Title: Drude continued and the Free Electron Gas

As was stated last Drude’s theory arrives at the empirical laws of Ohm for DC fields

\[
\vec{j} = \frac{ne^2\tau}{m} \vec{E} \quad \sigma = \frac{ne^2\tau}{m}
\]

This formalism can be extended to encompass AC fields.

Let

\[
\vec{E}(t) = \vec{E} e^{i\omega t} \quad q = -e = \text{unit of charge}
\]

\[
m\vec{a} = -e\vec{E} \exp(i\omega t) - \frac{m}{\tau} \vec{v}
\]

Assume a solution

\[
\vec{v} = \vec{v}_0 e^{i\omega t}
\]

\[
\vec{a} = +i\omega \vec{v}_0 e^{i\omega t}
\]

and

\[
im\omega \vec{v}_0 = -e\vec{E} - \frac{m}{\tau}\vec{v}_0
\]

\[
\vec{v}_0 = -e\vec{E}/m(1/\tau + i\omega)
\]

Now multiply by \(-ne:\)

\[
-ne\vec{v}_0 = \vec{j} = \frac{\tau ne^2\vec{E}/m}{(1 + i\omega\tau)}
\]

\[
\vec{j} = \sigma\vec{E} = \frac{\sigma_e \vec{E}}{(1 + i\omega\tau)}
\]

If \(\omega \rightarrow 0\) then we reduce back to the DC field expression. If \(\omega >> \frac{1}{\tau}\) then the response is out of phase with the applied field, no net current. (Electrons do not get a chance to scatter.) This implies that at some frequency, the electric field can propagate through the electron “gas”. For alkali metals (Na, K, etc.) this occurs in the UV. Thus, another success for Drude’s model.

Failures of the Drude theory:

1. The expected \(\frac{3}{2}k_BT\) contribution for each electron in the classical gas is not observed.

2. There is no fundamental method to determine the relaxation time \(\tau\).

\(v_{\text{electron}}\tau >> \text{lattice constant.}\)

3. Measured magnetic susceptibility, \(\chi\) (to be presented later), is much too small.
4. Experimentally some materials have positive Hall coefficients.

The solution to all above shortcomings was with the introduction of the Quantum Mechanical theory of Sommerfeld.

Thus we must replace classical electron gas Boltzmann distribution with Fermi-Dirac statistics which are appropriate for spin 1/2 particles.

\[
\text{Boltzmann: } f(\vec{v}) = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m v^2/2 k_B T}
\]

\[
\text{F-D: } f(\vec{v}) = \frac{(m/\hbar)^{3}}{4\pi^{3}} \frac{1}{\exp\left[(\frac{1}{2}mv^2 - k_B T_0)/k_B T\right] + 1}
\]

or more conventionally

\[
f(\epsilon_s) = \text{occupancy of a state, } s = \frac{1}{\exp[(\epsilon_s - \mu)/k_B T] + 1}
\]

\(\epsilon_s\) is the energy of an allowed electron state
\(\mu\) is the chemical potential (i.e., just the energy required to add an additional particle to the system.)

The explicit calculation for F-D statistics appears in myriad of thermodynamics texts.
This is my crude "intuitive" approach:

Examine a particular state, \(\epsilon_s\), for a single electron

<table>
<thead>
<tr>
<th>Energy</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>unoccupied</td>
<td>0</td>
</tr>
</tbody>
</table>

The Boltzmann occupancy factor

\[
< n_s > \equiv f(\epsilon_s) = \frac{0e^{-0/k_B T} + 1e^{-\epsilon_s/k_B T}}{e^{-0/k_B T} + e^{-\epsilon_s/k_B T}} = \frac{1}{e^{\epsilon_s/k_B T} + 1}
\]

In actuality, there are many electrons and many states which can be occupied. Consequently we must modify the previous expression with an appropriate weighting factor. Hence a factor \(\lambda\) is multiplied by \(e^{-\epsilon_s/k_B T}\).

\(\lambda \equiv \text{activity coefficient} = e^{\mu/k_B T}\) where \(\mu \equiv \text{chemical potential.}\)

This gives the familiar form of Fermi-Dirac statistics.
Another important aspect of the Sommerfeld model is to treat electrons as waves, not ballistic particles, which satisfy the Schrödinger wave equation:

\[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})] \Psi_k(\vec{r}) = \varepsilon_k \Psi_k(\vec{r})\]

If \(V(\vec{r}) = 0\) then \(\Psi_k = A e^{i\vec{k} \cdot \vec{r}}\) and \(E_k = \frac{\hbar^2 k^2}{2m}\) \(\vec{p} = \hbar \vec{k}\) \(\vec{p} = -i\hbar \nabla\)

subject to the normalization condition

\[\int \Psi^* \Psi dV = 1 \quad A^2 = \text{Volume} = V \quad \Psi_k = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}\]

Since we will be considering electrons in a crystal, we once again invoke periodic boundary conditions \(\Psi_k(x, y, z) = \Psi_k(x + L, y, z)\) and so on.

Thus

\[\begin{align*}
k_x L &= n_x 2\pi \quad \rightarrow \quad k_x = n_x \frac{2\pi}{L} \\
k_y L &= n_y 2\pi \quad \rightarrow \quad k_y = n_y \frac{2\pi}{L} \\
k_z L &= n_z \pi \quad \rightarrow \quad k_z = n_z \frac{\pi}{L}
\end{align*}\]

(This should look familiar)

So we have once again “digitized” reciprocal space.

Since

\[\begin{align*}
\vec{k} &= n_x \frac{2\pi}{L} \hat{x} + n_y \frac{2\pi}{L} \hat{y} + n_z \frac{2\pi}{L} \hat{z} \\
k^2 &= \left(\frac{2\pi}{L}\right)^2 n^2 \\
E &= \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{2\pi^2}{L}\right) n^2
\end{align*}\]

In reciprocal space each allowed \(k\)-vector occupies \((\frac{2\pi}{L})^3\)

volume in \(k\)-space

\[\mathcal{D}(\vec{k}) \, d^3k = \frac{V}{(2\pi)^3} d^3k\]
To find the ground state (lowest energy state) at $T=0$, one fills all the lowest energy levels subject to the constraints of the Pauli exclusion principle. The last state's energy is the Fermi Energy, $\varepsilon_F$, (or equivalently, the chemical potential at zero temperature).

Recall that the chemical potential, $\mu(T)$, is just the change is free energy, $F$, with changes in number of particles.

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V}$$

If there are $N$ total free electrons in a system,

$$2 \int_0^{k_F} \mathcal{D}(\vec{k}) d^3 k = N \quad \text{factor of 2 for spin degeneracy (\uparrow or \downarrow)}$$

or

$$\frac{4\pi k_F^3}{(2\pi)^3} = \frac{N}{2} \quad \Rightarrow \quad k_F = \left( \frac{3\pi^2 N}{V} \right)^{1/3}$$

$k_F$ is just the wave vector of an electron at the Fermi energy.

A sphere of radius $k_F$ is called the Fermi sphere. At $T = 0$, all states $k \leq k_F$ are occupied, and all states $k > k_F$ are unoccupied.

Since

$$E = \frac{\hbar^2 k^2}{2m}$$

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}$$

Typical values for $\epsilon_F$ range from 2-10 eV

$$\frac{1}{2}mv_F^2 = \epsilon_F \quad v_F \approx 10^6 \text{ m/sec} \text{ or about 1% of } c \text{ (the speed of light)}$$

Rather focusing on $\mathcal{D}(k)$, we can obtain $\mathcal{D}(\epsilon)$ or $\mathcal{D}(\hbar\omega)$.

$$\mathcal{D}(\epsilon) = \frac{dN(\epsilon)}{d\epsilon} \quad E = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}$$

$$N = \frac{V}{3\pi^2} \left( \frac{2mE}{\hbar^2} \right)^{3/2}$$
\[ D(\varepsilon) = \frac{3}{2} \left( \frac{2m}{\hbar^2} \right)^{1/2} \frac{V}{3\pi^2} E^{1/2} \]

\[ D(\varepsilon) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} \quad \text{in 3 dimensions} \]

In 1D \( D(\varepsilon) \propto E^{-1/2} \)

2D \( D(\varepsilon) \) is constant

Note: \( E = \frac{\hbar^2 k^2}{2m} = \hbar \omega \)

\[ D(\varepsilon) \]

\[ E^{1/2} \]

\[ \varepsilon \text{ (energy)} \]