

**Introduction to Solid State Physics**  
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**Lecture – 21**

**Understanding the electronic contribution to the specific heat of a solid Part-III**

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$$\begin{aligned}
 N &= 2 \sum_k f_D(\epsilon_k - \mu) = 2 \sum_k f_D(\epsilon_k - \mu(\tau)) = 2 \sum_k f_D(\epsilon_k - \epsilon_F) \\
 \frac{N}{V} &= \int_0^{\epsilon_F} g(\epsilon_k) f_D(\epsilon_k - \mu(\tau)) d\epsilon_k = \int_0^{\epsilon_F} g(\epsilon_k) f_D(\epsilon_k - \mu(\tau=0)) d\epsilon_k \\
 &\quad \text{for } \epsilon_k - \epsilon_F = 0 \Rightarrow \epsilon_k = \epsilon_F \\
 &\quad \text{for } \epsilon_k - \epsilon_F < 0 \Rightarrow \epsilon_k < \epsilon_F \\
 &\quad \text{for } \epsilon_k - \epsilon_F > 0 \Rightarrow \epsilon_k > \epsilon_F \\
 \epsilon_F &\int_0^{\epsilon_F} g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k + \int_{\epsilon_F}^{\infty} g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k = \int_0^{\epsilon_F} g(\epsilon_k) d\epsilon_k \\
 &\int_0^{\epsilon_F} g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k + \int_{\epsilon_F}^{\infty} g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k = \int_0^{\epsilon_F} g(\epsilon_k) d\epsilon_k \\
 &\int_{\epsilon_F}^{\infty} g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k = \int_{\epsilon_F}^{\infty} g(\epsilon_k) d\epsilon_k - \int_0^{\epsilon_F} g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k \\
 &\int_{\epsilon_F}^{\infty} g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k = \int_{\epsilon_F}^{\epsilon_F} g(\epsilon_k) (1 - f_D(\epsilon_k - \mu)) d\epsilon_k \quad \text{--- (2)}
 \end{aligned}$$

Now, in the earlier lecture, we had used this expression for the total number of particles and we had reached up to this expression which is shown here we can simplify this expression a bit further.  $\int_0^{\epsilon_F} g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k + \int_{\epsilon_F}^{\infty} g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k = \int_0^{\epsilon_F} g(\epsilon_k) d\epsilon_k$  is equal to  $\int_0^{\epsilon_F} g(\epsilon_k) (1 - f_D(\epsilon_k - \mu)) d\epsilon_k$ . This is equation 2, instead of calling the above equation 2, we call this as equation number 2. Now, let us go back and copy this equation.

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$$E(0) = \int_0^{E_F} \epsilon_k g(\epsilon_k) f_D(\epsilon_k - \epsilon_F) d\epsilon_k + \int_{E_F}^{\infty} \epsilon_k g(\epsilon_k) f_D(\epsilon_k - \epsilon_F) d\epsilon_k$$

$$E(0) = \int_0^{E_F} \epsilon_k g(\epsilon_k) d\epsilon_k$$

$$\Delta E = E(T) - E(0)$$

$$= \int_0^{E_F} \epsilon_k g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k - \int_0^{E_F} \epsilon_k g(\epsilon_k) d\epsilon_k$$

$$\Delta E = \int_0^{\epsilon_F} \epsilon_k g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k + \int_{\epsilon_F}^{\infty} \epsilon_k g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k - \int_0^{\epsilon_F} \epsilon_k g(\epsilon_k) d\epsilon_k \quad (1)$$

Let us rewrite this expression once again, ok.

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$$\Delta E = \int_0^{\epsilon_F} \epsilon_k g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k + \int_{\epsilon_F}^{\infty} \epsilon_k g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k - \int_0^{\epsilon_F} \epsilon_k g(\epsilon_k) d\epsilon_k$$

$$= \int_0^{\epsilon_F} \epsilon_k g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k + \left[ \int_{\epsilon_F}^{\infty} \epsilon_k g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k + \int_{\epsilon_F}^{\infty} \epsilon_k g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k \right] - \int_0^{\epsilon_F} \epsilon_k g(\epsilon_k) d\epsilon_k$$

$$= \int_0^{\epsilon_F} \epsilon_k g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k + \int_{\epsilon_F}^{\infty} (\epsilon_k - \epsilon_F) g(\epsilon_k) f_D(\epsilon_k - \mu) d\epsilon_k + \int_{\epsilon_F}^{\infty} \epsilon_F g(\epsilon_k) (1 - f_D(\epsilon_k - \mu)) d\epsilon_k - \int_0^{\epsilon_F} \epsilon_k g(\epsilon_k) d\epsilon_k$$

So, the change in energy  $\Delta E$  let me rewrite this expression as integral 0 to  $E_F$   $E g$  of  $E f_D E$  minus  $\mu dE$  plus integral  $E_F$  to infinity  $E g$  of  $E f_D E$  minus  $\mu dE$ . These are all momentum states with momentum state  $k$  where  $k$  identifies the state minus integral 0 to  $E_F$   $E k g E k dE$ , and this I can rewrite it as integral 0 to  $E_F$   $E k g E k f_D E k$  minus  $\mu dE k$  plus integral  $E_F$  to infinity  $E k$  minus  $E_F$ . This I am now rewriting it as  $E k$  minus  $E_F g E k f_D E k$  minus  $\mu dE k$  because I have subtracted a minus  $E_F$  from here

I will add a plus  $E_F$ . So,  $E_F$  to infinity the same term, but I have just add  $E_F g(E) k f_D$   
 $E_k$  minus  $\mu$   $dE_k$ . So, these two terms is nothing else, but this term which I have here,  
 this term is now rewritten as this term and then I have the same expression as earlier this  
 extra term is still the same 0 to  $E_F$   $E_k g(E) k dE_k$ .

And, now for this I will substitute my expression which I have got earlier which is this  
 term that for  $E_F g(E) k f_D$   $E_k$   $E_F$  to infinity I will substitute from 2, which you already  
 have and then if I substitute that I will end up with an expression which is integral 0 to  $E_F$   
 $E_k g(E) k f_D$   $E_k$  minus  $\mu$   $dE_k$  plus integral  $E_F$  to infinity  $E_k$  minus  $E_F g(E) k f_D$   
 $E_k$  minus  $\mu$   $dE_k$  and now, this term is going to be replaced by the term which I have  
 already derived here.  $E_F$  into  $g(E) k 1 - f_D$  this term is going to be replaced by this.

So, now, you will get your limits of integration as 0 to  $E_F$   $E_k g(E) k 1 - f_D$   $E_k$   
 minus  $\mu$   $dE_k$  minus integral  $E_k g(E) k dE_k$  0 to  $E_F$ . This is the only odd one out  
 because this is  $E_F$  to infinity rest of all of them have got converted to 0 to  $E_F$ . So, by  
 substituting this one here you get this term now. Now, you will have to regroup terms.  
 You will have to regroup terms, you will have to take you can see that these two are  
 similar. When you take these two terms together you will have a  $1 - f_D$  which you  
 will have to combine with this is  $E_F$ .

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Handwritten mathematical derivation on a grid background:

$$\Delta E = E(T) - E(0)$$

$$dE = \Delta E = \int_0^{E_F} (\epsilon_F - \epsilon) g(\epsilon) (1 - f_D(\epsilon, \mu)) d\epsilon + \int_{E_F}^{\infty} (\epsilon - \epsilon_F) g(\epsilon) f_D(\epsilon, \mu) d\epsilon$$

*Temp dependent*

$$C_V = \frac{dE}{dT} = - \int_0^{E_F} (\epsilon_F - \epsilon) g(\epsilon) \frac{df_D}{dT} d\epsilon + \int_{E_F}^{\infty} (\epsilon - \epsilon_F) g(\epsilon) \frac{df_D}{dT} d\epsilon$$

$$C_V = \int_0^{E_F} (\epsilon_F - \epsilon) g(\epsilon) \frac{df_D}{dT} d\epsilon + \int_{E_F}^{\infty} (\epsilon - \epsilon_F) g(\epsilon) \frac{df_D}{dT} d\epsilon$$

$$C_V = \int_0^{E_F} (\epsilon_F - \epsilon) g(\epsilon) \left( \frac{df_D}{dT} \right) d\epsilon$$

$\epsilon = \frac{\hbar^2 k^2}{2m}$   
 $\vec{k} = (k_x, k_y, k_z)$   
 $\epsilon_x = \frac{\hbar^2 k_x^2}{2m}, k_y, \dots, k_z$

So, the change in energy is integral of 0 to  $E_F$  the Fermi energy  $E_F$  minus  $E_k g(E) k 1$   
 minus  $f_D$  plus integral 0 to infinity  $E_k$  minus  $E_F g(E) k dE_k$ . The specific heat now can

be calculated because this is nothing else, but if you take the derivative of this change in energy if the change in temperature is infinitesimal. For an infinitesimal change in energy, for a infinitesimal change in temperature the infinitesimal change in energy is the following and so, you take a derivative  $dE$  by  $dT$ , it is specific heat. So, if you take the derivative of the above ok, then all of these are of course, not temperature dependent  $E_F$ ,  $E_k$  and  $g(E_k)$  these are not temperature dependent, but the Fermi Dirac distribution is definitely temperature dependent ok.

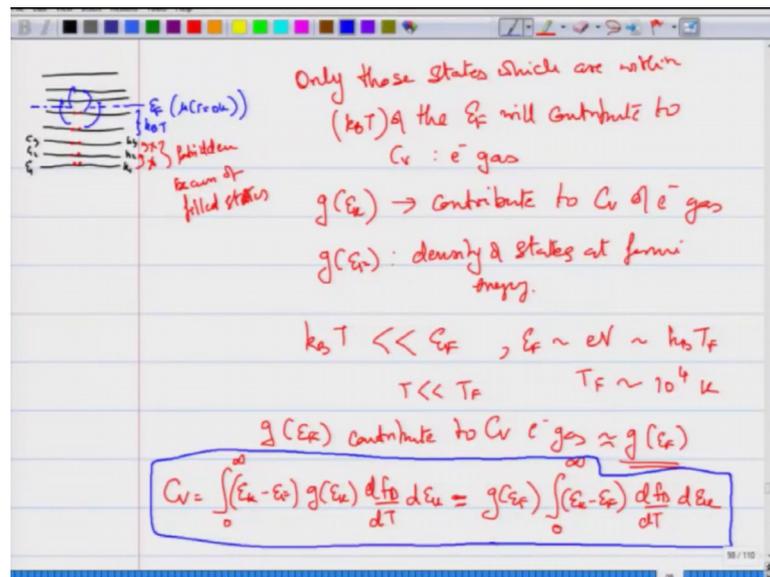
So, then you will land up with an expression  $0$  to  $E_F$   $E_F$  minus  $E_k$   $g(E_k) df(D)$  by  $dT$  plus integral  $E_F$  to infinity  $E_k$  minus  $E_F$   $g(E_k) df(D)$  by  $dT$   $dE_k$   $dE_k$ , this is  $dE_k$  plus this term. So, when you take the derivative of the above expression which corresponds to the change in energy when you change the temperature, then this is the only one which is temperature dependent. This term is temperature dependent, ok.

So, you get this expression and therefore, you can rewrite this expression as  $C_V$ . Now, you can take it as  $E_k$  my this negative sign will make it  $E_k$  minus  $E_F$ . So, finally,  $0$  to  $E_F$   $E_k$  minus  $E_F$   $g(E_k) df(D)$  by  $dT$   $dE_k$  plus integral  $E_F$  to infinity  $E_k$  minus  $E_F$   $g(E_k) df(D)$  by  $dT$   $dE_k$  or the specific heat now you can take the limits of integration from  $0$  to infinity. These two terms are exactly identical  $E_k$  minus  $E_F$   $g(E_k) df(D)$  by  $dT$   $dE_k$ .

So, this is your expression for the specific heat of the electron gas.  $E_k$  minus  $E_F$  where  $E_k$  is  $\hbar^2 k^2 / 2m$ , the energy of the free electron gas and  $k$  is the vector  $k$  is  $k_x, k_y, k_z$  where  $k_x$  is equal to  $2\pi n_x / L$  and similarly  $k_y$  and similarly  $k_z$ , ok. This we have already seen and this gives you the  $E_k$  the energy of the free electron with respect to the Fermi energy which is  $E_F$ ;  $E_F$  is temperature dependent. This is the density of states at any energy  $E_k$ . This is the derivative of the Fermi distribution Fermi Dirac distribution with respect to temperature and this gives you the specific heat.

Now, let us try and calculate this quantity, but before we go along we will do an approximation.

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And, the first approximation that we will do is that in the model of the specific heat which I have described to you earlier you have these states which is  $E_1$ ,  $E_2$ ,  $E_3$  and you can identify it with  $k_2$ ,  $k_3$  these are the different moment or the energy states and the electrons are filling up these states and this is where your Fermi energy is sitting in the this is the location of the Fermi energy in the system which is the chemical potential at temperature  $T$  equal to 0 Kelvin.

Now, within the Sommerfeld's model what does it say that when you apply a temperature or when you increase the temperature from 0 temperature then the electrons which are within  $k_B T$  of this Fermi energy will undergo excitation. These will excite those which are within  $k_B T$  of the Fermi energy will get excited to the higher energy states. Only those states which are within  $k_B T$  of the Fermi energy will contribute to the specific heat of the electron gas. These cannot make any transitions because these are forbidden these cannot be forbidden because of filled states; because these are completely filled states.

So, states which are very far away from the Fermi energy much beyond  $k_B T$  will not contribute anything to the specific heat because you cannot cause any excitations within this state. Only those electrons which are within  $k_B T$  of the Fermi energy are the ones which will contribute to the. So, therefore, in the expression; so, if you are looking at the density of states  $E_k$  the density of states which will contribute to the specific heat which

will contribute to specific heat of the electron gas will essentially be the density of states at the Fermi energy.

Remember that  $k_B T$  is far far smaller than the Fermi energy because the Fermi energy  $E_F$  is of the order of few electron volts which if you write it as  $k_B T_F$  as some temperature then this  $T_F$  we know turns out to be of the order of  $10^4$  Kelvin. Your metal is sitting at a few tens to hundreds of Kelvin and in fact, at low temperature where you are really seeing the contribution which is coming from the electron gas by eliminating the vibrations of the solid which only happens at very low temperatures. There the temperature is far far smaller than  $T_F$  the Fermi temperature.

So, the density of states which contribute to the specific heat of the electron gas are the states which are near the Fermi energy because this  $k_B T$  is really very small compared to the Fermi energy. So, the states which are very close to the Fermi energy those are the ones which will contribute to the density of states and therefore, the specific heat which is integral of 0 to infinity  $E^k \text{ minus } E_F \text{ g}(E) dE$  is for all practical purposes it is approximately  $g(E_F)$  the density of states at the Fermi energy. This was the density of states at any energy and then you will integrate it.

But, as you know that because of the temperatures being far smaller than the Fermi temperature the density of states which really contribute to the specific heat are the ones which are very close to the Fermi energy. These states which are far away from the Fermi energy do not contribute, so, their density of states will have no contribution to this process. So, we can replace this density of states which is entering in the discussion of specific heat. We can take it as approximately the density of state at the Fermi energy integral 0 to infinity  $E^k \text{ minus } E_F \text{ df}(E)$ . This is a very important expression which will help us to calculate the specific heat of the electron gas.