Physics 0551 Lecture #17

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.

$$\begin{aligned}
\text{Let} \qquad \vec{E}(t) &= \vec{E}e^{i\omega t} \qquad\qquad q = -e = \text{ unit of charge} \\
m\vec{a} &= -e\vec{E}\exp(i\omega t) - \frac{m}{\tau}\, v
\end{aligned}$$

$$\begin{aligned}
\text{Assume a solution} \quad \vec{v} &= \vec{v_0}e^{i\omega t} \\
\vec{a} &= +i\omega\vec{v_0}e^{i\omega t}
\end{aligned}$$

$$\begin{aligned}
\text{and} \qquad im\omega\vec{v_0} &= -e\vec{E} \,-\, \frac{m}{\tau}\vec{v_0} \\
\vec{v_0} &= -e\vec{E}/m(1/\tau + i\omega)
\end{aligned}$$

$$\begin{aligned}
\text{Now multiply by } -ne: \quad -ne\vec{v_0} &= \vec{j} \,=\, \frac{\tau ne^2\vec{E}/m}{(1+i\omega\tau)} \\
\vec{j} &= \sigma\vec{E} = \frac{\sigma_o\vec{E}}{(1+i\omega\tau)}
\end{aligned}$$

If $\omega \to 0$ 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 <u>not</u> observed.

2. There is no fundamental method to determine the relaxation time τ.
   $v_{\text{electron}}\tau >>$ lattice constant.

3. Measured magnetic susceptibility, χ (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.

$$\begin{aligned}\text{Boltzmann:}\quad f(\vec{v}) &= n(\frac{m}{2\pi k_B T})^{3/2} e^{-mv^2/2k_BT} \\ \text{F-D:}\quad f(\vec{v}) &= \frac{(\frac{m}{\hbar})^3}{4\pi^3} \quad \frac{1}{\exp[(\frac{1}{2}mv^2 - k_BT_0)/k_BT] + 1}\end{aligned}$$

or more conventionally

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

ϵ_s is the energy of an allowed electron state
μ 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, ϵ_s, for a single electron		Energy
F-D statistics implies two possibilities $\rightarrow$	unoccupied	0
	occupied	ϵ_s

The Boltzman occupancy factor

$$< n_s > \equiv f(\epsilon_s) = \frac{0e^{-0/k_BT} + 1e^{-\epsilon_s/k_BT}}{e^{-0/k_BT} + e^{-\epsilon_s/k_BT}} = \frac{1}{e^{\epsilon_s/k_BT} + 1}$$

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 λ is multiplied by $e^{-\epsilon_s/k_BT}$.

$\lambda \equiv$ activity coefficient $= e^{\mu/k_BT}$ where $\mu \equiv$ 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:

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

If $V(\vec{r}) = 0$ then $\Psi_k = Ae^{i\vec{k}\cdot\vec{r}}$ and $E_k = \dfrac{\hbar^2 k^2}{2m}$ $\quad \vec{p} = \hbar\vec{k} \quad \vec{p} = -i\hbar\nabla$

subject to the normalization condition

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

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

Thus

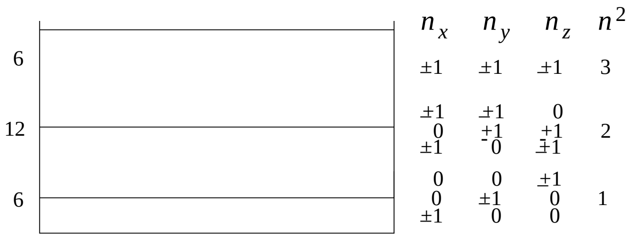
$$\begin{aligned} k_x L &= n_x 2\pi & \rightarrow \quad k_x &= n_x \tfrac{2\pi}{L} \\ k_y L &= n_y 2\pi & \rightarrow \quad k_y &= n_y \tfrac{2\pi}{L} \\ k_z L &= n_z 1\pi & \rightarrow \quad k_z &= n_z \tfrac{2\pi}{L} \end{aligned}$$

(This should look familiar)

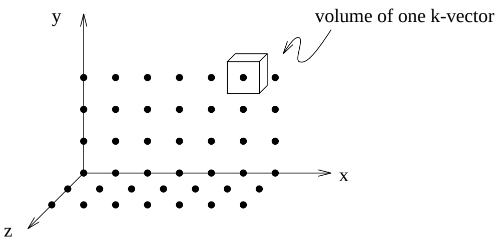
So we have once again "digitized" reciprocal space.

Since

$$\begin{aligned} \vec{k} &= n_x \frac{2\pi}{L}\hat{x} + n_y \frac{2\pi}{L}\hat{y} + n_z \frac{2\pi}{L}\hat{z} \\ k^2 &= (\frac{2\pi}{L})^2 n^2 \quad \text{and} \quad n^2 = n_x^2 + n_y^2 + u_z^2 \\ E &= \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(\frac{2\pi}{L}^2)n^2 \end{aligned}$$

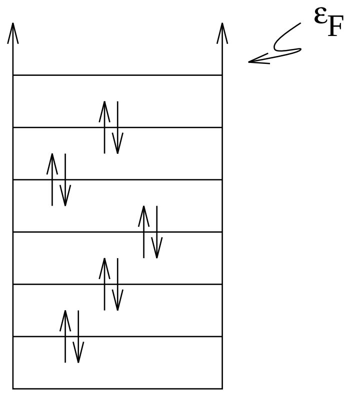


In reciprocal space each allowed k-vector occupies $(\frac{2\pi}{L})^3$ volume in k-space



$$\mathcal{D}(\vec{k})\; d^3k = \frac{V}{(2\pi)^3} d^3k$$

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, ε_F, (or equivalently, the chemical potential at zero temperature).



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

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

If there are N total free electrons in a system,

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

$$\text{or} \quad \frac{\frac{4}{3}\pi k_F^3}{(\frac{2\pi}{L})^3} = \frac{N}{2} \qquad\qquad k_F = (3\pi^2\frac{N}{V})^{1/3}$$

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
$$E \;=\; \hbar^2k^2/2m$$
$$\epsilon_F \;=\; \hbar^2k_F^2/2m = \frac{\hbar}{2m}(3\pi^2\frac{N}{V})^{2/3}$$

Typical values for ε_F range from 2-10 eV
$\frac{1}{2}mv_F^2 \;=\; \varepsilon_F \quad v_F \approx 10^6$ m/sec or about 1% of c (the speed of light)
Rather focusing on $\mathcal{D}(k)$, we can obtain $\mathcal{D}(\varepsilon)$ or $\mathcal{D}(\hbar\omega)$.

$$\mathcal{D}(\varepsilon) = \frac{dN(\varepsilon)}{d\varepsilon} \qquad E \;=\; \frac{\hbar^2}{2m}(3\pi^2\frac{N}{V})^{2/3}$$
$$N \;=\; \frac{V}{3\pi^2}(\frac{2mE}{\hbar^2})^{3/2}$$

$$\mathcal{D}(\varepsilon) = \frac{3}{2}(\frac{2m}{\hbar^2})^{1/2}\frac{V}{3\pi^2} \quad E^{1/2}$$

$$\mathcal{D}(\varepsilon) = \frac{V}{2\pi^2}\,(\frac{2m}{\hbar^2})^{3/2}E^{1/2} \qquad \text{in 3 dimensions}$$

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

2D $\mathcal{D}(\varepsilon)$ is constant

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