# Chapter 9: Electronic Transport

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As we have seen, transport in insulators (of heat mostly) is dominated by phonons. The thermal conductivity of some insulators can be quite large (cf. diamond). However most insulators have small and uninteresting transport properties.

Metals, on the other hand, with transport dominated by electrons generally conduct both heat and charge quite well. In addition the ability to conduct thermal, charge, and entropy currents leads to interesting phenomena such as thermoelectric effects.

1 Quasiparticle Propagation

In order to understand the transport of metals, we must understand how the metallic state propagates electrons: ie., we must know the electronic dispersion $\omega(k)$. The dispersion is obtained from band structure $E(k) = \hbar\omega(k)$ in which the metal is approximated as an almost free gas of electrons interacting weakly with a lattice potential $V(r)$, but not with each other.
The dispersion is obtained from band structure $E(k) = \hbar \omega(k)$ in which the metal is approximated as an almost free gas of electrons interacting weakly with a lattice potential $V(r)$, but not with each other.

The Bloch states of this system

$$\phi_k(r) = U_k(r) e^{i k \cdot r}, \quad U_k(r) = U_k(r + r_n)$$

may be approximated as plane waves $U_k(r) = U_k$. Then, the state describing a single quasiparticle may be expanded.

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d k U(k) e^{i(k \cdot x - \omega(k)t)}$$

If $U(k) = c\delta(k - k_0)$ then $\psi(x, t) \propto e^{i(k_0 \cdot x - \omega t)}$ and the quasiparticle is delocalized. On the other hand, if $U(k) = \text{constant}$ then $\psi(x, t) \propto \delta(x)$ and the quasiparticle is perfectly localized.

This is an expression of the uncertainty principle

$$\Delta k \Delta x \sim 1 \quad \text{or} \quad \Delta p \Delta x \sim \hbar,$$
If \( U(k) = c\delta(k - k_0) \) then \( \psi(x, t) \propto e^{i(k_0 \cdot x - \omega t)} \) and the quasiparticle is delocalized.

so that we cannot know both the momentum and location of the quasiparticle to arbitrary precision.

\( \omega(k) \neq \) constant, so the different components propagate with different phase velocities, so the quasiparticle spreads as it propagates. This is also the reason why the group velocity of the quasiparticle is not the phase velocity. Consider the propagation of \( \psi(x, t) \) which when \( t = 0 \).

\[
\psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk U(k) e^{ik \cdot x}. \tag{4}
\]

Suppose that \( U(k) \) has a well-defined dominant peak (See Fig. 3) so that

\[
\omega(k) \simeq \omega(k_0) + \nabla_k \omega(k)|_{k_0} \cdot (k - k_0)t \tag{5}
\]

then

\[
\psi(x, t) \simeq \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk U(k) e^{i(k \cdot x - \omega_0 t - \nabla_k \omega(k)|_{k_0} \cdot (k - k_0)t)} \tag{6}
\]
I.e., aside from a phase factor, the quasiparticle travels along with velocity $\nabla_k \omega(k)|_{k_0} = v_g$. (If we had considered higher order terms, we would have seen the quasiparticle distorts as it propagates. (c.f. Jackson p.305). In general,

$$v_g = \nabla_k \omega(k) = \frac{1}{\hbar} \nabla_k E(k)$$  \hspace{1cm} (8)

### 1.1 Quasiparticle Equation of Motion and Effective Mass

We are ultimately interested in the transport; i.e. the response of this quasiparticle to an external electric field $\mathcal{E}$, from which
it gains energy.

\[ \delta E = -e\mathcal{E} \cdot v \delta t \quad \text{(i.e. force \times distance)} \quad (9) \]

This energy is reflected by the quasiparticle ascending to higher energy \( \mathbf{k} \) states.

\[ \delta E = \nabla_k E(\mathbf{k}) \cdot \delta \mathbf{k} = \hbar v \cdot \delta \mathbf{k} \quad (10) \]

So

\[ \hbar \delta \mathbf{k} = -e\mathcal{E} \delta t \quad (11) \]

\[ \hbar \dot{\mathbf{k}} = -e\mathcal{E} \quad \text{E.O.M} \quad (12) \]

This equation of motion is identical to that for free electrons (c.f. Jackson); however, it may be shown to be applicable to general Bloch states provided that \( \mathcal{E} \) is smaller than the atomic fields, and it must not vary in space or time too fast.

We may put this EOM in a more familiar form

\[ \dot{v}_i = \frac{1}{\hbar} \frac{d}{dt} (\nabla_k E(\mathbf{k}))_i = \frac{1}{\hbar} \sum_j \frac{\partial^2 E}{\partial k_i \partial k_j} \frac{dk_j}{dt} \]

\[ = \frac{1}{\hbar} \sum_j \frac{\partial^2 E}{\partial k_i \partial k_j} (-e\mathcal{E}_j) \quad (13) \]

This will have the form \( \mathbf{F} = m\mathbf{a} \), if we define the mass tensor

\[ \left( \frac{1}{m^*} \right)_{ij} = \left( \frac{1}{m^*} \right)_{ji} = \frac{1}{\hbar^2} \frac{\partial E}{\partial k_i \partial k_j} \quad \text{symmetric \\ & real} \quad (14) \]
which may be diagonalized to define three principle axes. In the simple cubic case, the matrix will have the same element along each principle direction and

\[ m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}}. \]  

(15)

In this way the effective mass of electrons on a lattice can vary strongly, the larger \( \frac{d^2E}{dk^2} \) is, the smaller \( \frac{m^*}{m} \) is. Consider the simple 1-d case (See Fig. 4)

Figure 4:
2 Currents in Bands

Our previous discussion of the motion of an electron (or a quasi-particle) in a metal under the influence of an applied field $E$, ignored the presence of other electrons and the Pauli principle.

2.1 Current in an Insulator

The Pauli principle insures that a full band of states is insulating. Consider the electric current due to $d^3k$ states

$$dJ = -e\mathbf{v}(k) \left( \frac{L}{2\pi} \right)^3 d^3k$$ (16)

The current density is then

$$dj = \frac{-e}{h} \nabla_k E(k) \frac{1}{(2\pi)^3} d^3k$$ (17)

ie., different occupied states in the Brillouin zone contribute differently to the current. The net current density $j$ is then the integral over all occupied states, which for our full band is the integral over the first Brillouin zone

$$j = -\frac{e}{8\pi^3\hbar} \int_{\text{1st B.Z.}} \nabla_k E(k) d^3k.$$ (18)

Thus for each $k$ vector in the integral, there is also $-k$. 
Now consider a lattice with inversion symmetry $k \rightarrow -k$ so that $E(k) = E(-k)$. Alternatively, recall that time-reversal invariance requires that
\[ E_\uparrow(k) = E_\downarrow(-k), \]
but since $E_\uparrow(k) = E_\downarrow(k)$ due to spin degeneracy, we must have that $E(k) = E(-k)$. Thus
\[ v_{-k} = \frac{1}{\hbar} \nabla_{-k} E(-k) = -\nabla_k E(k) = -v_k! \]
i.e., for the insulator
\[ j = \frac{-e}{8\pi^3\hbar} \int_{\text{1st B.Z.}} d^3k \nabla_k E(k) \equiv 0 \]  
Now imagine that the band is not full (See Fig. 6, left). Then, if we apply an external field $\mathcal{E}$, so that
\[ \dot{k} = -\frac{e\mathcal{E}}{\hbar} \quad e > 0! \]
Figure 6: The Fermi sea of a partially filled band will shift under the influence of an applied field $E$. This destroys the inversion symmetry of the Fermi sea, causing a net current.

the electrons will redistribute as the Fermi surface shifts (See Fig. 6 right).

$$j = \frac{-e}{8\pi^3} \int_{\text{occupied}} v(k) d^3k$$

$$= \frac{-e}{8\pi^3} \int_{1\text{st B.Z.}} d^3k v(k) - \frac{-e}{8\pi^3} \int_{\text{empty}} d^3k v(k)$$

$$= \frac{e}{8\pi^3} \int_{\text{empty}} d^3k v(k)$$ (23)

Thus the current may be formally described as a current of positive charge particles (holes) assigned to the unoccupied states in the band.
2.2 Currents in a Metal

Now imagine that the band is almost full. Near the top of the

\[ E(k) = E_0 - \frac{\hbar^2 k^2}{2|m^*|} \quad k = \text{deviation from top!} \quad (24) \]

or

\[ \dot{\mathbf{v}} = \frac{1}{\hbar} \frac{d}{dt} \nabla_k E_k = -\frac{\hbar \mathbf{k}}{|m^*|} = \frac{e \mathcal{E}}{|m^*|} \quad (25) \]

This is the EOM of a positively charged particle with positive mass in an electric field \( \mathcal{E} \). \textit{I.e., holes at the top of the band have positive mass.}
We have just shown that a material with full bands is an insulator (See Fig. 8 left). I.e., it carries no current, as least at

\[ T = 0 \] and for a small \( \mathcal{E} \). However we ignored the presence of other bands. If there is a conduction band, for \( T \neq 0 \), and a reasonably small \( E_g \), there will be conductivity due to a small number of thermally excited holes and electrons \( n \sim \exp(-E_g/K_B T) \) (See Fig. 8 right). Thus perhaps a better definition of an insulator is a material for which the conductivity increases with \( T \).
3 Scattering of Electrons in Bands

According to the EOM for hole at the top of a band

\[ \mathbf{v} = \frac{e}{m^*} \mathcal{E} \]  

as long as \( \mathcal{E} \) is finite, these holes will continue to accelerate and \( \mathbf{j} \) will increase accordingly. Of course, this does not happen. Rather the material simply heats up (ie., has a finite \( R \)). In addition, if \( \mathcal{E} \) is returned to zero, then \( \mathbf{j} \) likewise returns to zero. Why?

In 1900 Drude assumed that the electrons scatter from the lattice yielding resistivity. Of course, as we have seen the quasi-

![Figure 9: Drude thought that electrons scatter off the lattice yielding resistivity. Bloch showed this to be wrong.](image)

particle state may be defined from a sum over Bloch waves (described by \( \mathbf{k} \)) each of which is a stationary state and describe
the unperturbed propagation of electrons. Thus a *perfect* lattice yields no resistivity. We can get resistivity in two ways.

1. Deviations from a perfect lattice
   
   (a) Defects (See Fig. 10a)
   
   (b) Lattice vibrations = phonons (See Fig. 10b)

2. Electron - electron interactions (See Fig. 11)

\[
\begin{align*}
E(k) - E(k+q) &= \hbar \omega(q) \\
c_{k+q}^\dagger c_k a_{-q}^\dagger \text{ or } c_{k+q}^\dagger c_k a_q &
\end{align*}
\]

Figure 10: Electrons do scatter from defects in the lattice or lattice vibrations. They contribute to the resistivity, with the phonon contribution increasing with temperature, and the defect contribution more-or-less constant.
Due to the strength of the electron-electron interaction and the
density of electrons, (2) should dominate. However, it is easy
to show, using the Pauli principle, that effect of (2) is quite
often negligible, so that we may return to regarding the pure
electronic system as a (perhaps renormalized) non-interacting
Fermi gas.

According to momentum and energy conservation Fig 11

\[ E_1 + E_2 = E_3 + E_4 \quad k_1 + k_2 = k_3 + k_4. \]  \hfill (27)

(Of course, momentum conservation is only up to a recipro-
cal lattice vector \( G \), \( k_1 + k_2 = k_3 + k_4 \). Electron-electron interactions
also contribute to the resistivity (from simple order of magnitude arguments based
on relative strengths of the interactions, their contribution should dominate—but due
to the Pauli principle, it does not).

Figure 11: \( E_1 + E_2 = E_3 + E_4 \) and \( k_1 + k_2 = k_3 + k_4 \). Electron-electron interactions
also contribute to the resistivity (from simple order of magnitude arguments based
on relative strengths of the interactions, their contribution should dominate—but due
to the Pauli principle, it does not).

cal lattice vector \( G \), \( k_1 + k_2 = k_3 + k_4 = G \); however, as with
phonon conductivity, these processes with finite \( G \) involve much
higher energies, and may be neglected near $T = 0$.) Furthermore, since all states up to $E_F$ are occupied, $E_3; E_4 > E_F$!

Suppose $E_1$ is (thermally) excited, so $E_1 > E_F$ and it collides with an occupied state $E_2 < E_F$. Then

$$(E_1 - E_F) + (E_2 - E_F) = (E_3 - E_F) + (E_4 - E_F) > 0 \quad (28)$$

$$\epsilon_1 + \epsilon_2 = \epsilon_3 + \epsilon_4 > 0, \quad \epsilon_3; \epsilon_4 > 0 \quad (29)$$

or $\epsilon_1 + \epsilon_2 > 0$, However, since $\epsilon_2 < 0$, if $\epsilon_1$ is small, then $|\epsilon_2| \leq \epsilon_1$, is also small, so only states with $\frac{\epsilon_2}{E_F} \leq \frac{\epsilon_1}{E_F}$ states may scatter with the state $k_1$ conserve energy and obey the Pauli principle, thus restricting $\epsilon_2$ to a narrow shell of width $\epsilon_1$ around the Fermi surface.

Now consider the restrictions placed on the states 3 and 4 by momentum conservation.

$$k_1 - k_3 = k_4 - k_2 \quad (30)$$

I.e. $k_1 - k_3$ and $k_4 - k_2$ must remain parallel, and since $k_1$ is fixed, this restriction on the final states further reduces the scattering probability by a factor of $\frac{\epsilon_1}{E_F}$. 

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Figure 12: Momentum and energy conservation severely restrict the states that an electron can scatter with and into.

Thus the total scattering cross section $\sigma$ is reduced from the classical result $\sigma_0$ by $\left(\frac{\epsilon_1}{E_F}\right)^2$. If the initial excitation $\epsilon_1$ is due to thermal effects, then $\epsilon_1 \sim k_B T$ and

$$\frac{\sigma}{\sigma_0} \sim \left(\frac{k_B T}{E_F}\right)^2 \ll 1! \quad (31)$$

The total scattering due to electron-electron repulsion is very small. Therefore, unless $E_F$ can be made small, the dominant contribution to a material’s resistivity is due to defects and phonons.
4 The Boltzmann Equation

The nonequilibrium (but steady-state) situation of an electronic current in a metal driven by an external field is described by the Boltzmann equation.

Figure 13: Electronic transport due to an applied field $\mathcal{E}$, is limited by inelastic collisions with lattice defects and phonons.

This differs from the situation of a system in equilibrium in that a constant deterministic current differs from random particle number fluctuations due to coupling to a heat and particle bath. Away from equilibrium ($\mathcal{E} \neq 0$) the distribution function may depend upon $\mathbf{r}$ and $t$ as well as $\mathbf{k}$ (or $E(\mathbf{k})$). Nevertheless, when $\mathcal{E} = 0$ we expect the distribution function of the particles
in $V$ to return to

$$f_0(k) = f(r, k, t)|_{\varepsilon=0} = \frac{1}{e^{\beta(E(k)-E_F)} + 1} \quad (32)$$

As indicated,

To derive a form for $f(r, k, t)$, we will consider length scales larger than atomic distances $\AA$, but smaller than distances in which the field changes significantly. In this way the system is considered essentially homogeneous with any inhomogeneity driven by the external field. Now imagine that there is no scattering (no defects, phonons), then since electrons are conserved

$$\frac{dr}{dt} dt \quad \bullet \quad \frac{dk}{dt} dt \quad \bullet \quad \frac{dt}{dt}$$

Figure 14: In lieu of scattering, particles flow without decay.

$$f(r, k, t) = f\left( r - v dt, k + \frac{e \varepsilon}{\hbar} dt, t - dt \right) \quad (33)$$

Now consider defects and phonons (See Fig. 15) which can scatter a quasiparticle in one state at $r - v dt$ and time $t - dt$, to another at $r$ and time $t$, so that $f(r, k, t) \neq f\left( r - v dt, k + \frac{e \varepsilon}{\hbar} dt, t dt \right)$. 

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We will express this scattering by adding a term.

\[ f(r, k, t) = f \left( r - v dt, k + e\mathcal{E} \frac{dt}{\hbar}, t - dt \right) + \left( \frac{\partial f}{\partial t} \right)_S dt \]  

(34)

For small \( dt \) we may expand

\[ f(r, k, t) = f(r, k, t) - v \cdot \nabla_r f + e\mathcal{E} \cdot \nabla_k f \frac{f}{\hbar} - \frac{\partial f}{\partial t} + \left( \frac{\partial f}{\partial t} \right)_S \]

(35)

or

\[ \frac{\partial f}{\partial t} + v \cdot \nabla_r f - e\mathcal{E} \cdot \nabla_k f = \left( \frac{\partial f}{\partial t} \right)_S \quad \text{Boltzmann Equation} \]

(36)

If the phonon and defect perturbations are small, time-independent, and described by \( H \), then the scattering rate from a Bloch state \( k \) to \( k' \) (occupied to unoccupied) is \( w_{k'k} = \frac{2\pi}{\hbar} |\langle k' | H | k \rangle|^2 \). Then

\[
\left( \frac{\partial f(k)}{\partial t} \right)_S = \left( \frac{L}{2\pi} \right)^3 \int d^3k' \left\{ \left( 1 - f(k) \right) w_{kk'} f(k') - \left( 1 - f(k') \right) w_{k'k} f(k) \right\} \]

(37)
Needless to say it is extremely difficult to solve these last two coupled equations.

4.1 Relaxation Time Approximation

As a result we make a series of approximations and ansatz. The first of these is the relaxation time approximation that the rate at which a system returns to equilibrium $f_0$ is proportional to its deviation from equilibrium

$$\left( \frac{\partial f}{\partial t} \right)_S = -\frac{f(k) - f_0(k)}{\tau(k)}. \quad (38)$$

Here $\tau(k)$ is called the relaxation time (for a spatially inhomogeneous system $\tau$ will also depend upon $r$). I.e., we make the assumption that scattering merely acts to drive a nonequilibrium system back to equilibrium.

If $\mathcal{E} \neq 0$ for $t < 0$ and then at $t = 0$ it is switched off so that for $t > 0 \mathcal{E} = 0$, then for a homogeneous system

$$\frac{\partial f}{\partial t} = \left( \frac{\partial f}{\partial t} \right)_S = -\frac{f - f_0}{\tau}. \quad (39)$$

so that

$$f - f_0 = (f(t = 0) - f_0) e^{-\frac{t}{\tau}} \quad (40)$$
ie., \( \tau \) is the time constant at which the system returns to equilibrium.

Now consider the steady-state situation of a metallic system in a time-independent external field \( \mathcal{E} = \mathcal{E} \hat{x} \). Then

\[
\frac{\partial f}{\partial t} = 0 \tag{41}
\]

Furthermore since the system is homogeneous

\[
\nabla_r f = 0 \tag{42}
\]

then

\[
-\frac{e}{\hbar} \mathcal{E} \cdot \nabla_k f(k) = \left( \frac{\partial f}{\partial t} \right)_S = -\frac{f(k) - f_0(k)}{\tau(k)} \tag{43}
\]

ie

\[
f(k) = f_0(k) + \frac{e}{\hbar} \tau(k) \mathcal{E} \cdot \nabla_k f(k) \tag{44}
\]

which may be solved iteratively, generating a power series in \( \mathcal{E} \) (or \( \mathcal{E}_x \)).

### 4.2 Linear Boltzmann Equation

For small \( \mathcal{E} \) (Ohmic conditions)

\[
f(k) \simeq f_0(k) + \frac{e}{\hbar} \tau(k) \mathcal{E} \cdot \nabla_k f_0(k) \quad \text{linear Boltzmann Eqn.} \tag{45}
\]
I.e. the lowest order Taylor series of $f(k)$. Or equivalently, if $\mathcal{E} = \mathcal{E}_x \hat{x}$

$$f(k) \simeq f_0 \left( k + \frac{e}{\hbar} \tau(k) \mathcal{E} \right)$$

(46)

I.e., the effect is to shift the Fermi surface from its equilibrium position by an amount

\[ \delta k_x = -e \tau \frac{\mathcal{E}_x}{\hbar} \]

(47)

Figure 16: According to the linear Boltzmann equation, the effect of a field $\mathcal{E}_x$ is to shift the Fermi surface by $\delta k_x = -e \tau \frac{\mathcal{E}_x}{\hbar}$

From the discussion in Sec.??, it is clear that a finite current results.

Interesting! Note that elastic scattering $|k| = |k'|$ cannot restore equilibrium. Rather they would only cause the Fermi
surface to expand. Inelastic scattering (i.e. from phonons) is needed to explain relaxation.

Figure 17: Note that elastic scattering $|\mathbf{k}| = |\mathbf{k}'|$ cannot restore equilibrium. Rather they would only cause the Fermi surface to expand.

5 Conductivity of Metals

5.1 Drude Approximation

As mentioned above, Drude calculated the conductivity of metals assuming that

- all free electrons participate, and

- electron-lattice scattering yields a scattering rate $1/\tau$.

Under these assumptions, the EOM is

$$m \ddot{\mathbf{v}} + \frac{m}{\tau} (\mathbf{v} - \mathbf{v}_{\text{therm}}) = -e\mathbf{E}$$ (48)
where \( v - v_{\text{therm}} = v_D \), the drift velocity, and \( \frac{m}{\tau} v_D \) is friction. Again when \( \mathcal{E} = 0 \), we again have an exponential decay of \( v \) so \( \tau \) is again the relaxation time.

In steady-state \( \dot{v} = 0 \)

\[
v_D = \frac{-e\tau}{m} \mathcal{E}
\]  

(49)

so that

\[
\dot{j} = -en v_D = \frac{ne^2\tau}{m} \mathcal{E}
\]  

(50)

or defining \( j = \sigma \mathcal{E}, \) and \( \sigma = \mu ne, \)

\[
\sigma = \frac{ne^2\tau}{m} \quad \mu = \frac{e\tau}{m}
\]  

(51)

5.2 Conductivity Using the Linear Boltzmann Equation

Of course, this is wrong since all free electrons do not participate in \( \sigma \) due to the Pauli principle. And a more careful derivation, using the Boltzmann Equation, is required. Again, the relationship between \( j \) and \( f(k) \) is

\[
j = \frac{-e}{8\pi^3} \int d^3k \ v(k) f(k)
\]  

(52)

\[
\approx \frac{-e}{8\pi^3} \int d^3k \ v(k) \left\{ f_0(k) + \frac{e\tau(k)}{\hbar} \mathcal{E}_x \frac{\partial f_0}{\partial k_x} \right\}
\]  

(53)
Figure 18: To calculate the conductivity, we apply a field in the x-direction only and use the linearized Boltzmann Eqn.

For an isotopic material $j_z = j_y = 0$, and the equation becomes scalar. Furthermore, again

$$\int v(k)f_0(k)d^3k = 0$$  \hspace{1cm} (54)

since $v_{-k} = -v_k$. Then as

$$\frac{\partial f_0}{\partial k_x} = \frac{\partial f_0}{\partial E} \frac{\partial E}{\partial k_x} = \frac{\partial f_0}{\partial E} \hbar v_x$$ \hspace{1cm} (55)

$$j_x \simeq -\frac{e^2}{8\pi^3} \epsilon_x \int d^3kv_x^2\tau(k)\frac{\partial f_0}{\partial E}$$ \hspace{1cm} (56)

Then as $\frac{\partial f_0}{\partial E} \simeq -\delta(E - E_F)$ for $T \ll E_F$ the integral in $k$ is confined to the surface of constant $E$, and

$$d^3k = dS_E dk_{\perp} = dS_E \frac{dE}{\hbar v(k)}$$ \hspace{1cm} (57)

then
As expected only the properties of the electrons on the Fermi surface are relevant.

We can now calculate the conductivity of a metal by aver-
aging $v_x^2 \tau(k)$ over the Fermi surface. Consider a simple system
with a spherical Fermi surface, then

$$\int dS_E \frac{\tau(k)v_x^2(k)}{v(k)} = \frac{4\pi}{3} k_F^2 \tau(E_F)v(E_F)$$

$$= \frac{4\pi}{3} k_F^2 \tau(E_F) \frac{\hbar k_F}{m^*} \quad (60)$$

or

$$\sigma = \frac{e^2}{8\pi^3 \hbar} \frac{4\pi}{3} k_F^2 \tau(E_F) \frac{\hbar k_F}{m^*}$$

$$\quad (61)$$

then as $k_B T \ll E_F, N = \frac{2}{3} \pi \frac{k_F^3}{(2\pi)^3} \Rightarrow k_F^3 = 3\pi^2 n$ we find that

$$\sigma = \frac{e^2 \tau(E_F)}{m^*} n \quad \mu = \frac{e \tau(E_F)}{m^*} \quad (62)$$

For semiconductors where $n$ is $T$ dependent, and for more realistic material where the Fermi surface $\neq$ sphere, the formula is more complicated.

However, for metals the temperature dependence of $\sigma$ is dominated by that of $\tau$; i.e., by the temperature dependence of phonons. However, before we can calculate $\sigma(T)$, we must first disentangle the phonon from the defect scattering. Assuming
that the two mechanisms are independent, they must add

\[ \frac{1}{\tau} = \frac{1}{\tau_{\text{ph}}} + \frac{1}{\tau_{\text{defect}}} \]  

(63)
i.e.

\[ \rho = \rho_{\text{ph}} + \rho_{\text{defect}} \quad \text{Matthiesen’s Rule} \]  

(64)
The defect contribution is proportional to the defect cross section \( \Sigma_{\text{defect}} \) and the current, or \( v(E_F) \), \( \frac{1}{\tau_{\text{defect}}} \propto \Sigma_{\text{defect}} v(E_F) \). Is is roughly temperature independent, since the cross section \( \Sigma_{\text{defect}} \) and \( v(E_F) \) are.

The phonon contribution, on the other hand, is highly temperature dependent since at zero temperature, there are no phonons. The scattering cross section is roughly proportional to the rms phonon excursion \( \langle S^2(q) \rangle \). However, from the equipartition theorem

\[ \frac{1}{2} M \omega_q^2 \langle S^2(q) \rangle = \frac{k_B T}{2} \quad T \gg \theta_D. \]  

(65)
Thus

\[ \frac{1}{\tau_{\text{ph}}} \propto \langle S^2(q) \rangle \propto \frac{k_B T}{m \omega_q^2} \]  

(66)
I.e., at high temperatures, all modes contribute a linear in \( T \)
scattering to \( \frac{1}{\tau_{\text{ph}}} \). Therefore, at \( T \gg \theta_D \) (\( \theta_D \) = debye temperature)

\[
\rho = \alpha T + \rho_{\text{defect}}
\]  

(67)

Figure 21: The phonon and defect contributions to the resistivity add (left), and the phonon contribution is linear at high temperatures \( T \gg \theta_D \).

6 Thermoelectric Effects

Until now, we have assumed that the transport system is thermally homogeneous. Of course this need not be the case since we can obviously maintain both an electrical and a thermal current. Here, each electron can carry a charge current \( \sim e \mathbf{v} \sim e^2 \mathcal{E} \) and a thermal current \( kT k \nabla T \). In fact, a heat current can be
Thermoelectric effects are important in systems with both electric potential and thermal gradients. We will assume both are in the x-direction used to induce an electrical potential (Seebeck or thermoelectric effect) and, conversely, an electric current can be used to move heat (Peltier effect) which makes the solid state refrigeration possible.

6.1 Linearized Boltzmann Equation

To allow for a thermal gradient $\nabla T$, our formalism must be modified. Imagine that $\nabla T$ and $\mathcal{E}$ are fixed in time, then the Boltzmann equation becomes

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{r} f - \frac{e}{\hbar} \mathbf{E} \cdot \nabla_{k} f = \left( \frac{\partial f}{\partial t} \right)_{S} = -\frac{f(k) - f_{0}(k)}{\tau(k)}$$  (68)
where in steady state $\frac{\partial f}{\partial t} \to 0$. After linearizing (replacing $f$ by $f_0$ in the left-hand side), we get

$$f(k) \simeq f_0(k) - \tau(k) \left\{ \mathbf{v} \cdot \nabla_r f_0 - \frac{e}{\hbar} \mathbf{E} \cdot \nabla_k f_0 \right\} \quad (69)$$

Then, as before

$$\frac{e}{\hbar} \mathbf{E} \cdot \nabla_k f_0 = \frac{e}{\hbar} \mathbf{E} \cdot \frac{\partial f_0}{\partial E} \hbar \mathbf{v} = \frac{e}{\hbar} \mathbf{E} \frac{\partial f_0}{\partial E} \hbar v_x \quad (70)$$

The spatial inhomogeneity is through $\nabla T$, and in a semiconductor for which $E_F$ depends strongly upon $T$, through $\nabla E_F$

$$\mathbf{v} \cdot \nabla_r f_0 = \mathbf{v} \cdot \left\{ \frac{\partial f_0}{\partial T} \nabla T + \frac{\partial f_0}{\partial E_F} \nabla E_F \right\} = \mathbf{v} \cdot \left\{ \frac{\partial f_0}{\partial T} \nabla T - \frac{\partial f_0}{\partial E} \nabla E_F \right\} \quad (71)$$

Apparently $\nabla E_F$ only contributes a term which modifies the electric field dependence

$$v_x \frac{\partial f_0}{\partial E} \left\{ e\mathbf{E}_x + (\nabla E_F)_x \right\} \equiv v_x \frac{\partial f_0}{\partial E} e\mathbf{E}'_x \quad (72)$$

Of course, in a metal $\mathbf{E}' = \mathbf{E}$.

### 6.2 Electric Current

Thus, we now have

$$f(k) = f_0(k) - \tau \frac{\partial f_0}{\partial T} v_x \frac{\partial T}{\partial x} + \frac{e}{\hbar} \tau\mathbf{E}' \hbar v_x \frac{\partial f_0}{\partial E} \quad (73)$$
Then for

\[ j_x = -\frac{e}{8\pi^3} \int d^3k v_x(k) f(k) \]  

\[ j_x = -\frac{e}{8\pi^3} \int d^3k v_x(k) \left\{ f_0(k) - \tau \frac{\partial f_0}{\partial T} v_x \frac{\partial T}{\partial x} + \frac{e}{\hbar} \tau \mathcal{E}'_x \frac{\partial f_0}{\partial E} h v_x \right\} \]  

(74)

recall that the last term yielded \( \sigma \) last time (and still will)

\[ j_x = \sigma \mathcal{E}'_x + \frac{e}{8\pi^3} \int d^3k v_x^2 \tau \frac{\partial f_0}{\partial T} \frac{\partial T}{\partial x} \]  

(75)

Again we will calculate the second term assuming a spherical Fermi surface. The term \( \frac{\partial f_0}{\partial T} \) confines the integral to the Fermi sphere and so again effectively it amounts to a Fermi-surface average, so \( \overline{v^2} \rightarrow \frac{1}{3} \mathbf{v}^2 \approx \frac{2}{3m^*} \frac{1}{2} m^* \mathbf{v}^2 = \frac{2}{3m^*} E \) or changing to an integral over the DOS

\[ j_x = \sigma \mathcal{E}'_x + \frac{2}{3m^*} \int dE \tau(E) E D(E) \frac{\partial f_0}{\partial T} \frac{\partial T}{\partial x} \]  

(76)

Figure 23: The derivative \( \frac{\partial f_0}{\partial E} \) is only significant near the fermi surface.
Assuming that $\tau(E) \sim \tau(E_F)$, we get

$$j_x = \sigma \mathcal{E}_x' + \frac{2}{3 m^*} \tau(E_F) \frac{\partial T}{\partial x} \int dE E \frac{\partial f_0}{\partial T} D(E) \quad (77)$$

$$j_x = \sigma \mathcal{E}_x' + \frac{e}{3 m^*} \tau(E_F) \frac{\partial T}{\partial x} c_v(T) \quad c_v \propto m^* \quad (78)$$

In general, this intuitive form is rewritten as

$$j_x = \sigma \mathcal{E}_x' + \mathcal{L}_{xx}^{12} \left( -\frac{\partial T}{\partial x} \right) \quad (79)$$

and from it we see that both an electric field (or the generalized field strength $\mathcal{E}'$), and the thermal gradient contribute to the electron current, $j_x$.

### 6.3 Thermal and Energy Currents

Of course one can have a thermal current without having an electric current (same number of electrons moving right and left, but more of the hot ones moving right). Thermodynamics is needed to quantify this though since these electrons will also carry entropy as well as energy and heat.

Imagine that a small subsection of our material is in thermal equilibrium and then some electrons are introduced/taken away
so that

\[ dQ = TdS = dU - \mu dN \quad \text{First Law of Thermodynamics} \]  

(80)

in terms of particle flow

\[ \mathbf{j}_Q = \mathbf{j}_E - E_F \mathbf{j}_n \quad -e \mathbf{j}_n = \mathbf{j} \]  

(81)

where this equation defines \( \mathbf{j}_Q \), the thermal current, and

\[ \mathbf{j}_E = \int \frac{d^3k}{8\pi^3} E(k) \mathbf{v}(k) f(k, \mathbf{r}) . \]  

(82)

Again one could work out the form of \( \mathbf{j}_Q \) for the spherical Fermi surface using the linearized Boltzmann equation. However one must obtain a form like

\[ \mathbf{j} = \mathcal{L}^{11} \mathcal{E}' + \mathcal{L}^{12} (-\nabla T) \]  

(83)

\[ \mathbf{j}_Q = \mathcal{L}^{21} \mathcal{E}' + \mathcal{L}^{22} (-\nabla T) \]  

(84)

(The fact that \( \mathcal{L}^{12} = \mathcal{L}^{21} \) is referred as the Onsager relation.)

These relationship between the \( \mathcal{L} \)'s and the transport coefficients depends upon what experiment is being done. For example in Fig. 24 there is a potential gradient \((V \neq 0)\) but no
Here, there is a potential gradient ($V \neq 0$) but no thermal gradient since $T_1 = T_2$. The electric field drives both electric and thermal currents. Thus, a heat bath is required to keep both sides of the sample at the same temperature.

Thus, we may identify

$$ j = \mathcal{L}^{11} \mathcal{E} $$

$$ j_Q = \mathcal{L}^{12} \mathcal{E} $$

(85)

Thus, we may identify

$$ \sigma = \frac{ne\tau}{m^*} = \mathcal{L}^{11} $$

(86)

Note that since there is a thermal current induced by the potential gradient, a heat bath is required to keep both sides of the sample at the same temperature.
In Fig. 25 we maintain a thermal gradient, but turn off the electric current. Here,

\[ T_1 \neq T_2 \]

\[ I = 0 \]

**Figure 25**: Here \( j = 0 = \mathcal{L}^{11} \mathcal{E}' + \mathcal{L}^{12} (\nabla T) \) and \( j_Q = (\mathcal{L}^{12} \left( \frac{\mathcal{E}^{12}}{\mathcal{T}^{11}} \right) + \mathcal{L}^{22}) (\nabla T) \)

where \( -\mathcal{L}^{12} \left( \frac{\mathcal{E}^{12}}{\mathcal{T}^{11}} \right) + \mathcal{L}^{22} = \kappa T \)

\[ j = 0 = \mathcal{L}^{11} \mathcal{E}' + \mathcal{L}^{12} (\nabla T) \] \hspace{2cm} (87)

and

\[ j_Q = \mathcal{L}^{21} \mathcal{E}' + \mathcal{L}^{22} (\nabla T) = \left( -\mathcal{L}^{21} \left( \frac{\mathcal{L}^{12}}{\mathcal{L}^{11}} \right) + \mathcal{L}^{22} \right) (\nabla T) \] \hspace{2cm} (88)

and since (you will show)

\[ \mathcal{L}^{12} = -\frac{2eT}{3m^*c_v} = \mathcal{L}^{21} \] \hspace{2cm} (89)

\[ \kappa = \mathcal{L}^{22} - \frac{(\mathcal{L}^{12})^2}{\mathcal{L}^{11}} \] \hspace{2cm} (90)
We could also measure the thermal conductivity by driving a heat current through the sample, maintaining the ends at the same potential (see Fig. 26 right). Here, we would find

\[ \kappa = L^{22} - \frac{(L^{12})^2}{L^{11}} \]

\[ j = L^{12}(\nabla T) \]
\[ j_Q = L^{22}(\nabla T) \]

\[ \kappa = L^{22} \]

Figure 26: Two methods for measuring \( \kappa \).

Thus, we can identify

\[ \kappa = L^{22} \text{ or } L^{22} - \frac{(L^{12})^2}{L^{11}} \]  

(92)

depending upon the experiment. These are the same if the sample is a good metal where \( L^{11} = \sigma \) is large (Young Kim).
David Mast measures $\kappa$ by the method of the left of Fig. 26. This yields the more conventional definition of $\kappa$.

6.4 Seebeck Effect, Thermocouples

These relations result in some interesting physical effects. Consider a bimetallic conducting loop with two junctions maintained at temperatures $T_1$ and $T_2$. Let metal A be different than B, so that $\mathbf{L}^{ij}_A \neq \mathbf{L}^{ij}_B$. If no current flows around the loop, then

$$\mathbf{j} = 0 = \mathbf{L}^{11} \mathbf{E}_x + \mathbf{L}^{22} (-\nabla T) \Rightarrow \mathbf{E}_x = \left(\frac{\mathbf{L}^{12}}{\mathbf{L}^{11}}\right) \frac{dT}{dx} \quad (93)$$

Figure 27: A bimetallic conducting loop with junctions maintained at $T_1$ and $T_2$. If $T_1 \neq T_2$, and $\mathbf{L}^{12}_A / \mathbf{L}^{11}_A \neq \mathbf{L}^{12}_B / \mathbf{L}^{11}_B$, then the heat current induces a potential $V \propto T_2 - T_1$. 

40
where \( S = \frac{L_{12}}{L_{11}} \) is called the thermopower and is a property of a material.

The potential measured around the loop is given by

\[
V = \int_{0}^{1} E_B dx + \int_{1}^{2} E_A dx + \int_{2}^{0} E_B dx
\]  

(94)

or

\[
V = S_B \left\{ \int_{0}^{1} \frac{\partial T}{\partial x} dx + \int_{2}^{0} \frac{\partial T}{\partial x} dx \right\} + S_A \int_{1}^{2} \frac{\partial T}{\partial x} dx
\]  

(95)

\[
= S_B \int_{2}^{1} \frac{\partial T}{\partial x} dx + S_A \int_{1}^{2} \frac{\partial T}{\partial x} dx
\]  

(96)

\[
= (S_A - S_B) \int_{T_1}^{T_2} dT = (S_A - S_B) (T_2 - T_1)
\]  

(97)

Or if \( S_A \) and \( S_B \) are not \( T \)-independent \( V = \int_{T_1}^{T_2} dT (S_A - S_B) \).

So if \( T_1 \neq T_2 \) and \( S_A \neq S_B \), then the heat current induces an emf! This is called the Seebeck effect ⇒ (solid state thermometer with ice \( H_2O \) as a reference).

### 6.5 Peltier Effect

Now consider the inverse situation where an electrical current \( j \) is driven through the loop which is held at a fixed temperature
Figure 28: An electrical current $j$ is driven through the loop which is held at a fixed temperature $\left( \frac{\partial T}{\partial x} = 0 \right)$. Then

$$j_Q = \mathcal{L}^{21} \mathcal{E} \quad j = \mathcal{L}^{11} \mathcal{E} \quad (98)$$

$$j_Q = \left( \frac{\mathcal{L}^{21}}{\mathcal{L}^{11}} \right) j = \tau j \quad (99)$$

This is known as the Peltier effect whereby heat is carried from one junction to the other or an electric current is accompanied by a heat current. One may use this effect to create an extremely simple (and similarly inefficient) refrigerator.
Figure 29: If $dT/dx = 0$ and $\pi_A = L_A^{21}/L_A^{11} \neq L_B^{21}/L_B^{11} = \pi_B$ then the electric current also induces a heat from one junction to another.

7 The Wiedemann-Franz Law (for good metals)

One may independently measure the thermal $\kappa$ and electrical $\sigma$ conductivities. However, in general one expects that $\kappa \propto \sigma T$

Figure 30: The thermal and electrical conductivities may be measured independently.

since in electrical conduction each election carries a charge $e$
and is acted on by a force $-e\mathbf{E}$. The current per unit electric field proportional to $e^2$. In thermal conduction each electron carries a thermal energy $k_B T$ and is acted on by a thermal force $-k_B \nabla T$. The heat current per unit thermal gradient is proportional to $k_B^2 T$, thus one expects

$$\frac{\kappa}{\sigma} \propto \frac{k_B^2 T}{e^2} \quad (100)$$

Due to the simplicity of these arguments, our formalism should reproduce this relationship. As we discussed before

$$\mathbf{j}_Q = \mathbf{j}_E - E_F \mathbf{j}_n \quad (101)$$

$$= \frac{1}{8\pi^3} \int d^3\mathbf{k} \ (E - E_F) \mathbf{v}(\mathbf{k}) f(\mathbf{k}) \quad (102)$$

In the linear approximation to the Boltzmann equation for $\mathcal{E}_x' = 0$, we get

$$\mathbf{j}_Q = \frac{1}{8\pi^3} \int d^3\mathbf{k} \ (E - E_F) \frac{\partial f_0}{\partial T} v_x^2 \tau \left(-\frac{\partial T}{\partial x}\right) \quad (103)$$

where $E - E_F$ and $\frac{\partial f_0}{\partial T}$ are odd in $(E - E_F)$, for the Fermi liquid

$$\mathbf{j}_Q \cong -\left(\frac{\partial T}{\partial x}\right) \frac{1}{3} v_F^2 \tau_F \int \frac{d^3\mathbf{k}}{3\pi^3} (E - E_F) \frac{\partial f_0}{\partial T} \quad (104)$$

$$\mathbf{j}_Q = -\left(\frac{\partial T}{\partial x}\right) \frac{1}{3} v_F^3 \tau_F c_v \quad (105)$$
Figure 31: The function \((E - E_F)\frac{\partial f_0}{\partial T}\) is sharply peaked at the fermi surface and even in \(E - E_F\).

\[
\kappa = \frac{1}{3} v_F^3 \tau_F c_v
\]  
(106)

Now recall that for the Fermi liquid \(c_v = k_B \frac{\pi^2}{2} n k_B \frac{T}{k_B T_F}\), so that

\[
\kappa = \frac{1}{3} \frac{m^* v_F^2}{m^*} \tau_F k_B \frac{\pi^2}{2} n k_B \frac{T}{E_F} = \frac{\pi^2}{3} \tau_F n k_B^2 T m^*
\]  
(107)

However, also for the Fermi liquid, we found that \(\sigma = e^2 \tau_F \frac{n}{m^*}\), so

\[
\frac{\kappa}{\sigma} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 T
\]  
(108)

Of course this relationship only holds in a good metal. There are two reasons for this. First we are neglecting terms like \(\frac{(\mathcal{L}^{12})^2}{\sigma}\) in \(\kappa\) which are unimportant for a good metal (or if we electrically short the sample.) Second, we are assuming that \(\kappa\) is dominated by electronic transport.