Lecture 12

Tuesday, February 08, 2011

Finite Temperature Physics of Free Electrons

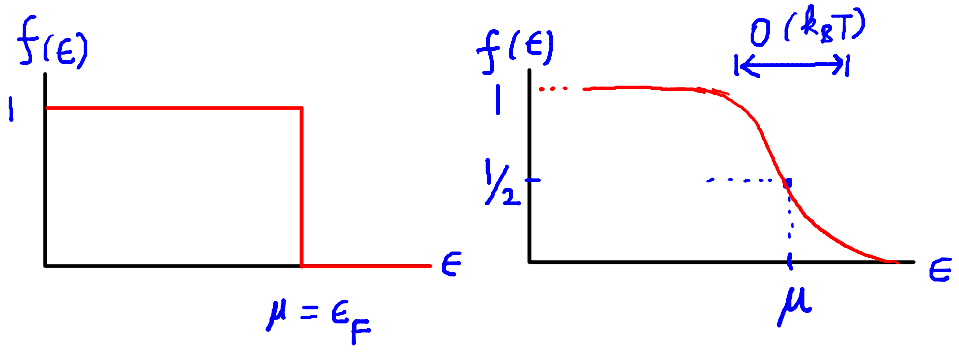
Since T_F is much larger than any interesting temperature scale (room temperature or melting temperature) for common metallic solids, it should be noted that any physical quantities that has a finite value at $T = 0$ for common metals will likely have only a small correction at a finite temperature.

Examples of such quantities are **pressure, bulk modulus, total energy, chemical potential**, etc. These quantities are basically determined by the property of the Fermi sea at $T = 0$, and the small perturbation of the Fermi surface at a finite temperature gives only a small correction.

Of course, there are quantities that vanish (or become negligible) as $T \to 0$, and for those quantities, the small perturbation of the Fermi surface at a finite temperature is the only reason that such quantities are significant. Examples include **entropy, heat capacity, thermally induced electron mean free path**, etc.

Fermi Dirac distribution function

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}$$



- At zero temperature, $f(\epsilon)$ is a "step-down" function and $\mu = \epsilon_F$.
- $f(\epsilon) = \frac{1}{2}$ at $\epsilon = \mu$.
- $f(\epsilon)$ is different from its $T = 0$ form only in the $O(k_B T)$ vicinity of μ.

Finite Temperature Physics -- Some important results

It is possible to derive the following (see Homework; or "Sommerfeld expansion" in A&M):

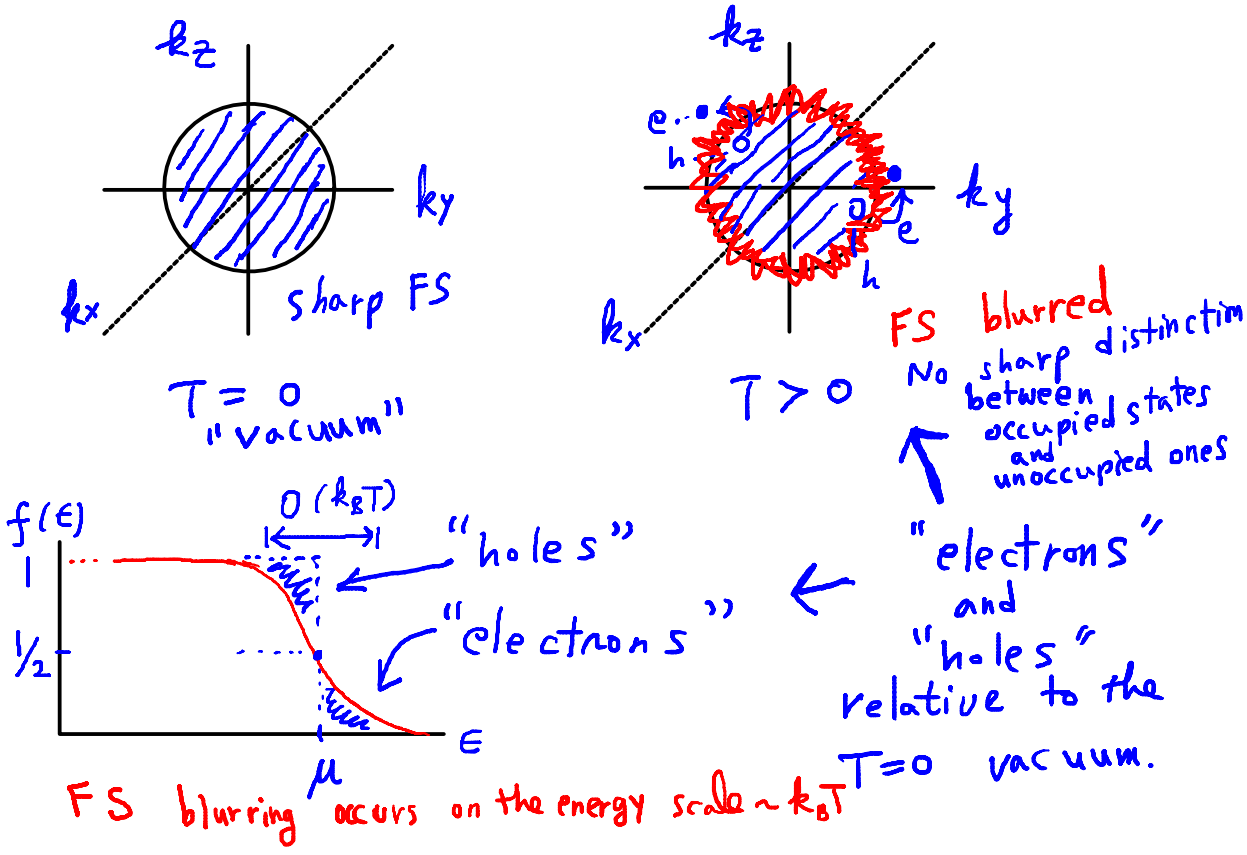
$$\mu \approx \epsilon_F \left(1 - \frac{1}{12}\pi^2 \left(\frac{T}{T_F}\right)^2\right)$$

$$E = \int_0^\infty \epsilon D(\epsilon) f(\epsilon) d\epsilon \approx \frac{3}{5} N\epsilon_F + \frac{\pi^2}{6}(k_B T)^2 D(\epsilon_F)$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\pi^2}{3} k_B (k_B T) D(\epsilon_F) = \frac{\pi^2}{2} N k_B \left(\frac{T}{T_F}\right)$$

where in the last step, $D(\epsilon_F) = \frac{3N}{2\epsilon_F}$, N = number of electrons, is used.

Physical picture of E and C_V



In analogy with Dirac's picture for electrons and positrons, the Fermi sea at T = 0 can be thought of as the vacuum. Relative to that vacuum, at finite temperatures electron-hole (e-h) pairs proliferate.

(1) Typical energy of such an electron or a hole excitation $\sim k_B T$. (Note that this is relative to the vacuum energy!)

(2) The number of such electrons and holes $\sim D(\epsilon_F)k_BT$ (Why? Electron-hole pairs occur within the energy $\sim k_BT$ of $\mu \approx \epsilon_F$. With $T \ll T_F$, the density of states $\approx D(\epsilon_F)$ is a very good approximation. $D(\epsilon_F)k_BT \approx$ the number of states within the energy range of k_BT near ϵ_F.)

(3) The total thermal energy = (1) x (2) $\sim D(\epsilon_F)(k_BT)^2$.

This is the physical reason why we have, in general,

$$E - E(T=0) \sim D(\epsilon_F)(k_BT)^2 \quad \text{and} \quad C_V \sim D(\epsilon_F)(k_BT)T$$

up to numerical factors.

Also, $D(\epsilon_F) \sim N/\epsilon_F$, and so $C_V \sim Nk_B\left(\frac{T}{T_F}\right)$, which means that the heat capacity is reduced by a factor $\sim \frac{T}{T_F}$ in the degenerate fermion gas relative to the classical gas.

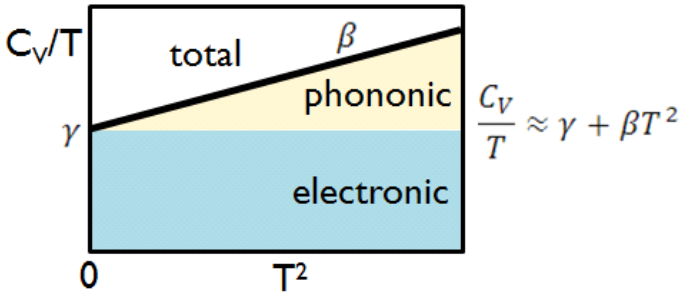
Heat capacity, electron gas plus phonon gas

In general, the heat capacity for a metal is the sum of the contribution from the electron gas and the phonon gas.

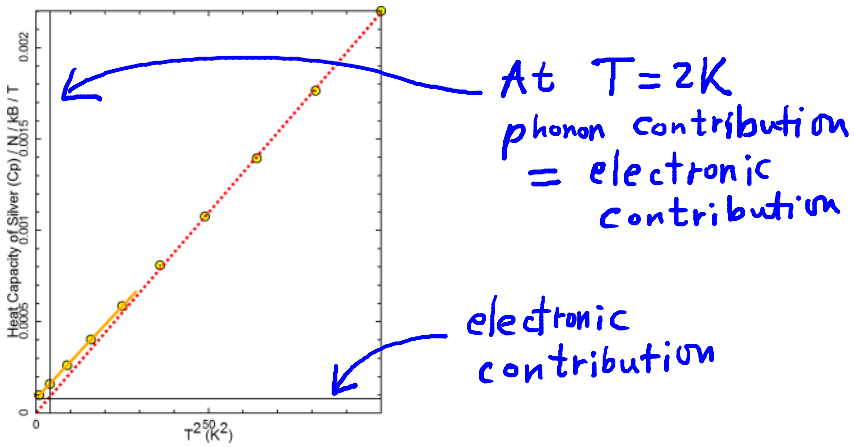
It can be written as (for $T \ll \theta_D, T_F$)

$$C_V \approx \gamma T + \beta T^3$$

$\gamma = \frac{\pi^2}{2} N_e k_B \frac{1}{T_F}$ and $\beta = \frac{12\pi^4}{5} N_m k_B \frac{1}{\theta_D^3}$. N_e = number of electrons. N_m = number of acoustical phonon modes = number of bases/lattice-points.



For this reason, many researchers plot the C_V function as above, where the y intercept directly gives the γ value. This is very important.



For instance, the above figure shows the heat capacity of Ag, revisited. In a previous lecture it was shown that the T^3 behavior does a good job (dotted line). However, you might have noticed that the last point at the low temperature end did not do a good job. Well, here is the full view, showing all the low temperature data. What it shows is that at 4 K and below, the electronic contribution, while small, does show the specific heat deviating from the pure phonon behavior. The y intercept can be easily obtained as 7.79e-5 in the unit shown above (1/K). Multiplying this by $R = N_A k_B = 8.314$e3 mJ/mole-K, we get the value of γ for the molar heat capacity: $\gamma = 0.65$ mJ/mole-K^2. This is very close to the value 0.61 calculated within the free electron model!

Generally, normal metals have $\gamma \sim 1$ mJ/mole-K^2. Thus, one might think that the electrons in normal metals are really like free electrons! This is quite mysterious since the bare Coulomb interaction between electrons is actually quite large ~ 10 eV ($\frac{e^2}{r} = \frac{e^2}{\hbar c}\frac{\hbar c}{r} = \frac{1}{137}\frac{1973}{r}$ eV if r is in Å). In real solids, the screening may reduce this energy, but still the Coulomb interaction remains to be significant ~ 1 eV, of the same order as the Fermi energy. One reason why such Coulomb interaction does not have a strong effect is due to the Pauli exclusion principle (read "Fermi liquid" in A&M), while the actual theory of a Fermi liquid is quite involved.

There are certain classes of materials where γ is very large ~ 1000. These materials (UBe_{13}, $CeCu_2Si_2$, …) are called "heavy fermions." Why?

$$\gamma \propto \frac{N_e k_B}{T_F} = \frac{N_e k_B^2}{\epsilon_F} = 2\frac{N_e k_B^2}{\hbar^2 k_F^2} m$$

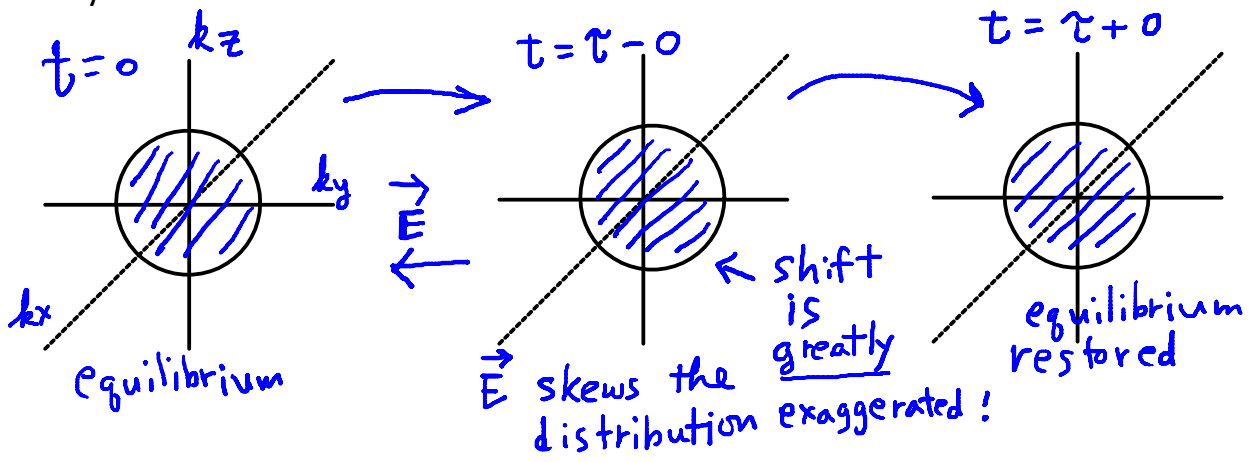
How can γ be so large? N_e and k_F are fixed by the chemistry (# of electrons per cell), and k_B and $\hbar$ are fundamental constants, and so the only way that γ can be so large is if m is very large. So, "heavy electrons" or "heavy fermions".

As the example of the heavy fermion shows, the "free electron" in the free

electron theory should be interpreted cautiously. It is better to call it "free quasi-electron" or "free Landau quasi-particle." However, these are the topics of higher level many body theory.

Conduction of electricity

The free electron theory explains why metals conduct electricity. Here is a simple theory.



In this picture, one imagines that the electron system is in an equilibrium, and is driven out of the equilibrium due to the electric field. On a time scale of τ, **the relaxation time**, the system goes through collisions and brought back to the equilibrium state again, the history of the past completely forgotten and the whole process starting all over again.

The relaxation time τ is **the average time** for the electron to travel before it is scattered.

How much current does the $\vec{E}$ field drive?

As we shall see, the relation $\hbar\dot{\vec{k}} = \vec{F}$ (a semi-classical equation of motion) is valid for free electrons or electrons in a crystalline potential, with $\hbar\vec{k}$ being the **crystal momentum** in general. We can use this equation for each electron state, with $\vec{F} = -e\vec{E}$. But what we ultimately want is the average over all electrons:

$$\frac{1}{N_e}\sum\hbar\dot{\vec{k}} = \frac{1}{N_e}\sum\vec{F}$$

The sum is over all occupied states. The RHS is simply $\vec{F}$, as $\vec{F}$ is a constant. Thus, this equation means that the average momentum $\frac{\sum\hbar\vec{k}}{N_e}$ increases gradually due to

$\vec{F}$. Note that at the equilibrium $\frac{\sum \hbar \vec{k}}{N_e} = 0$, while it will be a certain finite value at $t = \tau - 0$. We call that value $m\,\vec{v}_d$, where $\vec{v}_d$ is the **drift velocity**. Note that the drift velocity has nothing to do with the individual velocity of each electron, which is on the order of the Fermi velocity. Instead, $\vec{v}_d$ is the average net velocity gained by the electron over the time scale τ. Thus we get:

$$\frac{m\vec{v}_d}{\tau} = \vec{F} = -e\vec{E}$$

The current density that is gained by the applied field is

$$\vec{j} = -ne\vec{v}_d = -ne\left(-\frac{e\vec{E}\tau}{m}\right) = \frac{ne^2\tau}{m}\,\vec{E}$$

which defines the conductivity

$$\sigma = \frac{ne^2\tau}{m}$$

This is called the **Drude conductivity**.

Typical values

For normal metals, the conductivity is on the order of $(\mu\Omega\, cm)^{-1}$, which is in the cgs unit 1e18 Hz (note that Ω is an SI unit).

With this value of σ, τ can be estimated from $\tau = \frac{m\sigma}{ne^2}$, with $n \approx 0.1\ \text{Å}^{-3}$, as 3e-14 sec. That is 30 femto seconds. For a typical range of conductivity encountered in normal metals, τ ranges from $\sim$1 femto second to $\sim$10 nano second (at low T, pure metal).

The **mean free path**, $l = v_F\tau$, measures the distance that the electron travels between collisions. This is given by ~ 10 Å to 1 mm with a more typical value being between 100 Å to 1 μm.

Lastly, the drift velocity for a very large current density such as $1000\ \text{A/cm}^2$ is very tiny. $v_d = \frac{j}{ne} \approx 10^{-11}\, c \sim 10^{-9}\, v_F$. This is a truly negligible fraction of v_F, but since $\vec{v}_d$ is all in the same direction, it adds up to a macroscopic effect, while $\vec{v}_F$ adds up to a zero macroscopic effect since it is in all directions.

NOTE: In "strongly correlated electron systems" (notably high temperature superconductors, manganites, and heavy fermions), unusually low conductivity is often observed in metals: $(\mathrm{m\Omega\ cm})^{-1}$ or less. Often this implies a mean free path less than the lattice constant! This is an indication that the "free electron physics" as we know it and as we introduced it here is in a serious trouble.

Thermal conductivity and Wiedemann-Franz law

The thermal conductivity $\kappa = \frac{1}{3}\, v\, l\, \frac{C}{V}$ (see Lecture 09). In this free electron model, $v = v_F$, $l = v_F\tau$, $C = \frac{\pi^2}{2} N_e k_B \left(\frac{T}{T_F}\right) = \frac{\pi^2}{2}\, N_e k_B^2 \frac{T}{\epsilon_F} = \pi^2 N_e k_B^2 \frac{T}{m v_F^2}$. Thus,

$$\kappa = \frac{1}{3} v_F^2 \tau \pi^2 N_e k_B^2\, \frac{T}{m v_F^2} \frac{1}{V} = \frac{\pi^2}{3} k_B^2 \tau\, n \frac{T}{m}$$

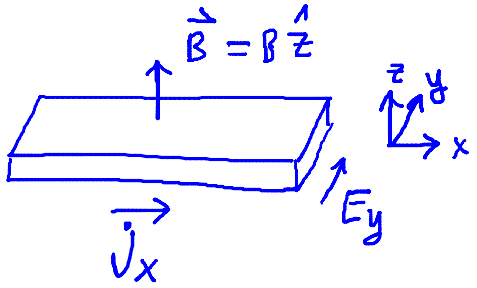
Note that $\frac{n\tau}{m}$ enters κ, as it enters $\sigma = \frac{n\tau e^2}{m}$. So, this suggests that

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 \equiv \text{Lorenz number}$$

The fact that this number is observed to be universal in many common metals (see table 5 of Kittel) is called **Wiedemann-Franz law**, lends much support to the free electron theory.

In pure metals, the electricity and the heat are both carried by the electron, and this fact underlies the Wiedemann-Franz law. However, note that the assumption of this law is that the same relaxation time τ applies to the electric conductivity and to the thermal conductivity, which was our assumption above. That this is *not* always the case can be realized when we consider the $T \ll \theta_D$ regime where the electron is scattered by a low energy phonon with $k \ll k_D$. Since, $k_D \sim k_F$, this means that the wave vector $\vec{k}$ of the electron hardly changes, meaning that the scattering is a forward scattering. Such forward scattering is not efficient at all in slowing down the electric current, while it is efficient in slowing down the heat current, since the typical energy of the phonon involved in such a scattering would be $k_B T$. So, Wiedemann-Franz law is not valid in this regime. Its ranges of validity are very low temperatures, where the impurity scattering dominates, and high temperatures ($T \gg \theta_D$), where short wave length phonons abound. In both cases, the change of the electron wave vector due to collisions is on the order of k_F.

Hall Effect



In this experiment, a B field is applied perpendicular to the sample (a "Hall bar"), say the z axis, while a current is induced by an electric field along the x axis. As the charge carrier experiences the Lorentz force, it will acquire some momentary current along the y direction. In the steady state, the Hall bar will develop a charge accumulation at the edges and the corresponding electric field E_y. The Hall coefficient R_H is defined as

$$R_H = \frac{E_y}{j_x B}$$

Within the free electron model, it is straightforward to calculate R_H. As before, we use the semi-classical equation of motion (which we will prove couple of lectures later): $\vec{F} = \hbar\dot{\vec{k}}$ with $\vec{F} = -e\left(\vec{E} + \frac{1}{c}\vec{v}_{\vec{k}} \times \vec{B}\right)$. Here, $\vec{v}_{\vec{k}}$ is the group velocity at $\vec{k}$, i.e. $\hbar\vec{k}/m$ for the current theory. Defining the drift velocity $\vec{v}$ as before (i.e. as the average of $\vec{v}_{\vec{k}}$ over all electrons) we get

$$m\frac{d\vec{v}}{dt} = -e\left(\vec{E} + \frac{1}{c}\vec{v} \times \vec{B}\right)$$

where $\vec{v}$ is the drift velocity. Note the transition from $\vec{v}_{\vec{k}}$ ($\sim$ Fermi velocity) to $\vec{v}$ (a very tiny fraction of Fermi velocity). As before, we apply the relaxation time approximation, which can be implemented by making the substitution $\frac{d}{dt} \to \frac{d}{dt} + \frac{1}{\tau}$. This substitution can be best understood as considering $\vec{v}$ as being related to the probability that the electron distribution will survive without collision $P(t)$: $P(t)\left(1 - \frac{dt}{\tau}\right) = P(t + dt)$ and so $\frac{dP}{dt} = -\frac{P}{\tau}$. Thus, in the absence of an external force, $\frac{d\vec{v}}{dt} + \frac{\vec{v}}{\tau} = 0$. In the presence of an external force

$$\frac{d\vec{v}}{dt} + \frac{\vec{v}}{\tau} = \frac{\vec{F}}{m}$$

In the current problem, we have

$$\frac{d\vec{v}}{dt}+\frac{\vec{v}}{\tau}=-\frac{e}{m}\left(\vec{E}+\frac{1}{c}\vec{v}\times\vec{B}\right)$$

We look for a steady state solution ($\frac{d\vec{v}}{dt}=0$) with $v_y=v_z=0$, $\vec{B}=B\hat{z}$, and $E_z=0$.

$$v_x=-\frac{\tau e}{m}E_x$$
$$v_y=0=-\frac{\tau e}{m}\left(E_y-\frac{1}{c}v_xB\right)$$

The first equation is what we already know. $j_x=-nev_x=\sigma E_x$, with $\sigma=\frac{ne^2\tau}{m}$. The second equation means: $\frac{E_y}{v_xB}=\frac{1}{c}$. Thus, $R_H=\frac{E_y}{j_xB}=-\frac{1}{nec}$.

$$R_H=-\frac{1}{nec}$$

This is the famous Hall coefficient (in the SI unit, $R_H=-\frac{1}{ne}$). The simplicity of this equation is the result of the simple model, the free electron model. While this theory is marvelously successful in many ways, it also comes short in important ways. According to this model, note that R_H is always negative. This is not true in general can be seen in Table 4. For instance, the Hall coefficient is positive for Be, Al, In, and As. It is also very large for Sb and Bi. All these anomalies need to be explained by the "band theory" which we will now explore. A more fundamental failure of the free electron theory is the inability to explain why certain substances such as Si, diamond or GaAs become insulators/semiconductors.