

## **Lecture #17**

Today:

1. The Sommerfeld expansion and the calculation of properties near the Fermi level
2. Calculating the electronic contribution to the heat capacity of a metal at moderate temperatures.
3. Semiclassical theory of electron dynamics
4. Results of the SCT in particular the behavior of electrons near the band edge
5. Effective mass.

## The Sommerfeld expansion

We saw in the last lecture that the one can use the density of states function and the occupation number (Fermi function) to calculate thermodynamic properties of the metal or electron gas:

$$u = \int g(\mathbf{e}) f(\mathbf{e}) d\mathbf{e}$$

$$n = \int g(\mathbf{e}) f(\mathbf{e}) d\mathbf{e}$$

where the  $g(\mathbf{e}) f(\mathbf{e})$  term is the density of occupied states just as a reminder

$$g(\mathbf{e}) = \frac{\text{\# of one electron levels in the } \mathbf{e} \rightarrow \mathbf{e} + d\mathbf{e} \text{ range}}{V}$$

$$f(\mathbf{e}) = \frac{1}{e^{(\mathbf{e}-\mathbf{m})/kT} + 1}$$

we also gave the specific form of the for the free electron density of levels:

$$g(\mathbf{e}) = \begin{cases} \mathbf{e} > 0 & \frac{m}{\hbar^2 \mathbf{p}^2} \sqrt{\frac{2m\mathbf{e}}{\hbar^2}} \\ \mathbf{e} < 0 & 0 \end{cases}$$

The form of the total energy per unit volume and density remains valid even if the density of states function assumes a more sophisticated form.

In general the form of these integrals is fairly complex and difficult to solve. However as we saw in the previous lecture the electrons that determine the properties of the metal at room temperature come from levels that are very close to the Fermi surface. Let us examine an integral of the form:

$$\int_{-\infty}^{\infty} H(\mathbf{e}) f(\mathbf{e}) d\mathbf{e}$$

since the Fermi function differs from its zero temperature value only in the vicinity of  $\mathbf{m}$  the value of the integral will depend only on the values of  $H(\mathbf{e})$  near  $\mathbf{m}$ . That opens the possibility of approximating  $H(\mathbf{e})$ .

$$H(\mathbf{e}) = \sum_{n=0}^{\infty} \left( \frac{d^n}{d\mathbf{e}^n} H(\mathbf{e}) \right)_{\mathbf{e}=\mathbf{m}} \frac{(\mathbf{e}-\mathbf{m})^n}{n!}$$

substituting in the above equation carrying out integration by parts and using the symmetry properties of the Fermi function.

$$\int_{-\infty}^{\infty} H(\mathbf{e}) f(\mathbf{e}) d\mathbf{e} = \int_{-\infty}^{\mathbf{m}} H(\mathbf{e}) d\mathbf{e} + \sum_{n=1}^{\infty} (k_B T)^{2n} \underbrace{a_n}_{\substack{\text{a dimensional} \\ \text{constants} \approx 1}} \left( \frac{d^{2n-1}}{d\mathbf{e}^{2n-1}} H(\mathbf{e}) \right)_{\mathbf{e}=\mathbf{m}}$$

In most cases it is sufficient to retain only the leading terms in the expansion

$$\int_{-\infty}^{\infty} H(\mathbf{e}) f(\mathbf{e}) d\mathbf{e} = \int_{-\infty}^{\mathbf{m}} H(\mathbf{e}) d\mathbf{e} + \frac{\mathbf{p}^2}{6} (k_B T)^2 H'(\mathbf{m}) + O\left(\frac{k_B T}{\mathbf{m}}\right)^4$$

Lets examine the density integral under a constant volume condition where we are retaining only terms in the expansion that are of  $T^2$  order

$$\begin{aligned}
 n &= \int_{-\infty}^{\infty} g(\mathbf{e}) f(\mathbf{e}) d\mathbf{e} = \int_{-\infty}^m g(\mathbf{e}) d\mathbf{e} + \frac{p^2}{6} (k_B T)^2 g(\mathbf{m})' + O\left(\frac{k_B T}{m}\right)^4 \\
 &\simeq \int_0^{e_F} g(\mathbf{e}) d\mathbf{e} + \underbrace{\int_{e_F}^m g(\mathbf{e}) d\mathbf{e}}_{\approx (\mathbf{m} - \mathbf{e}_F) g(\mathbf{e}_F)} + \frac{p^2}{6} (k_B T)^2 g(\mathbf{e}_F)' \\
 &\rightarrow (\mathbf{m} - \mathbf{e}_F) g(\mathbf{e}_F) + \frac{p^2}{6} (k_B T)^2 g(\mathbf{e}_F)' = 0
 \end{aligned}$$

and the expression for the chemical potential becomes:

$$\mathbf{m} = \mathbf{e}_F - \frac{p^2}{6} (k_B T)^2 \frac{g(\mathbf{e}_F)'}{g(\mathbf{e}_F)}$$

where the Fermi energy is defined by the zero temperature values which we derived in class last lecture using this form:

$$\mathbf{m} = \mathbf{e}_F \left( 1 - \frac{1}{3} \left( \frac{p k_B T}{2 \mathbf{e}_F} \right)^2 \right)$$

Using a similar derivation for the energy density one can obtain:

$$u = u_0 + \frac{p^2}{6} (k_B T)^2 g(\mathbf{e}_F)$$

and the specific heat at constant density is given by

$$c_v = \left( \frac{\partial u}{\partial T} \right)_v = \frac{p^2}{3} (k_B)^2 T g(\mathbf{e}_F) = \frac{p^2}{2} \left( \frac{k_B T}{\mathbf{e}_F} \right) n k_B$$

which shows that the effect of the FD statistics on the specific heat is to depress it compared to the ideal gas value by a factor of

$$\sim \left( \frac{k_B T}{\mathbf{e}_F} \right)$$

A simple way to obtain the value of the energy is via the following argument:

$g(\mathbf{e}_F) k_B T \approx$  the number of electrons excited

$k_B T \approx$  the energy added by the excited electrons

$(g(\mathbf{e}_F) k_B T) k_B T \approx$  the addition to the energy contributed by thermal excitation

It turns out that at room temperatures the specific heat is dominated by ionic contributions which have a much stronger temperature dependence. At low temperatures the electronic degrees of freedom become the dominating factor in determining the specific heat.

## Failures of the free electron model

While the free electron was highly successful in predicting the linear term in the heat capacity it did not account for most of the significant properties of metals in particular: T dependence of conductivity, cubic term in specific heat, sign of the thermoelectric effect, directional dependence of conductivity.

## Semiclassical theory of electron dynamics

Table 12.1  
COMPARISON OF SOMMERFELD AND BLOCH ONE-ELECTRON EQUILIBRIUM LEVELS

	SOMMERFELD	BLOCH
QUANTUM NUMBERS (EXCLUDING SPIN)	$\mathbf{k}$ ( $\hbar\mathbf{k}$ is the momentum.)	$\mathbf{k}, n$ ( $\hbar\mathbf{k}$ is the crystal momentum and $n$ is the band index.)
RANGE OF QUANTUM NUMBERS	$\mathbf{k}$ runs through all of $k$ -space consistent with the Born-von Karman periodic boundary condition.	For each $n$ , $\mathbf{k}$ runs through all wave vectors in a single primitive cell of the reciprocal lattice consistent with the Born-von Karman periodic boundary condition; $n$ runs through an infinite set of discrete values.
ENERGY	$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$	For a given band index $n$ , $\varepsilon_n(\mathbf{k})$ has no simple explicit form. The only general property is periodicity in the reciprocal lattice: $\varepsilon_n(\mathbf{k} + \mathbf{K}) = \varepsilon_n(\mathbf{k})$ .
VELOCITY	The mean velocity of an electron in a level with wave vector $\mathbf{k}$ is: $\mathbf{v} = \frac{\hbar\mathbf{k}}{m} = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial \mathbf{k}}$	The mean velocity of an electron in a level with band index $n$ and wave vector $\mathbf{k}$ is: $\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}$
WAVE FUNCTION	The wave function of an electron with wave vector $\mathbf{k}$ is: $\psi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{V^{1/2}}$	The wave function of an electron with band index $n$ and wave vector $\mathbf{k}$ is: $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$ where the function $u_{n\mathbf{k}}$ has no simple explicit form. The only general property is periodicity in the direct lattice: $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$ .

The semiclassical theory assumes that the electrons suffer collisions which account for the emergence of finite conductivity. The motion of the electrons between collisions is governed by classical equations of motion:

$$\vec{p} = m\vec{\dot{r}} = \hbar\vec{k}$$

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

The interpretation of these equations of motion for a free electron from a QM point of view involves the motion of a wave packet of the form:

$$\mathbf{y}(\vec{r}, t) = \sum_{\mathbf{k}'} a(\mathbf{k}') e^{i\vec{k}' \cdot \vec{r} - i \frac{\hbar^2 k'^2}{2m} t}$$

$$a(\mathbf{k}') \approx 0 \text{ for all } |\mathbf{k}' - \mathbf{k}| > 0$$

where  $\mathbf{k}$  and  $\mathbf{r}$  represent the mean position and momentum about which the free electron wavepacket is localized subject to the uncertainty principle. We know though that the electrons in the metal are moving under the effects of a periodic potential and thus should

have the Bloch form. The question that surfaces is how do we take the collision effects into account. Keep in mind that the Bloch waves do have a velocity associated with them which just depends on the derivative of the band energy with respect to  $\vec{k}$ .

$$v_n(\vec{k}) = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} \epsilon_n(\vec{k})$$

this implies an infinite conductivity for a perfect crystal! So the intuitive picture of an electron colliding with the ions is absolutely wrong. This is a manifestation of the wave properties of the electrons and implies that a wave can propagate through an array of periodic scatterers with out loss. Any real crystal has defects in it and it is those defects that give rise to the finite conductivity. It is important to note that even a perfect crystal will exhibit finite conductivity due to thermal vibrations leading to deviations from perfect periodicity.

In order to treat the motion of electrons in between collisions we construct a wavepacket made of Bloch electrons:

$$\Psi(\vec{r}, t) = \sum_{\vec{k}'} a(\vec{k}') u_{n, \vec{k}'}(\vec{r}) e^{-i\epsilon_n(\vec{k}')t}$$

$$a(\vec{k}') \approx 0 \text{ for all } |\vec{k}' - \vec{k}| > 0$$

since  $\vec{k}$  is restricted to lie in the first BZ and  $\Delta k$  is thus small compared to  $1/a$  where  $a$  is the lattice constant it follows that the spread of a wavepacket of Bloch waves in real space is large compare to the lattice constant (draw the wavepacket and lattice comb).

The semiclassical model predicts how the position and wavevector of each electron varies under the influence of external electric and magnetic fields which are varying on a length scale that is much larger than the spatial extent of the wavepacket. The key piece of information that is used in the semiclassical model is the band structure of the metal  $\epsilon_n(\vec{k})$  which is then related to the transport properties of the electrons.

The evolution of the wavepacket under this model is in accordance with the following rules:

1. The band index is a constant of motion, interband transitions are assumed to be negligible.
2. The time evolution of the position and wavevector of an electron with band index  $n$  are determined by the following equations of motion:

$$\dot{\vec{r}} = v_n(\vec{k}) = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} \epsilon_n(\vec{k})$$

$$\hbar \dot{\vec{k}} = -e \left( \vec{E} + \frac{1}{c} v_n(\vec{k}) \times \vec{H} \right)$$

Note:

- (a) One should keep in mind that since we are using the Bloch form of the electron two wavefunctions which differ by a reciprocal lattice vector are identical.
- (b) The contribution of the electrons in the  $n$ -th band with wavevectors  $\vec{k}$  are given by the fermifunction.

$$f(\epsilon_n(\vec{k})) \frac{d^3k}{4\pi^3} = \frac{1}{e^{(\epsilon_n(\vec{k}) - \mu)/kT} + 1}$$

### Some basic results of the semiclassical equations of motion

1. Filled bands are inert and do not contribute to the electrical properties of the solid. Conduction is only due to those electrons that are in partially filled bands. Thus a solid which has filled bands will be an electrical and thermal (considering the electronic contribution to the heat conduction) insulator. The number of levels in each band is equal to twice the number of primitive cells in the crystal thus a solid can have completely full or empty bands only if it has an even number of electrons per primitive cell. This is a sufficient though not necessary condition for being an insulator.

1. Semiclassical motion of an electron in a DC field.

In a uniform electrical field:

$$k(t) = k(0) - \frac{eEt}{\hbar}$$

thus in a time  $t$  every electron changes its wavevector by the same amount.

The current is obtained:

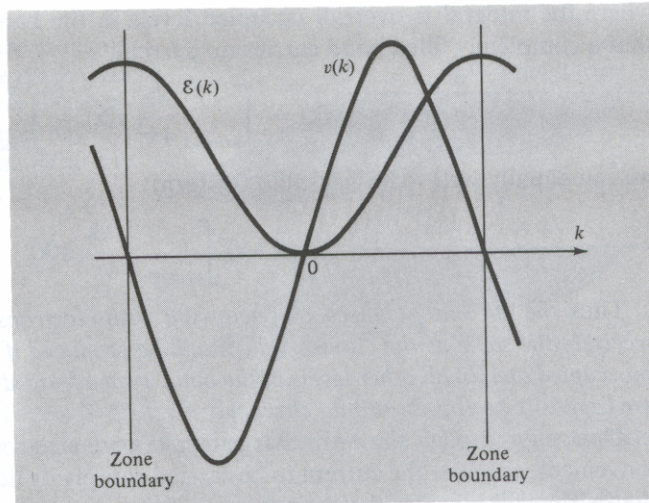
$$v_n(\vec{k}(t)) = v_n\left(k(0) - \frac{eEt}{\hbar}\right)$$

since  $v$  is periodic in  $k$  the velocity is a bounded function which is periodic in the field!

Let's examine the  $k$  dependence of the velocity carefully:

**Figure 12.4**

$\varepsilon(k)$  and  $v(k)$  vs.  $k$  (or vs. time, via Eq. (12.17)) in one dimension (or three dimensions, in a direction parallel to a reciprocal lattice vector that determines one of the first-zone faces.)



As the  $k$  vector is increased (by increasing the external field) the velocity reaches a maximum and then starts to decrease?! This is the result of the force applied by the periodic lattice the coherent scattering from the periodically spaced scatterers. As the  $k$  approaches the zone boundary the electron approaches levels where it would be moving in the opposite direction.

The electron responds to the applied field as if it had a negative mass.

One way to convince yourself of this is to consider the band shape near its maximum:

$$\varepsilon(k) \approx \varepsilon(k_0) - A(k - k_0)^2$$

for levels with  $k$ 's close to the band edge:

$$v(k) = \frac{1}{\hbar} \frac{\partial \epsilon}{\partial k} \approx -\frac{\hbar}{m^*} (k - k_0)$$

$$a = \frac{d}{dt} v = -\frac{\hbar}{m^*} \dot{k}$$

where

$$A = \frac{\hbar^2}{2m^*}$$

### **Justifying the independent electron model**

We have described the wavefunctions of the electrons in the conduction band of a metal by assuming that they consist of a Slater determinant of one level eigenfunctions. Thus the structure of the N electron eigenfunction is thus identical to that of the eigenfunction of a system of N non-interacting particles this is called the independent electron approximation which neglects the e-e interactions. There are a number of approximations which do allow us to include the effects of the interaction one very famous one is the Hartree Fock approximation which leads to the H-F equations. The essence and structure of the eigenfunction remains though the same – what changes is the form of the single electron eigenfunction that is used to construct the Slater determinant. As we saw earlier it is in fact those electrons that are closest to the Fermi level that determine the properties of the metal. In order to justify why the independent electron approximation works so well in particular in describing those electrons that are close to the Fermi level we need to look at the effects of the electron-electron interactions and try to describe those in a qualitative way. Naively one would think that the electron-electron scattering rate should be high this due to the strong coulombic interaction it turns out that Pauli's exclusion principle actually decreases that rate dramatically.