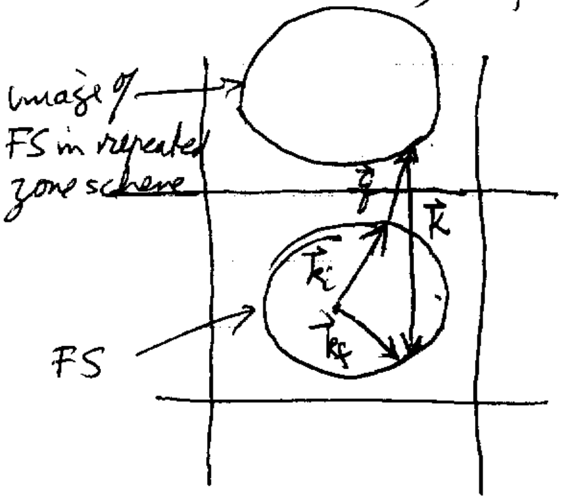
normal process

crystal momentum conserved with $\vec{K} = 0$, ie $\vec{k}_f = \vec{k}_i \pm \vec{q}$



Umklapp processes

Crystal momentum conserved with $\vec{K} \neq 0$, ie $\vec{k}_f = \vec{k}_i \pm \vec{q} + \vec{K}$



But when $\hbar\omega_D \gg k_B T$ only phonon modes with $\hbar\omega_s(q) \lesssim k_B T$ are thermally excited and can lead to scattering by phonon absorption. Moreover scattering by phonon emission can also only take place with phonons with $\hbar\omega_s(\vec{q}) \lesssim k_B T$. The reason is as follows. For an electron to scatter by emission of a phonon $\hbar\omega$

the initial electron state must be occupied

$\rightarrow \quad \mathcal{E}(\vec{k}_i) \lesssim \mathcal{E}_F + k_B T$ since occupied states must be no more than $k_B T$ above the FS for metal at finite temperature

But the final state must be unoccupied

$\rightarrow \quad \mathcal{E}(\vec{k}_f) = \mathcal{E}(\vec{k}_i) - \hbar\omega \gtrsim \mathcal{E}_F - k_B T$

since at finite T there are unoccupied states only with $k_B T$ below $\mathcal{E}_F$.

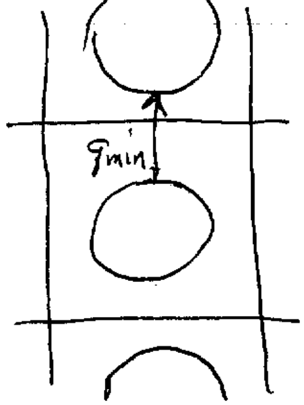
The only way to satisfy both conditions is for $\hbar\omega \lesssim k_B T$

Now as T decreases, the wave vectors of phonons that can cause scattering similarly decreases

$$\hbar c_s q = \hbar\omega_s(q) \lesssim k_B T$$

so $q_{max} \lesssim \dfrac{k_B T}{\hbar c_s}$ is largest wave vector electron can scatter by

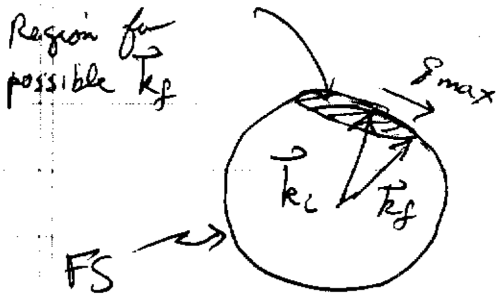
For an Umklapp process however, there is a q_{min} needed for scattering between repeated images of the FS



q_{min} is smallest distance between the repeated images of the FS in the repeated zone scheme

So when T is low enough that $q_{max} \simeq \frac{k_B T}{\hbar c_s}$ is such that $q_{max} < q_{min}$, then Umklapp processes are frozen out and only normal process scattering takes place!

We now consider this limit of sufficiently small T, so that we have only normal processes. In this case the possible $\vec{q}$'s that are consistent with both energy conservation and crystal momentum conservation are those with $\hbar c q \lesssim k_B T$ and are in the region illustrated below



The number of phonon modes allowed for electron scattering is just the area of the circle on the FS whose radius is $q_{max} \simeq \frac{k_B T}{\hbar c_s}$

This area is $\sim q_{max}^2 \sim T^2$

So number of phonon modes that can scatter is $\propto T^2$

Next we want to look at the amplitude of such scatterings

$$A \propto \sqrt{\frac{\hbar}{2M\omega_s(q)}}\; V_q \;\vec{q}\cdot\vec{\epsilon}_s(\vec{q})$$

($\vec{K}=0$ in above since we only have normal processes)

The scattering rate is $\sim |A|^2$

$$|A|^2 \sim \frac{\hbar}{2M\omega_s(q)} |V_q|^2 (\vec{q}\cdot\vec{\epsilon}_s(\vec{q}))^2$$

For small q, $V_q \to V_0$ a constant
(we can imagine V_q is that of a screened Coulomb interaction)

For longitudinal acoustic mode, $\omega_s(q) \simeq c_s q$
$\vec{\epsilon}_s(\vec{q}) \to \hat{q}$ as $q \to 0$

So $|A|^2 \sim \frac{1}{q} q^2 \sim q$

For transverse acoustic mode, $\omega_s(q) \simeq c_s q$

$\vec{\epsilon}_s(\vec{q}) \cdot \hat{q} \to 0$ as $q \to 0$ since $\vec{\epsilon}_s \perp \hat{q}$ for transverse mode.

Suppose $\vec{\epsilon}_s(\vec{q}) \cdot \hat{q} \sim q^\alpha$ $\quad \alpha > 0$

Then $|A|^2 \sim \frac{1}{q} q^2 \cdot q^{2\alpha} \sim q^{1+2\alpha}$

So as $q \to 0$ rate of scattering by transverse modes vanishes much faster than rate of scattering by longitudinal modes

$$q^{1+2\alpha} \ll q \quad \text{as } q \to 0$$

So at sufficiently small T, where scatterings are only by small q phonons, it is ~~the~~ scattering by longitudinal acoustic phonons that dominates (optical phonons, where $\omega_s(q) \to \omega_0 > 0$ as $q \to 0$ are frozen out at low T where $\hbar\omega_0 \gg k_B T$)

~~Putting it together~~ So scattering rate by a particular longitudinal acoustic mode is

$$|A|^2 \sim q \sim q_{max} \sim \frac{k_B T}{\hbar c}$$

Putting it all together we then get

~~total~~ scatterg rate $\frac{1}{\tau_s} = \left(\text{scattering rate of particular mode}\right) \times \left(\text{number of modes that can scatter}\right)$

$$\sim (T) \times (T^2) \sim T^3$$

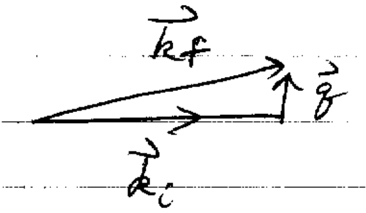
If we used this in the Drude model we would predict for the resistivity

$$\rho \simeq \frac{m}{ne^2 \tau_s} \sim \frac{1}{\tau_s} \sim T^3$$

But this is not correct!

Drude model assumed that after a collision, $\vec{k}_f$ was randomly selected from all equilibrium possibilities ie, $\vec{k}_f$ was not correlated with $\vec{k}_i$.

But for the small $\vec{q}$ scatterings we have been describing, $|\vec{q}|$ is small on the scale of the Fermi wave vector k_F and so scattering looks like



scattering is strongly peaked in the forward direction!
NOT randomly in ~~all~~ any possible direction.

However, after N such scatterings, if N is large enough, the total momentum transfer of the N scatterings will be enough to randomize the wave vector.

$$\vec{Q} = \sum_{i=1}^{N} \vec{q}_i$$

mean square momentum transfer is

$$\langle \vec{Q}^2 \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \vec{q}_i \cdot \vec{q}_j \rangle = \sum_i \sum_j \langle q_i^2 \rangle \delta_{ij}$$

since $\vec{q}_i$ and $\vec{q}_j$ are uncorrelated and $\langle \vec{q}_i \rangle = 0$

$$\langle \vec{Q}^2 \rangle = N \langle q^2 \rangle \approx N \left(\frac{k_B T}{\hbar c_s} \right)^2$$

To randomize we want $\langle \vec{Q}^2 \rangle \sim k_F^2$
with k_F the Fermi wavevector
(since $|\vec{k}_i| \approx |\vec{k}_f| \approx k_F$)

$$\Rightarrow \quad k_F^2 \simeq N \left(\frac{k_B T}{\hbar c_s}\right)^2 \Rightarrow N \sim \left(\frac{k_F \hbar c_s}{k_B T}\right)^2$$

or $N \sim \frac{1}{T^2}$

The τ we use in Drude model should now be the time to randomize the electron's momentum, and so

$$\tau \sim N \tau_s \sim \left(\frac{1}{T^2}\right)\left(\frac{1}{T^3}\right) \sim \frac{1}{T^5}$$

and so resistivity is

$$\boxed{\rho \sim \frac{1}{\tau} \sim \frac{1}{N\tau_s} \sim T^5}$$

This is Bloch's T^5 law for low temperature resistivity of metals due to phonon scattering.

To see the T^5 law in practice in a real material there has to be a window of T that is low enough to freeze out the Umklapp processes, but not too low. As T decreases too small, electron scattering becomes dominated by scattering off randomly positioned material impurities rather than by phonons.