Introduction to Solid State Physics

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Lecture – 20
Understanding the electronic contribution to the specific heat of a solid Part-II

We had started looking at the behaviour of specific heat of the electron gas and trying to understand from where from does the specific heat of the electron gas arise and what is it is value. If you consider the electron gas as was considered by Drude within the purview of kinetic theory of gases then you will get a number like 3 by 2 R.

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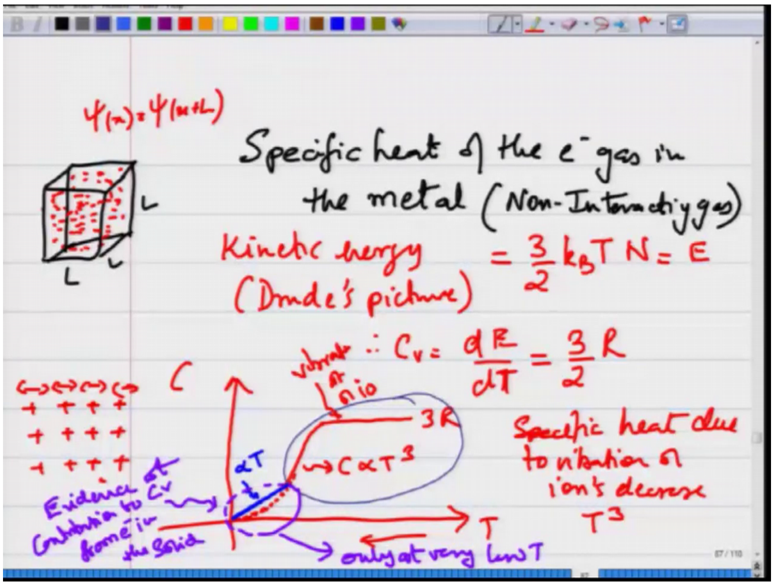
Specific heat of the e^- gas in the metal (Non-Interacting gas)

Kinetic energy (Drude's picture) $= \frac{3}{2} k_B T N = E$

$\therefore C_v = \frac{dE}{dT} = \frac{3}{2} R$

Specific heat due to vibration of ion's decrease T^3

Evidence of contribution to C_v from e^- in the solid

only at very low T

However, what was seen as I have already discussed was that the specific heat way of the solid which has the atomic lattice, the ionic lattice, which is the arrangement of this ions and it also has the electron gas inside it. So, the net specific heat is the specific heat of the ions inside the solid as well as the electrons and if you measure the specific heat of the solid it is nowhere close to 3 by 2 R, but it is actually 3 R as you reduce the temperature the specific heat goes down as T cube and then at very low temperatures you have a linear temperature dependence of the specific heat.

This entire regime of temperature where you see the T cube dependence and the 3R dependence this is all coming from the vibration of these ions inside the lattice.

However, you get this linear temperature dependence at very low temperatures which are sub Kelvin's often sub Kelvin temperatures very very low temperature is below 4 Kelvin. In this very low temperature regime you start seeing rather than this T cube dependence you see a linear dependence and this linear dependence is arises because you have actually frozen out the vibrations of the ions.

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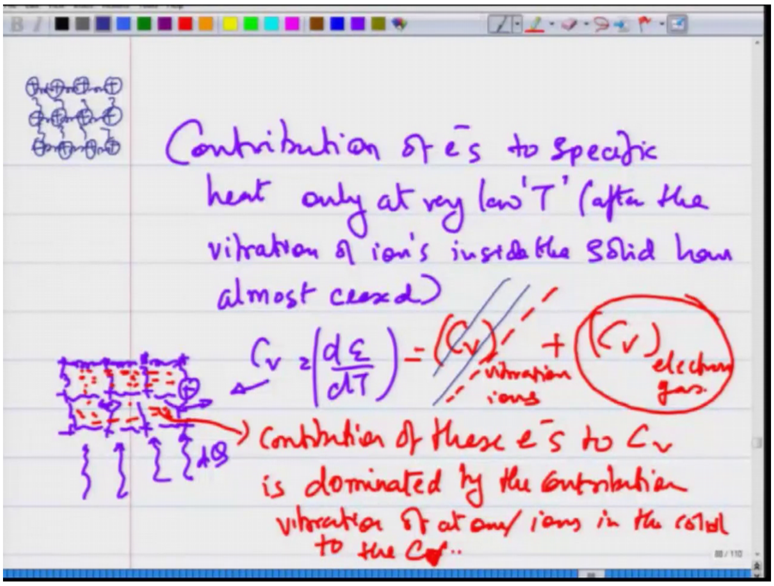

Contribution of $\bar{e}$s to specific heat only at very low 'T' (after the vibration of ion's inside the solid have almost ceased)

$$C_v = \left(\frac{d\varepsilon}{dT}\right) = \cancel{(C_v)}_{\text{vibration ions}} + (C_v)_{\text{electron gas}}$$

Contribution of these $\bar{e}$s to C_v is dominated by the contribution vibration of atom/ions in the solid to the C_v..

So, you no longer have this term which is coming from the specific heat of the behaviour of the ions, from the vibration of the ions is no longer present, what you have only present is the electrons. And these electrons now start contributing to the specific heat. So, if you change the temperature at these low temperatures, slight variation in temperature actually changes the energy of this electron gas and that gives rise to the specific heat.

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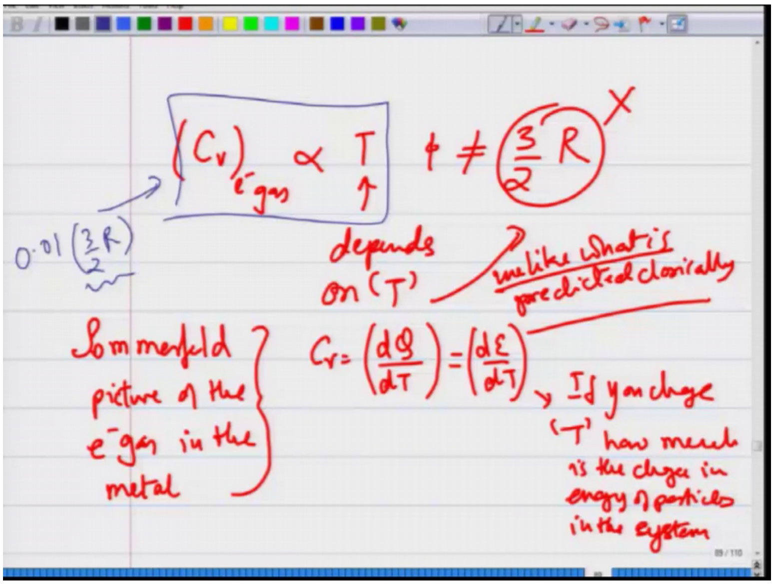

$\left(C_v\right)_{e^- gas} \propto T \uparrow \neq \left(\frac{3}{2}R\right)$ X

$0.01\left(\frac{3}{2}R\right)$

depends on 'T' unlike what is predicted classically

Sommerfeld picture of the e^- gas in the metal

$C_v = \left(\frac{dQ}{dT}\right) = \left(\frac{dE}{dT}\right)$ → If you change 'T' how much is the change in energy of particles in the system

And what was seen was that it has a linear temperature dependence and this specific heat of the electron gas is almost 0.01 of 3 by 2 R. This is the value which you get from kinetic theory of gases or within the Drude's model, but the actual specific heat of the electron gas is far lower. This value of the specific heat is far lower than 3 by 2 R, it is typically 0.01 of R. So, where from is the specific heat of the electron gas coming and this is where Sommerfeld's idea became very successful.

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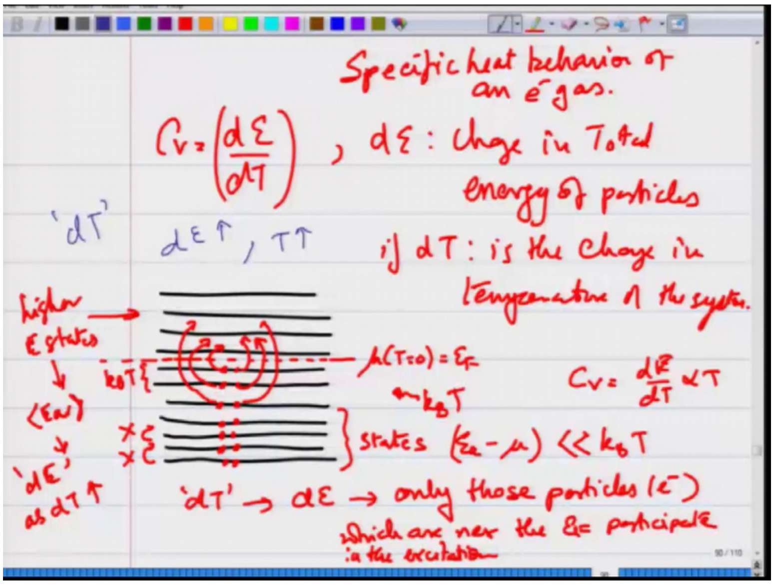

Specific heat behavior of an e^- gas.

$C_v = \left(\frac{dE}{dT}\right)$, dE : change in Total energy of particles

'dT' $dE\uparrow$, $T\uparrow$

if dT : is the change in temperature of the system.

higher E states → $\langle E_N \rangle$ → 'dE' as $dT\uparrow$

k_BT

$\mu(T=0) = E_F$

$\sim k_BT$

$C_v = \frac{dE}{dT} \propto T$

× ×

states $(E_n - \mu) << k_BT$

'dT' → dE → only those particles (e^-) which are near the E_F participate in the excitation

In explaining this linear temperature dependence of the specific heat and why is it. So, much lower than 3 by 2 R and where from does the specific heat arise within the Sommerfeld's model, you have these different energy states which you have from the periodic boundary conditions you have different energy states. You start filling up these states at low temperatures up to the Fermi level the states are all filled up.

And, at this low temperature if you change the temperature slightly, say you increase the temperature slightly by dT then the electrons which are present within kB dT of this Fermi energy though electrons which are present within a small region of the Fermi energy which is of the order of k B T those electrons will observe the thermal energy and will get excited to higher energy states. And as a result the electrons which were initially occupying only up to this energy level will now start occupying higher energy levels and so, therefore, the dE will also go up.

So, as you increase the temperature at the low temperature because of these excitations of the order of k B T around the Fermi energy, the average energy of the system also rises. And intuitively you can guess that as you increase the temperature you can acquire higher and higher energy states there will be more change in the average energy of the system and so, the specific heat should start increasing as a function of temperature. And this was a very successful contribution and the basic idea of calculating the specific heat of the electron gas inside a solid. So, let us go about calculating this specific heat. Now, that the picture is in mind let us calculate the specific heat of the solid.

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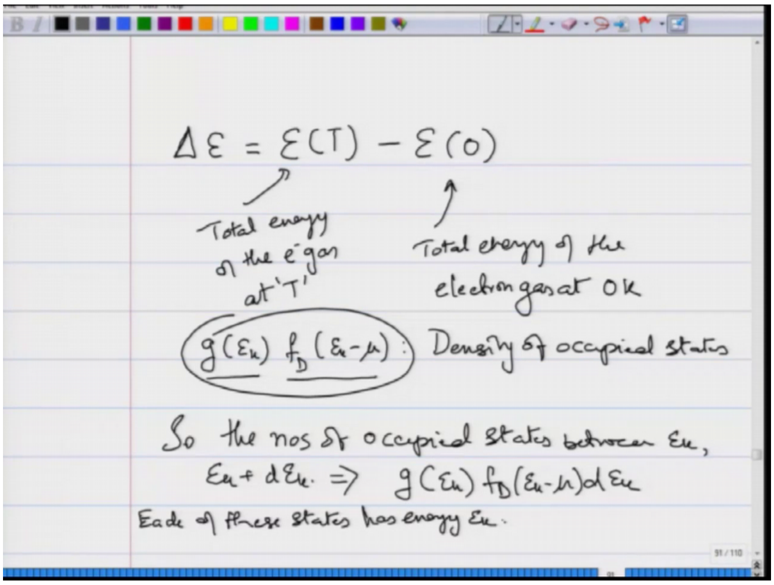

$$\Delta \varepsilon = \mathcal{E}(T) - \mathcal{E}(0)$$

Total energy of the e^- gas at 'T'

Total energy of the electron gas at 0K

$\boxed{\underline{g(\varepsilon_k)}\ \underline{f_D(\varepsilon_k-\mu)}}$: Density of occupied states

So the nos of occupied states between ε_k, $\varepsilon_k + d\varepsilon_k \Rightarrow g(\varepsilon_k) f_D(\varepsilon_k-\mu) d\varepsilon_k$

Each of these states has energy ε_k.

And the first thing to do is that we would like to know how much is the change in energy of the system which is defined as the total energy of the system the total energy of the electron gas at temperature T minus the total energy of the electron gas at 0 Kelvin.

Now, if you recall we had introduced the concept of the density of states and g of E k Fermi Dirac E k minus mu was the occupancy of states at E k. This is the density of states at E k and this is the probability of occupying those states. So, what is the density of occupied states you may also call this as that the density of occupied states is nothing else, but this quantity density of occupied states.

So, the number of occupied states between energy range E k and E k plus dE k will be g E k f D E k minus mu d E k. This is the total number of states between E k and E k plus dE k which are occupied. Each of these states has energy E k.

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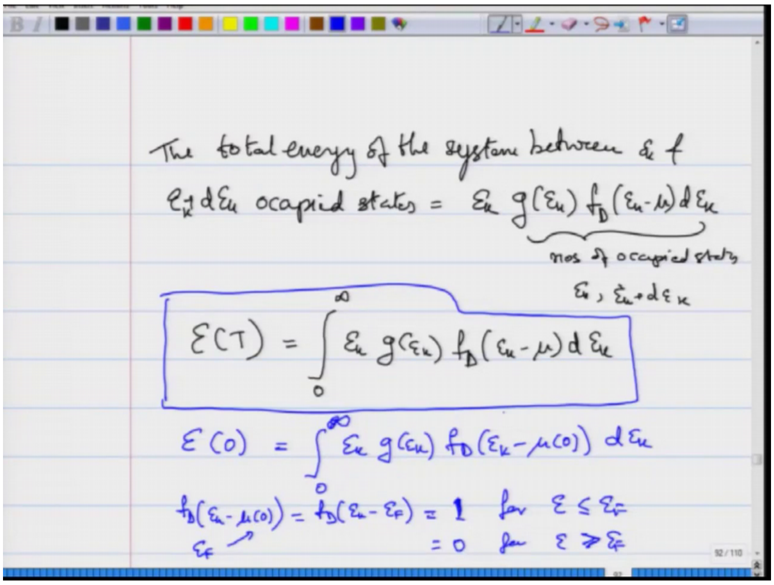

The total energy of the system between ε_k & $\varepsilon_k + d\varepsilon_k$ ocapied states $= \varepsilon_k \underbrace{g(\varepsilon_k) f_D(\varepsilon_k - \mu) d\varepsilon_k}_{\text{nos of occupied states } \varepsilon_k,\ \varepsilon_k + d\varepsilon_k}$

$$\boxed{\mathcal{E}(T) = \int_0^\infty \varepsilon_k\, g(\varepsilon_k)\, f_D(\varepsilon_k - \mu)\, d\varepsilon_k}$$

$$\mathcal{E}(0) = \int_0^\infty \varepsilon_k\, g(\varepsilon_k)\, f_D(\varepsilon_k - \mu(0))\, d\varepsilon_k$$

$$f_D(\varepsilon_k - \underset{\varepsilon_F \nearrow}{\mu(0)}) = f_D(\varepsilon_k - \varepsilon_F) = 1 \quad \text{for } \varepsilon \leq \varepsilon_F$$
$$= 0 \quad \text{for } \varepsilon > \varepsilon_F$$

So, the total energy of the system between E k and E k plus dE k occupied states is equal to E k g E k f D E k minus mu dE k. This is the number of occupied states between E k and E k plus dE k and this is the energy of each of the states. So, this gives you the total energy of which is present between E k and E k plus dE k ok.

And so, the total energy of the system is nothing else, but if I integrate from 0 to infinity all the energy states which are available from 0 to infinity E k g E k f D E k minus mu dE k, this give me the expression for the total energy of the system for this Sommerfeld's system where the electron is a quantum particle and this is the total energy at a given temperature T. And what is the energy at 0 temperature? The energy at 0 temperature is nothing else, but 0 to infinity E k g E k f D E k minus mu at 0 temperature dE k.

But, what is the Fermi derive distribution? E k minus the chemical potential at 0 temperature the chemical potential at 0 temperature is nothing else, but the Fermi energy which we have already calculated. This is E k minus E F the Fermi derive distribution E k minus E f which at 0 temperature is 1 for all energies which are less than or equal to E F and it is equal to 0 for all energies greater than E F. So, this range of energy which is going from 0 to infinity this will pick up a 1 only from 0 to E F and for all energies above E F this factor will become equal to 0.

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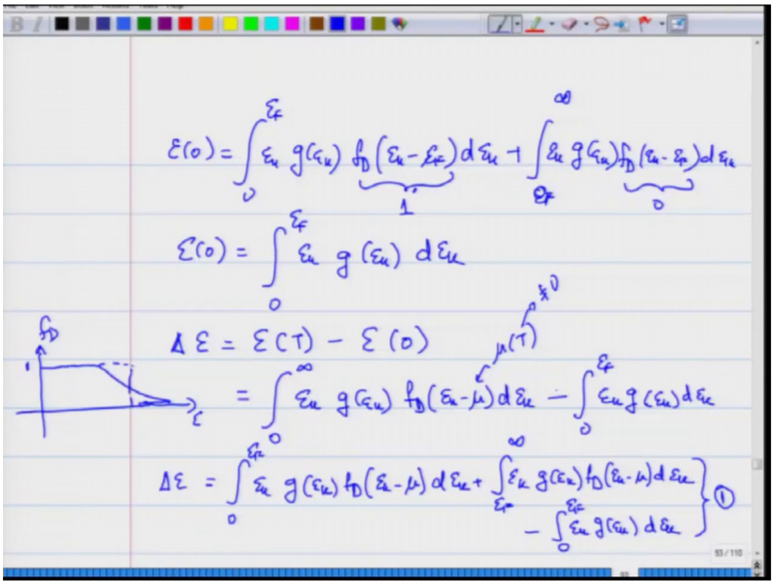

$$\mathcal{E}(0) = \int_0^{\varepsilon_F} \varepsilon_k\, g(\varepsilon_k)\, \underbrace{f_D(\varepsilon_k - \varepsilon_F)}_{1}\, d\varepsilon_k + \int_{\varepsilon_F}^{\infty} \varepsilon_k\, g(\varepsilon_k)\, \underbrace{f_D(\varepsilon_k - \varepsilon_F)}_{0}\, d\varepsilon_k$$

$$\mathcal{E}(0) = \int_0^{\varepsilon_F} \varepsilon_k\, g(\varepsilon_k)\, d\varepsilon_k$$

$$\Delta\mathcal{E} = \mathcal{E}(T) - \mathcal{E}(0)$$

$$= \int_0^{\infty} \varepsilon_k\, g(\varepsilon_k)\, f_D(\varepsilon_k - \overset{\mu(T),\ T\neq 0}{\mu})\, d\varepsilon_k - \int_0^{\varepsilon_F} \varepsilon_k\, g(\varepsilon_k)\, d\varepsilon_k$$

$$\left.\begin{aligned}\Delta\mathcal{E} = \int_0^{\varepsilon_F} \varepsilon_k\, g(\varepsilon_k)\, f_D(\varepsilon_k - \mu)\, d\varepsilon_k + \int_{\varepsilon_F}^{\infty} \varepsilon_k\, g(\varepsilon_k)\, f_D(\varepsilon_k - \mu)\, d\varepsilon_k \\ - \int_0^{\varepsilon_F} \varepsilon_k\, g(\varepsilon_k)\, d\varepsilon_k\end{aligned}\right\} ①$$

So, therefore, the energy at 0 temperature will be integral 0 to E F E k g E k f D E k minus E F dE k plus integral E f to infinity E k g E k f D E k minus E F dE k; this is 1, this is 0. In this range from energy is which are above E F the Fermi derive distribution is 0. So, this becomes equal to 0 to E F E k g E k dE k. So, therefore, if I write how much is the change in energy which is equal to the total energy at a given temperature minus the energy at 0 temperature, this can be written as 0 to infinity E k g E k f D E k minus mu dE k minus integral 0 to E F E k g E k dE k.

Now, this integral we start now this is the chemical potential at a finite temperature T which is not equal to 0, this is T is not equal to 0. Now, this integration I changed from 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 g of E k f D E k minus mu dE k minus integral 0 to E F E k g E k dE k. Let us call this equation as equation 1, where I have just read it in this by taking it from 0 to E F and E F to infinity.

And, then let us look at what are the contributions. Because, you know that at finite temperature the distribution becomes is no longer like this, but the distribution. So, there are electrons from below the Fermi energy have got excited to states which are available above the Fermi energy. This is the Fermi derive distribution, this is 1, this is the energy. So, for electrons which are roughly below the chemical potential those states have got unoccupied and electrons have got excited. So, we are breaking it up into two parts; one is up to E F and the other is from E F to infinity. Let us look at another term.

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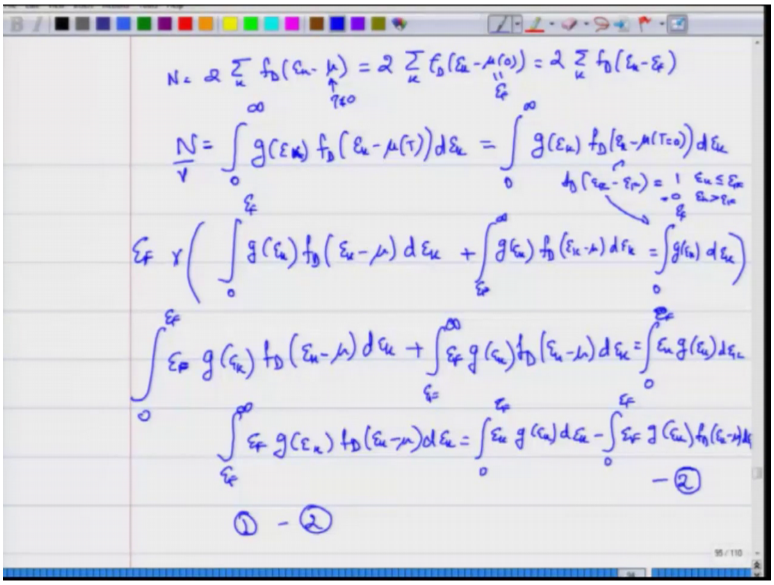

$$N = 2\sum_k f_D(\varepsilon_k - \underset{T\neq 0}{\underset{\uparrow}{\mu}}) = 2\sum_k f_D(\varepsilon_k - \underset{\varepsilon_F}{\underset{\shortparallel}{\mu(0)}}) = 2\sum_k f_D(\varepsilon_k - \varepsilon_F)$$

$$\frac{N}{V} = \int_0^\infty g(\varepsilon_k)\, f_D(\varepsilon_k - \mu(T))\, d\varepsilon_k = \int_0^\infty g(\varepsilon_k)\, f_D(\varepsilon_k - \mu(T=0))\, d\varepsilon_k$$

$$f_D(\varepsilon_k - \varepsilon_F) = 1 \quad \varepsilon_k \le \varepsilon_F$$
$$= 0 \quad \varepsilon_k > \varepsilon_F$$

$$\varepsilon_F \times \left(\int_0^{\varepsilon_F} g(\varepsilon_k) f_D(\varepsilon_k - \mu)\, d\varepsilon_k + \int_{\varepsilon_F}^\infty g(\varepsilon_k) f_D(\varepsilon_k - \mu)\, d\varepsilon_k = \int_0^{\varepsilon_F} g(\varepsilon_k)\, d\varepsilon_k \right)$$

$$\int_0^{\varepsilon_F} \varepsilon_F\, g(\varepsilon_k) f_D(\varepsilon_k - \mu)\, d\varepsilon_k + \int_{\varepsilon_F}^\infty \varepsilon_F\, g(\varepsilon_k) f_D(\varepsilon_k - \mu)\, d\varepsilon_k = \int_0^{\varepsilon_F} \varepsilon_k\, g(\varepsilon_k)\, d\varepsilon_k$$

$$\int_{\varepsilon_F}^\infty \varepsilon_F\, g(\varepsilon_k) f_D(\varepsilon_k - \mu)\, d\varepsilon_k = \int_0^{\varepsilon_F} \varepsilon_k\, g(\varepsilon_k)\, d\varepsilon_k - \int_0^{\varepsilon_F} \varepsilon_F\, g(\varepsilon_k) f_D(\varepsilon_k - \mu)\, d\varepsilon_k \quad - ②$$

① - ②

The total number of electrons; the total number of electrons can be written as 0 to infinity g of E k f D E k minus mu which is a function of temperature dE k this is at finite temperature which is also equal to integral of this is N by v the density which is equal to 0 to infinity g E k f D E k minus mu at temperature T equal to 0 dE k. This is the definition of the total number of electrons if you recall the total number of electrons was twice summation of k f D E k minus mu.

This is the definition at any temperature which can be written as per 0 temperature f D E k minus mu at 0 Kelvin which is twice of summation over k f D E k minus E F because mu at 0 temperature is E k this at 0 temperature is at E F and this is at finite temperature, this is T not equal to 0.

So, this expression can be read it and like this density of states at E k. The density of states into this and 0 to infinity this we can break it up in to two limits. So, we can rewrite this as 0 to E F g E k f D E k minus mu dE k plus integral E F to infinity g E k f D E k minus mu dE k is equal to integral 0 to E F g E k dE k, because f D E k minus E F is equal to 1 for E k less than or equal to E F and is equal to 0 for E k greater than E F. So, if you put that here in this expression anything which is greater than E F will pick up a 0, so you will not have the and there was below 0 is into 1, so this.

And now this expression this entire expression you multiply it by E F. So, you will get integral 0 to E F; E F into g E k f D E k minus mu d E k plus integral E F to infinity E k g E k f D E k minus mu dE k is integral 0 to E F E k g E k dE k. So, I can write my integral E F to infinity E k g not E k, this is E F this should be E F, this is E F. So, this integral E F g E k f D E k minus mu d E k is equal to integral 0 to E F E k g E k d E k minus integral 0 to E F E F g E k f D E k minus mu dE k. And, this is my expression 2 and I take expression 1 minus expression 2, where expression 1 is the earlier expression this expression from this expression I subtract this. So, with that we can get a term for this.