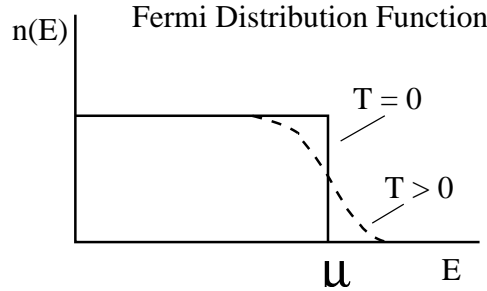# Lecture 3

Fermi-Dirac Distribution at Finite Temperature

Accepting well-known results of statistical mechanics, we know that the number of electrons in a given state at finite T is

$$n_n = \frac{1}{e^{\beta(\epsilon_n - \mu)} + 1} = f(\epsilon_n) \qquad \beta \equiv \frac{1}{kT}$$

This, of course, is the Fermi-Dirac distribution. The chemical potential

$$\mu = \left(\frac{\partial E}{\partial N} \right)_S = \left(\frac{\partial F}{\partial N} \right)_T$$

The Fermi distribution is symmetric about μ. This is particle-hole symmetry which means that the distribution of particles is the same as the distribution of holes. Note that at $\epsilon_n = \mu$, the occupation $f(\epsilon_n = \mu) = 1/2$. The smearing of the distribution $\sim kT$. At $T = 0$, distribution has an infinitely sharp-edge with $\mu(0) = \epsilon_F$.

What happens to μ at finite T? If the metal is isolated, μ must be fixed implicitly from the condition
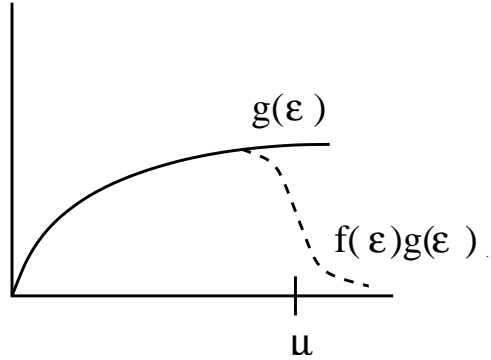
$$N = \sum_{k,\sigma} f_{k\sigma}(\mu, T) = \sum_{k,\sigma} \frac{1}{e^{(\epsilon_k - \mu)/kT} + 1}$$

(N = number of conduction electrons available.)

Converting the sum to an integral gives

$$N = \int_0^\infty d\epsilon \, f(\epsilon) g(\epsilon)$$

3.1

What happens to μ when T increases? The Fermi function $f(\epsilon)$ is symmetric around $\epsilon = \mu$, but $g(\epsilon)$, the density of states, is not - there are more states available at higher energies.

To keep the integral of $f(\epsilon)g(\epsilon)$ equal to N, $f(\epsilon)$ must decrease $\Rightarrow \mu$ moves down slightly as T increases. How much does μ decrease? A formal analysis is given in AM, pp. 45-57, and Appendix C. The informal argument goes as follows: If the density of states (DOS) $g(\epsilon)$ were constant, μ would stay exactly at ϵ_F for all T. At finite T, the average excitation is $\sim kT$ above ϵ_F, and so the average increase in the contribution of the density of states is

$$\delta g(\epsilon) \sim kT \frac{dg(\epsilon)}{d\epsilon}\bigg|_{\epsilon_F} \sim \frac{kT}{\epsilon_F} g(\epsilon_F) \quad (g(\epsilon) \sim \epsilon^{\frac{1}{2}})$$

Thus the total increase in $\int d\epsilon\, g(\epsilon)f(\epsilon)$ that would occur if $\mu = \epsilon_F$ is

$$\sim kT \left(\frac{kT}{\epsilon_F} \right) g(\epsilon_F).$$

To compensate for this increase, we have to shift μ down by an amount proportional to this. Since $[\mu] =$ energy, we expect

$$\Delta\mu \sim -kT \left(\frac{kT}{\epsilon_F} \right) \sim - \left(\frac{kT}{\epsilon_F} \right)^2 \mu(0)$$

(using $\mu(0) = \epsilon_F$). The precise answer is

$$\mu(T) = \mu(0) - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \mu(0)$$

3.2

Since $(T/T_F) \lesssim 1\%$ at most, $\mu(T)$ is nearly constant (and equal to ϵ_F) for the whole temperature region corresponding to the solid phase. Since electrons are thermally excited to within $\sim kT$ of ϵ_F, the thermal equilibrium properties, as well as some others, are determined entirely by states near the Fermi energy. Hence, we can take $g(\epsilon) \cong g(\epsilon_F)$. The density of states at the Fermi energy is

$$\overset{\nearrow \text{ No. of states}}{g(\epsilon_F)} = \frac{dn}{d\epsilon}\bigg|_{\epsilon_F} = V\frac{mk_F}{\hbar^2\pi^2} = \frac{Vm}{\hbar^2\pi^2}\underbrace{\sqrt{\frac{2m}{\hbar^2}}}_{k_F}\epsilon_F^{\frac{1}{2}} = V\frac{3n}{2\epsilon_F} \overset{\nwarrow \text{No. of electrons} \nearrow \text{per unit volume}}{}$$

$$\text{use} \Uparrow \epsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$$

$$\text{Note } g(\epsilon_F) = V\frac{mk_F}{\hbar^2\pi^2} \sim n^{1/3}m$$

$\left(n = \frac{k_F^3}{3\pi^2}\right)$. Order of magnitude estimate:

$$\frac{g(\epsilon_F)}{V} \sim 10^{23}\frac{1}{eV}\text{ per cm}^3 \gg \frac{1}{kT} \qquad\qquad \left(g(\epsilon_F) = V\frac{3n}{2\epsilon_F}\right)$$

$$g(\epsilon_F) = \frac{3}{2}\frac{N}{\epsilon_F}$$

From now on, we will approximate $g(\epsilon) \sim g(\epsilon_F)$ in integrals. We will also take the limits to be $\pm\infty$. Energies are centered on ϵ_F.

Thermodynamic Properties of Free-Electron Fermi Gas

1. **Specific Heat** $(C \sim T)$

(a) Qualitative Argument: At finite T, the characteristic energy $\sim kT$, number of states involved $\sim g(\epsilon_F)k_B T$,

$$\Rightarrow E \sim (kT)^2 g(\epsilon_F) \Rightarrow C_V = \frac{\partial E}{\partial T}\bigg|_v \sim k_B^2 T\, g(\epsilon_f)$$

$$\nwarrow \text{measure energy from } \epsilon_F = 0$$

3.3

(b) Quantitative Argument:

$$\bar{E}(T) \;=\; \sum_{k\sigma} n_{k\sigma}\epsilon_k$$

$$C_V \equiv \frac{d\bar{E}}{dT} \;=\; \sum_{k\sigma}\frac{dn_{k\sigma}}{dT}(\epsilon_k - \mu(0))$$

$$\left(\text{Note that the second term } \mu(0)\sum_{k\sigma}\frac{dn_{k\sigma}}{dT} = \mu(0)\frac{d}{dT}\underbrace{\left(\sum_{k\sigma}n_{k\sigma}\right)}_{=N} = 0\right)$$

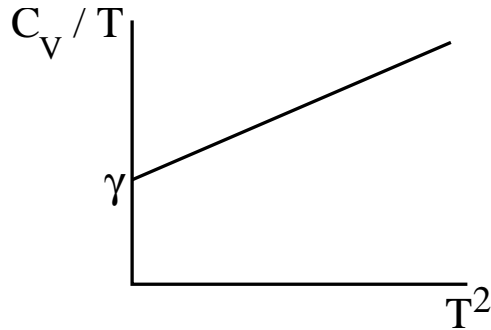$$C_V \;=\; \int g(\epsilon)(\epsilon - \mu)\frac{df}{dT}d\epsilon \qquad (n_{k\sigma} \to f(\epsilon))$$

$$\cong\; g(\epsilon_F)\int_{-\infty}^{\infty}(\epsilon - \mu)\frac{df}{dT}d\epsilon$$

$$=\; g(\epsilon_F)\frac{1}{k_B T^2}\int_{-\infty}^{\infty}(\epsilon - \mu)^2\frac{e^{(\epsilon-\mu)/kT}}{(e^{(\epsilon-\mu)/kT}+1)^2}d\epsilon$$

$$\equiv\; g(\epsilon_F)k_B^2 T\int_{-\infty}^{\infty}\frac{x^2 e^x}{(e^2+1)^2}dx$$

$$=\; \frac{\pi^2}{3}k_B^2 T\, g(\epsilon_F) = \gamma T$$

In the second step above, note that $\partial f/\partial T$ is nonzero in the vicinity of the Fermi energy. Comparison with experiment (AM Table 2.3): the linear T-dependence is roughly right (note that the ionic specific heat $\sim T^3$). Often plot C_V/T versus T^2.

The coefficient of T is wrong if the free electron DOS is used. It is customary to write $C_V = \gamma T$. Note that $g(\epsilon_F)$, when expressed in terms of n, etc., is directly proportional

3.4

to m

$$\left(g(\epsilon_F) = \frac{Vmk_F}{\hbar^2\pi^2} = \frac{Vm(3\pi^2n)^{1/3}}{\hbar^2\pi^2} \right) \Rightarrow \gamma \propto g_{eff}(\epsilon_F) \propto m^*$$

Thus the fact that γ is not the free electron value γ_0 can be described by saying that the electron has an effective mass m^* that gives it a different DOS. We can define

$$g_{eff}(\epsilon_F) \equiv \frac{C_v^{exp}}{\frac{\pi^2}{3}k_B^2 T}$$

and

$$\frac{m^*}{m} = \frac{g_{eff}(\epsilon_F)}{g(\epsilon_F)} = \frac{\gamma}{\gamma_0}$$

(It turns out that there are lots of different ways to define the effective mass and they tend to give somewhat different numbers. What we have in the case of the specific heat is the thermal effective mass.) Typically, $m^* \sim$ few $\cdot m$. But heavy fermion systems have $m^*/m \sim 10^2 - 10^3$!

2. **Pauli Paramagnetism** (AM pp. 663-6)

What happens when we apply a magnetic field? The response of the electrons is reflected in the susceptibility: $\vec{M} = \chi\vec{H}$. In the case of an electron gas, there are two contributions to the susceptibility: Orbital diamagnetism and spin (Pauli paramagnetism). These two effects can be separated in NMR. Here we will consider the paramagnetic term.

The electron has a magnetic moment $\vec{\mu}_B$ directed along its spin which interacts with $\vec{H}$. The energy is $\pm\mu_B H$ (the sign depends on the spin). Thus energy of up (down) spins is shifted down (up) by $\mu_B H$.

g$_+(\varepsilon)$

T = 0, H = 0

ε_F

ε

g$_-(\varepsilon)$

g$_+(\varepsilon)$

μH

μH

ε_F

ε

g$_-(\varepsilon)$

T = 0, H $\neq$ 0
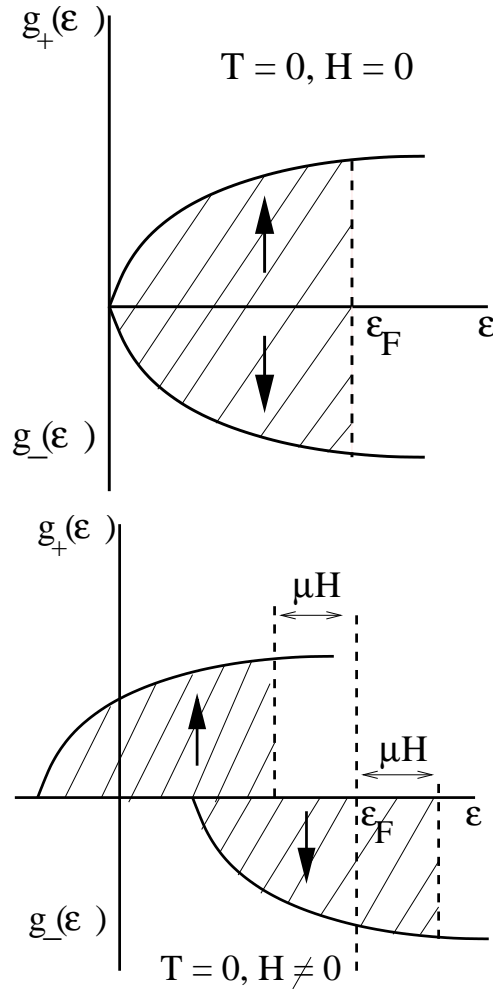
In equilibrium, spins will flow over from down to up to compensate, and the resulting magnetization will be $2 \times \mu_B \times$ (number flowing). The "2" comes because flipping a spin from $\downarrow$ to $\uparrow$ changes its magnetization from $+\mu_B$ to $-\mu_B \Rightarrow \delta \vec{M} = 2\mu_B$. The number flowing = (number in the surplus region above ϵ_F) = $\frac{1}{2}g(\epsilon_F)\mu_B H$ since $g(\epsilon_F)$ is the density of states for both spins. Hence

$$M = \mu_B^2 g(\epsilon_F) H$$

$$\boxed{\chi = \mu_B^2 g(\epsilon_F)}$$

This should be approximately independent of T since the picture is the same at finite T. Comparison with experiment (AM Table 31.5, p. 664): qualitative agreement but not quantitative.

Suppose there were simply an error in the DOS: $g(\epsilon_F) \Rightarrow g_{\mathit{eff}}(\epsilon_F)$, i.e., $m \to m^*$. We would still predict a unique ratio for $C_V/\chi T$ since $g(E_F)$ cancels out.

$$\boxed{\frac{C_v}{\chi T} = \frac{\pi^2}{3}\frac{k_B^2}{\mu_B^2}}$$

This is the right order of magnitude but it is not exactly the right number. This indicates that things cannot in general just be fixed up by attributing an effective mass to the electron. (Electron-electron interactions need to be taken into account.)
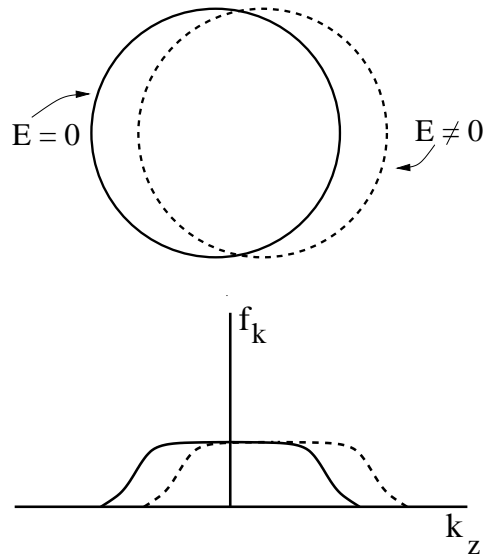
Transport properties

How do the transport principles change when we replace Boltzmann statistics with Fermi-Dirac statistics?

(Note that we can define the position as well as the momentum of electrons as long as everything varies over length scales $\gg k_F^{-1}(\sim 2-3\mathring{A})$. Strictly: $\Delta k \cdot \Delta r \gtrsim 1$, relevant values of $\Delta k \sim k_B T/v_F \Rightarrow \Delta r \gtrsim \frac{v_F}{k_B T} \sim \left(\frac{T_F}{T}\right) k_F^{-1} \sim \frac{10^4}{10^2} \cdot 2\mathring{A} \sim 200\mathring{A}$))

Electrical Conductivity

$(T = 0)$

(Note: displacement $\ll k_F$, and thermal smearing at reasonable T.) Two ways to look at this: Either the whole Fermi Sea is accelerated or the electrons are taken from one side to the other. Scattering processes either slow down whole sea or scatter across the

Fermi surface. Energy conservation implies the latter is true $\Rightarrow$ all the action goes on at the Fermi surface.

The DC conductivity turns out to be the same as before.

Let's calculate $\left.\dfrac{dj}{dt}\right|_{field}$:

Rate of change of electric current $= (e/m) \times$ rate of change of total momentum $= (e/m) \times$ total force $= \dfrac{e}{m} ne \vec{E} = \dfrac{ne^2}{m} \vec{E}$

$$\Rightarrow \left.\frac{d\vec{J}}{dt}\right|_{field} = \frac{ne^2}{m} \vec{E} \quad \text{as in Drude theory}$$

Now calculate $\left.\dfrac{dj}{dt}\right|_{collision}$. As before,

$$\left.\frac{d\vec{J}}{dt}\right|_{collision} = -\frac{\vec{J}}{\tau}$$

$$\Rightarrow \left.\frac{d\vec{J}}{dt}\right|_{total} = \left.\frac{d\vec{J}}{dt}\right|_{field} + \left.\frac{d\vec{J}}{dt}\right|_{coll} = \begin{cases} 0 & \text{for DC} \\ \dfrac{d}{dt}\left(\vec{J_0} e^{i\omega t}\right) & \text{for AC} \end{cases}$$

$$\Rightarrow \sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau} \quad \text{where} \quad \sigma_0 = \frac{ne^2\tau}{m}$$

Same as before. Hence all EM properties are identical in the two theories (including Hall effect, etc.).

One difference: $\ell = v\tau$ where v is "typical" velocity. In Drude theory v was the classical thermal velocity $v_{th} \sim \sqrt{kT/m}$. In Sommerfeld theory, v should be the Fermi velocity: $v_F \gg v_{th}$. Hence ℓ is much longer: at room temp. $\tau \sim 10^{-14}$ sec, $v_F \sim 10^8 \frac{cm}{s}$, $\Rightarrow \ell \sim 10^{-6}$ cm $\sim 100\text{Å}$.

Thermal Conductivity

Higher-energy particles tend to move in the positive direction, so the distribution is distorted.

3.8
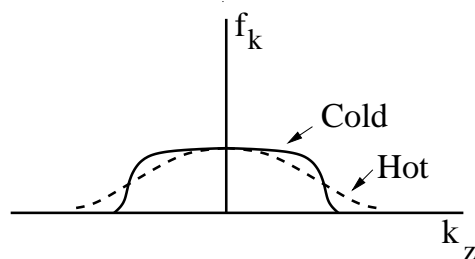
Note: No net electron current in this approximation. $\langle \vec{j} \rangle = -ne\langle \vec{v} \rangle = 0$ since $\langle \vec{v} \rangle = 0$.

Derivation of formula goes as before:

$$\left(\frac{d\vec{J}_Q}{dt} \right)_{diff} = -\frac{1}{3}\overline{v^2}C_V \nabla T$$

but $\overline{v^2}$ must now refer to the "active" electrons, so $\overline{v^2} = v_F^2$. Also

$$\left(\frac{d\vec{J}_Q}{dt} \right)_{coll} = -\frac{\vec{J}_Q}{\tau} \qquad \text{as before}$$

$$
\begin{aligned}
\frac{d\vec{J}}{dt}\bigg|_{tot} &= \frac{d\vec{J}}{dt}\bigg|_{diff} + \frac{d\vec{J}}{dt}\bigg|_{coll} = 0 \\
\frac{d\vec{J}}{dt}\bigg|_{diff} &= -\frac{d\vec{j}}{dt}\bigg|_{coll} \\
\vec{j}_Q &= -\kappa \nabla T \\
\kappa &= \frac{1}{3}C_V\overline{v^2}\tau = \frac{1}{3}C_V v_F^2 \tau
\end{aligned}
$$

Wiedemann-Franz Law

Derivation proceeds as before up to

$$\frac{\kappa}{\sigma T} = \frac{1}{3}\frac{C_V \overline{v^2} m}{ne^2 T}$$

But now $m\overline{v^2} = mv_F^2 = 2\epsilon_F$ and

$$C_V = \frac{\pi^2}{3}k_B^2 T g(\epsilon_F) = \pi^2 k_B^2 T \frac{n}{2\epsilon_F} \qquad \left(g(\epsilon_F) = \frac{3n}{2\epsilon_F} \right)$$

$$\Rightarrow \boxed{\frac{K}{\sigma T} = \frac{\pi^2}{3}\frac{k_B^2}{e^2}} \left(\text{Instead of } \frac{3}{2}(\frac{k_B}{e})^2 \right)$$

$$\frac{K}{\sigma T} \sim 2.44 \times 10^{-8}\frac{W-\Omega}{k^2}$$

which is in very good agreement with experiment for most regimes.

Thermopower:

Again, the derivation goes through as in the Drude model up to the point $Q = -\frac{1}{3e}\frac{C_V}{n}$. Now, however, $C_V = \frac{\pi^2}{3}k_B^2 T g(\epsilon_F) = \frac{\pi^2}{2}k_B(T/T_F)n$ so $Q = -\frac{\pi^2}{6}\frac{k_B}{e}(T/T_F)$.

3.9

This is in much better agreement with experiment (but still not quantitatively right, and can even have the wrong sign).

Electron-electron collisions - Effect on σ and κ

Any collision between electrons must conserve both energy and momentum (or $\vec{k}$):

$$\epsilon_1 + \epsilon_2 = \epsilon_1' + \epsilon_2'$$
$$\vec{p}_1 + \vec{p}_2 = \vec{p}_1' + \vec{p}_2'$$

Now the electrical current carried by a single electron is $(-e)\vec{v} = (-e/m)\vec{p}$. Hence the total electrical current is unchanged by electron-electron collisions, so there is no contribution to the relaxation rate $\tau_{e\ell}^{-1}$.

On the other hand, the heat current carried by an electron is $(\epsilon_k - \mu)\vec{v} = (\epsilon - \mu)(\vec{p}/m)$. The sum of this quantity *can* be changed by collisions. Hence, it contributes to τ_Q^{-1}. (Consider for example $(\epsilon_1 = 2\epsilon_F, \ \vec{p}_1 = p_F\hat{x}; \ \epsilon_2 = 3\epsilon_F, \ \vec{p}_2 = -p_F\hat{x}) \rightarrow (\epsilon_1' = \epsilon_F, \ \vec{p}_1' = -p_F\hat{x}; \ \epsilon_2' = 4\epsilon_F, \ \vec{p}_2' = +p_F\hat{x})$. Energy and momentum are conserved. But $\Sigma(\epsilon - \mu)\vec{p}/m$ goes from $-\epsilon_F\frac{p_F}{m}\hat{x}$ to $+3\epsilon_F\frac{p_F}{m}\hat{x}$) (the product $(\epsilon - \mu)\frac{\vec{p}}{m}$ is not conserved in collisions.)

Thus, if electron-electron collisions are important, we would expect W-F law to be violated. Experimentally, however, it appears to hold very well (in most regimes). Why? (answer below)

Effect of Exclusion Principle on Electron-Electron Collisions

For this purpose, we can forget all about the conservation of momentum and just concentrate on the conservation of energy. According to Fermi's Golden Rule, the scattering probability $\propto$ (total) density of final states available. For example, consider a "typical" electron with energy $(\epsilon - \mu) \sim kT$ making a collision. It can collide with an electron down to $\sim -kT$ of the Fermi surface (if below, no final states available): The total "rearrangeable" energy in the collision is $\sim 2kT$. Of the final energies, ϵ_1' and ϵ_2', one is fixed by energy conservation; the other is free and clearly ranges over $\sim kT$ $(\epsilon_F - kT \lesssim \epsilon' \lesssim \epsilon_F + kT)$. Hence we have one factor of $[kTg(\epsilon_F)]$ for the electron collided with, and another for the final state. Thus, the collision prob. $\propto [kTg(\epsilon_F)]^2$, or since

3.10

$g(\epsilon_F) \sim T_F^{-1}$, $\tau_{e\ell-e\ell}^{-1} \sim (T/T_F)^2 \tau_{classical}^{-1}$ (relative to what it would be in a classical gas). So, even if the mean free path ℓ in a classical gas was approximately the inter-electron spacing (say $\sim 1 \mathring{A}$), for any realistic degenerate system, it will be about 10^4 times this ($\ell \sim 10^4 \ell_{classical} \sim 10^4 \mathring{A}$). Hence, electron-electron collisions are negligible compared to other scattering mechanisms.

Successes and Failures of the Free Electron Model (after AM, Ch 3)

1. **Static Thermodynamic Properties**

   Compressibility : Right order of magnitude but not quantitatively right

   Specific Heat : the linear term seen experimentally and has right order of magnitude, but model gives wrong quantitative value.

   Pauli Paramagnetism : Temperature independence is as predicted, order of magnitude right, quantitatively wrong. *Cannot* fix by simply introducing effective mass m^*.

2. **Transport Properties**

   - DC conductivity is plausible, but τ (or ℓ) has to be put in by hand - difficult to understand T-dependence within free electron model. Also resistivity ρ can be anisotropic. Recall Matthiessen's rule: $\tau^{-1} \sim \tau_o^{-1} + (\tau^{-1})'T$

   - AC conductivity qualitatively right, but wrong ω-dependence in optical regime

   - Wiedemann-Franz law: very well obeyed for $T \sim 300$ K and $T \lesssim$ few Kelvin; otherwise it appears to fail ($C \sim T^3$ due to phonons, κ due to phonons too)

   - Hall coefficient - order of magnitude is right, but exact magnitude and sometimes even the sign is wrong

   - Thermopower - ditto

   - magnetoresistance - not in general zero as predicted by model (ρ_{xx})

3. **Fundamental Difficulties**

Why are some elements nonmetals? What determines the number of conduction electrons? (It isn't just the valence - consider, e.g., diamond and other forms of carbon.)

We have made 3 major approximations:

(1) Free-electron approx. (ignore ions)

(2) Independent electron approx. (ignore electron-electron interactions)

(3) Relaxation-time approx. (ignore dependence of scattering process on history, etc. of electrons)

Most of the difficulties are resolved if we keep (2) and (3) but relax (1). Thus we must

(a) discuss ions as independent dynamic entities

(b) discuss effect of ions on electrons *between* collisions (periodic potential)

(c) discuss effect of ions on electrons as source of collisions (electron-phonon interactions)

We now turn our discussion to (b). (a) and (c) come later.