Lecture 11

Tuesday, February 14, 2012

Free electrons

This childish-sounding theory turns out to be not only very useful but also very deep.

In Kittel, some discussions are made with the fixed boundary condition (p. 134, 137). This is useful, but we will stick with the Born-von Karman boundary condition. Kittel chooses to work with the following free-particle wave function without any normalization factor.

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$$

An alternative choice would be to normalize this function with $\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$ where V is the volume. In this lecture note, we will follow Kittel, and will not worry about the normalization (until we have to, if ever, that is).

This wave function is an eigenstate in free space, with the energy eigenvalue:

$$\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$$

Here, m is the electron mass. Let us recall that the above wave function shows only the spatial part. Including the spin part, the wave function needs to be written as:

$$\psi_{\vec{k},s}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\ \chi_s$$

where χ_s can be $\chi_{1/2}$ ("up" spin) or $\chi_{-1/2}$ ("down" spin).

Following our discussion of any general form of wave in crystal, $P(\vec{r})e^{i\vec{k}\cdot\vec{r}}$, where $P(\vec{r})$ is the lattice periodic function, which in this case is simply a constant (number one), we should have

$$k_a = \frac{2\pi}{L_a} l, \qquad k_b = \frac{2\pi}{L_b} m, \qquad k_c = \frac{2\pi}{L_c} n$$

where $l, m, n =$ integers, k_a, k_b, k_c are the components of $\vec{k}$ along the $\vec{a}^*, \vec{b}^*, \vec{c}^*$

axes respectively, and L_a, L_b, L_c are the dimensions of the crystal along the $\vec{a}, \vec{b}, \vec{c}$ axes respectively. The volume per $\vec{k}$ value is $\frac{(2\pi)^3}{V}$ as in the previous lectures.

Thus, the periodic boundary condition "quantizes" $\vec{k}$, which in free space is proportional to the momentum $\vec{p} = \hbar\vec{k}$.

Fermi surface, and all other Fermi quantities ($\epsilon_F, T_F, k_F, p_F, v_F$)

In a cubic cm of a common metal such as Na, Ag, Au, Al, there are typically $10^{22} \sim 10^{23}$ conduction electrons, which are described as free electrons to a good approximation.

Consider $T = 0$. What is the ground state of this collection of free electrons? Recall that the electron is a spin 1/2 particle, which means that it is a Fermion. Thus, the ground state is formed by putting electrons one by one at the lowest energy level, as given by $\vec{k}$, $\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$ and spin "up" or "down."

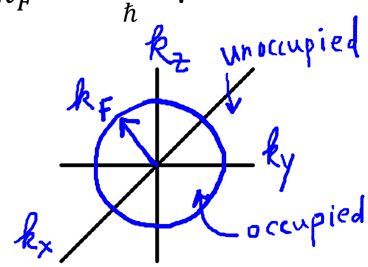
Filling electrons to the energy levels available, it is then obvious that there must be the maximum energy occupied. This energy is the **Fermi energy** ϵ_F. Now, here are a bunch of definitions. These definitions are given in general form (applicable even if the electron dispersion is not a free electron dispersion), and then the expression appropriate for the free electron dispersion is given.

The **Fermi temperature**: $T_F = \epsilon_F / k_B$.

The **Fermi wave vector**: $\vec{k}_F$ defined by $\epsilon_F = \epsilon_{\vec{k}=\vec{k}_F}$. Thus, $k_F = \frac{\sqrt{2m\epsilon_F}}{\hbar}$.

The **Fermi momentum**: $\vec{p}_F = \hbar\vec{k}_F$.

The **Fermi velocity**: $\vec{v}_F = \frac{1}{\hbar}\frac{\partial \epsilon_{\vec{k}}}{\partial \vec{k}}\Big|_{\vec{k}=\vec{k}_F}$. Thus, $v_F = \frac{\hbar k_F}{m}$.



Let N be the total number of electrons. k_F is determined from

Spin up and $\frac{4}{3}\pi k_F^3 \longrightarrow$ volume in $\vec{k}$ space

$$\text{spin up and down} \leftarrow 2\frac{\frac{4}{3}\pi k_F^3}{\frac{(2\pi)^3}{V}} = N$$

$\frac{4}{3}\pi k_F^3 \longrightarrow$ volume in $\vec{k}$ space

$\frac{(2\pi)^3}{V} \longrightarrow$ volume per $\vec{k}$ point

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

$n \longrightarrow$ electron # density

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

The typical number density is $10^{-22} \sim 10^{-23}\ \mathrm{cm}^{-3}$. And, thus **the typical Fermi energy is a few eV**. Converting this to temperature, **the typical Fermi temperature is 10,000 to 100,000 K**. $k_F \sim O(1)\ \text{Å}^{-1}$. $v_F \sim \frac{\hbar k_F}{m} = \frac{\hbar c}{mc^2} k_F c \sim \frac{1}{100} c$ (thus, the non-relativistic mechanics). [Note that the speed of sound is about 100 times smaller than v_F.]

Given the dispersion relation $\epsilon_{\vec{k}}$, the DOS is easily obtained as in the phonon problem.

$$\text{number of states in } d^3\vec{k} = \underbrace{2}_{\text{spin up and down}}\frac{d^3\vec{k}}{\frac{(2\pi)^3}{V}} = \frac{V}{4\pi^3}k^2 dk d\Omega$$

dN, the number of states between ϵ and $\epsilon + d\epsilon$ is obtained by integrating over the solid angle, since the dispersion relation ϵ is a function of k. [Note that here we use the energy variable ϵ, which is equivalent to ω, up to $\hbar$, in the phonon problem.]

$$dN = D(\epsilon)d\epsilon = \frac{V}{4\pi^3}k^2 dk 4\pi = \frac{V}{\pi^2}k^2 dk = \frac{V}{\pi^2}k\frac{m}{\hbar^2}d\epsilon = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2}d\epsilon$$

$$D(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2}$$

Density of states at ϵ_F is very important. By noting that $N \propto k_F^3 \propto \epsilon_F^{3/2}$, we get

$$\frac{dN}{d\epsilon_F} = D(\epsilon_F) = \frac{3}{2}\frac{N}{\epsilon_F}$$

Electrons and phonons -- different scales

The electronic energy scale ($1 \sim 10$ eV) is much higher, 100 to 1000 times higher than the phonon energy scale ($10 \sim 100$ meV). Equivalently, the Fermi temperature is much higher than the Debye temperature ($\sim O(100)$ K).

Thus, electrons are in a quantum mechanical state at room temperature, while phonons are more or less classical. It is often said that the electron gas is **degenerate**. What this means is that the system is in a quantum regime so that the identical nature of electrons is important. The density is high enough so that the mean distance between electrons r_s, defined through $\frac{V}{N} = \frac{4\pi}{3} r_s^3$, is much shorter than the thermal De Broglie wave length, about ten times as large as r_s at room temperature (calculation left for your exercise).

Another thing to take notice of is the difference in speeds. Ions vibrate with roughly the speed of sound while the electrons zip around 100 to 1000 times faster.

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

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

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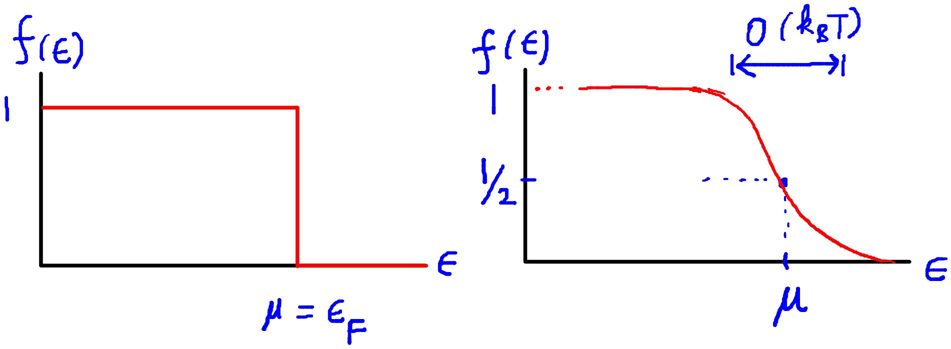


- At zero temperature, $f(\epsilon)$ is a "step-down" function and $\mu = \epsilon_F$.
- $f(\epsilon) = \frac{1}{2}$ at $\epsilon = \mu$.
- $f(\epsilon)$ is different from its $T = 0$ form only in the $O(k_B T)$ vicinity of μ.

Finite Temperature Physics -- Some important results

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

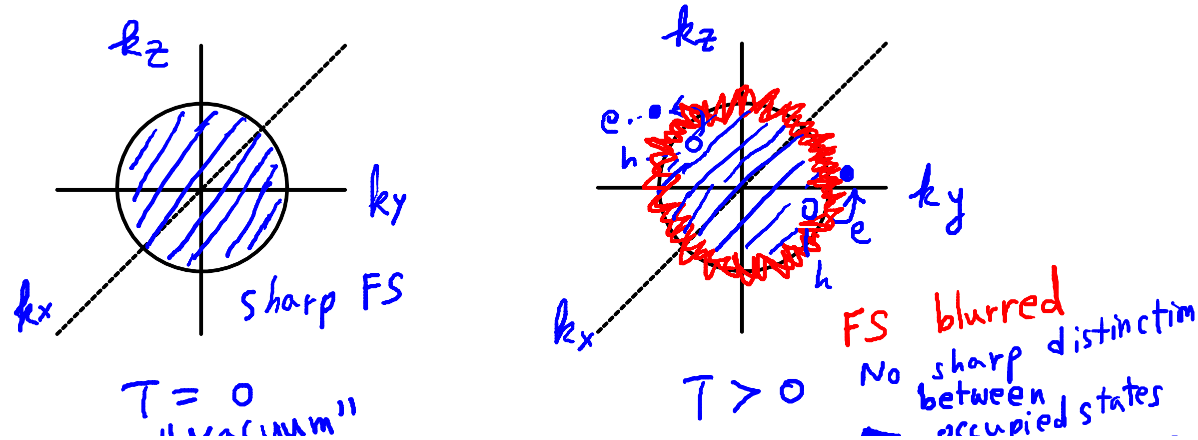
$$\mu \approx \epsilon_F \left(1 - \frac{1}{12}\pi^2 \left(\frac{T}{T_F}\right)^2\right)$$

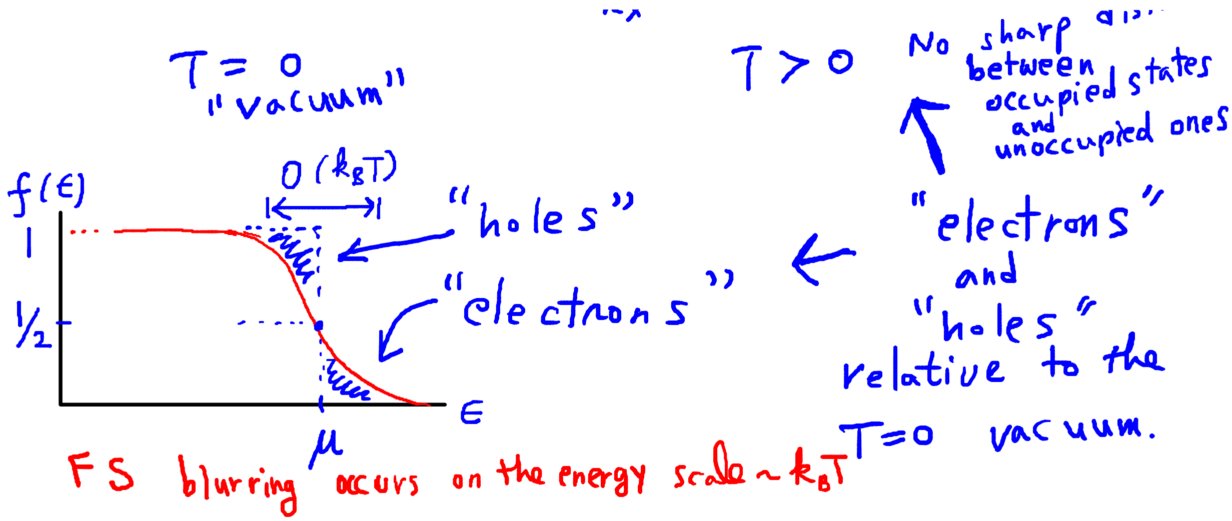
$$E = \int_0^\infty \epsilon D(\epsilon) f(\epsilon) d\epsilon \approx \frac{3}{5} N \epsilon_F + \frac{\pi^2}{6} (k_B T)^2 D(\epsilon_F)$$

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

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

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

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

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

up to numerical factors.

Also, $D(\epsilon_F) \sim N/\epsilon_F$, and so $C_V \sim N k_B \left(\frac{T}{T_F}\right)$, 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.

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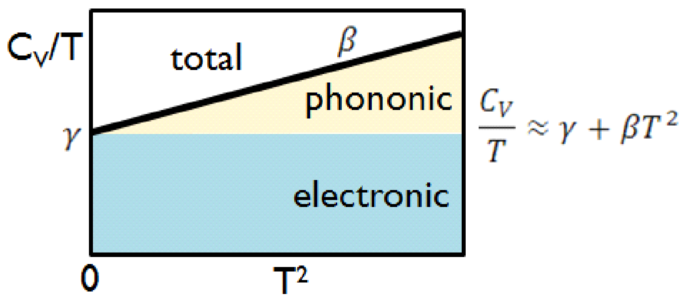
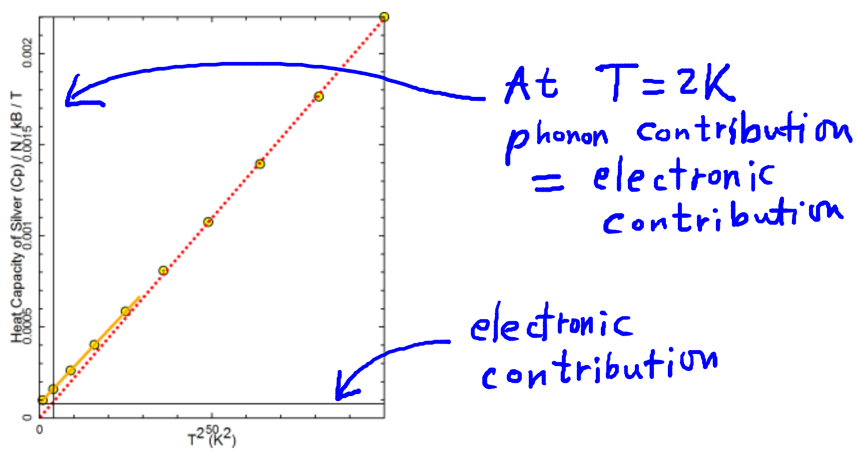
It can be written as (for $T \ll \theta_D, T_F$)

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

$\gamma = \frac{\pi^2}{2} N_e k_B \frac{1}{T_F}$ 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 $R = N_A k_B =$ 8.314e3 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 ($\mathrm{UBe}_{13}, \mathrm{CeCu}_2\mathrm{Si}_2$, …) 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.