**Electronic Properties of the Materials: Computational Approach**
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**Lecture - 13**
**Quantum Free Electrons: Sommerfeld Theory (Part 3)**

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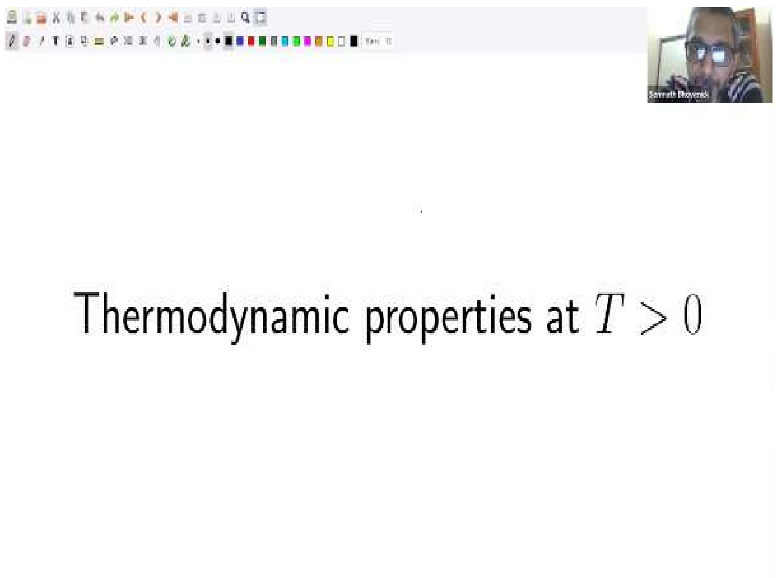


Hello friends, so, for we have discussed thermodynamic properties of free electron gas at 0 Kelvin. In this lecture, we are going to explore thermodynamic properties at finite temperature.

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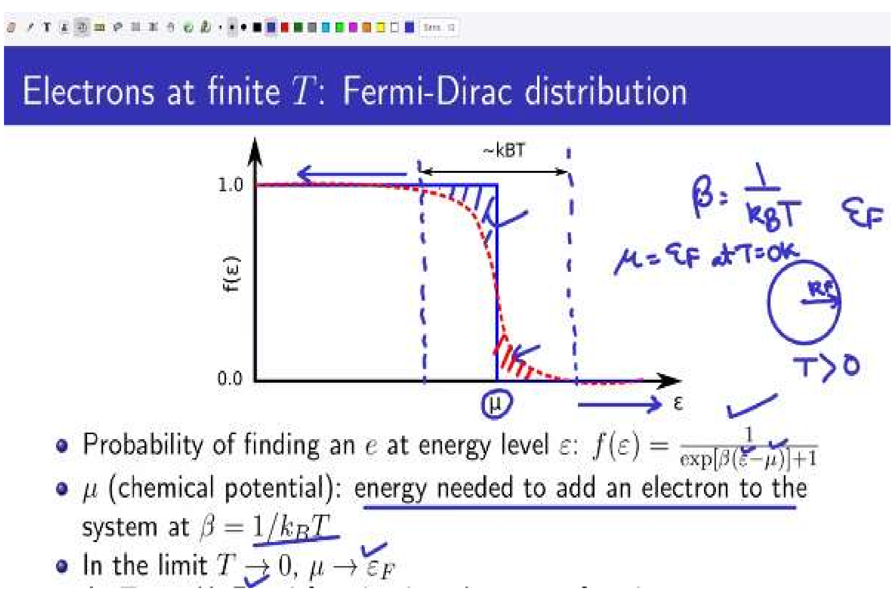

At p greater than 0 we have to examine the excited state of electron system probability of finding an electron at some excited state is given by the formula basically. In this equation beta = 1 by k B T, k B is the Boltzmann constant and T is the temperature E is energy the mu is the chemical potential chemical potential is defined as the energy needed to add an electron to the system at some given temperature. Now, what is mean can we relate it with something which we already have learned.

Now, know that to be consistent with whatever we have done at T = 0 Kelvin correct in the limit T going to 0 mu should be going to Fermi energy what does that mean? So, you see that at a t equal to 0 Kelvin, what we know that the ground state is given by this Fermi sphere correct that means, all the states up to k f is filled and all the states beyond f is empty. So, in the energy scale what we can say is that all the steps up to some energy level f is full add beyond this all the steps are empty.

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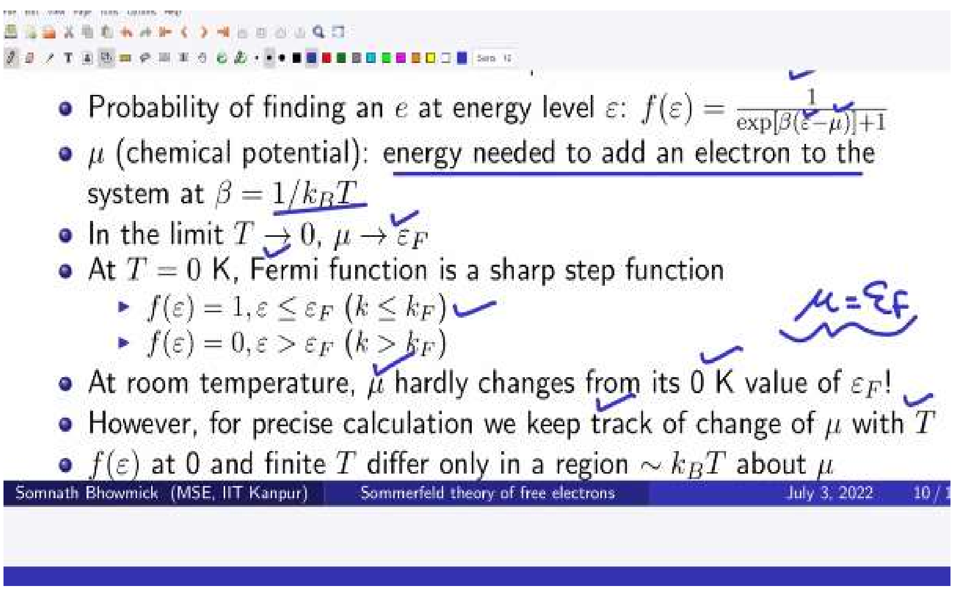


So, that means, at T = 0 this Fermi function this should look like a step function like this. So, that means mu this should become equal to E F at T = 0, mu = EF at T = 0 Kelvin so, that means this binary function is a sharp step function. So, up to this F the Fermi energy all states are full and beyond Fermi energy all the states are empty. Now, the question is what happens at finite temperature at some finite temperature this is shown by the dotted red line correct.

The Fermi function looks like this and you will see that some electrons which were in this portion, they have been excited to this portion. So, these electrons initially they were like below the Fermi energy, but at finite temperature, these electrons have been excited over the Fermi energy. Now, the question is how does mean change from E F as temperature increases? So, we know that mu = EF at T = 0 Kelvin.

Now, as T becomes greater than 0 the question is that what is the value of mu? It is no longer equal to Fermi energy but what will be the value of mu. In fact, we will see that even at room temperature mu the chemical potential it hardly changes from its 0 Kelvin value of EF. So, we know that at 0 Kelvin mu = EF, and we will see that even at room temperature this hardly changes. However, note that for precise calculation, we have to keep track of change of mu with T although the change is very small.

But still we have to keep track of this change for precise calculation. Note that if F E the Fermi function differs from its 0 Kelvin value only in a region we have with k B T. For example, let us compare the Fermi function at 0 and non 0 temperature at temperature T = 0 the Fermi function is given by this step function shown by the blue color. And at temperature greater than 0 the Fermi function is shown by this red dotted line.

Now, if you look at the figure then you see that in this region the Fermi function at 0 and non 0 temperature they are same, they have a value equal to 1. Similarly, in this region the Fermi function at 0 and non 0 temperature they are same and both of them have a value of 0 only in this region which is lie which has a width of k B T around this mu the chemical potential only in this region the blue line and the red dot a dashed line they differ from each other.

Thus, we can conclude that the Fermi function at 0 and non0 temperature they only differ within a region of with k B T around the chemical potential.

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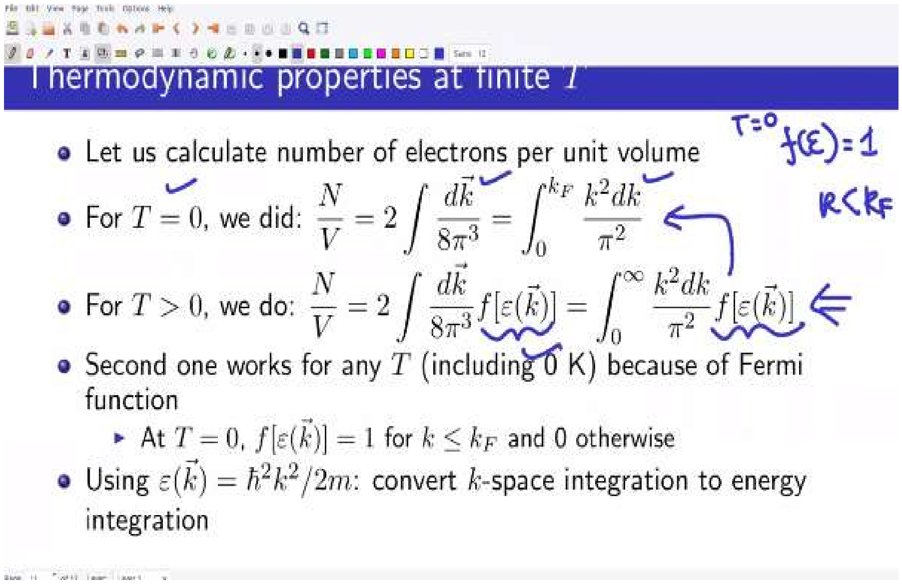


Let us calculate the number of electrons per unit volume for T = 0 Kelvin, what we did we calculated this integral N by V is equals to this integral. Now, for T greater than 0, we do almost the same thing now, you will see that we have one additional term which is that Fermi function note that the second formula that means, this formula works for any temperature including 0 Kelvin because of the Fermi function.

Now, what does it mean that we know that this Fermi function f of E will be equal to 1 when k is less than k F at T = 0 Kelvin this is how the Fermi function looks. So, that means, this integral can be written in this form at 0 Kelvin. So, that means, this second formula is a more general formula this will work for T = 0 Kelvin as well as when E is 1. Now, we know that E is equal to h cross square k square by 2m. So, using this formula, we are going to convert the k-space integration to energy integration. So, let us see that how we can do that.

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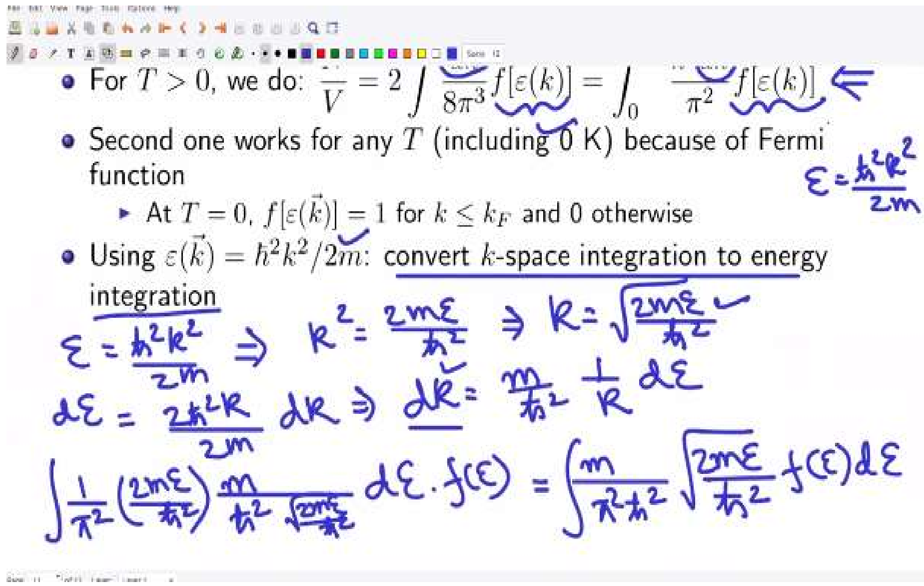


So, since

$$\varepsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k^2 = \frac{2m\varepsilon}{\hbar^2} \Rightarrow k = \sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

Now, what we do is that we can be at this term d of E because what we want to do is that? Right now, this is an integral over the k case what we want to do is that we want to convert the integral to some integral with energy. So,

$$d\varepsilon = \frac{2\hbar^k}{2m} dk \Rightarrow dk = \frac{m}{\hbar^2 k} d\varepsilon$$

Now, that means now let us just replace dk in this equation. So, that means, we have to evaluate this integral 1 by pi square so, look at so, we just right now replace this k with E in this equation. So,

$$\int \frac{1}{\pi^2} \frac{2m\varepsilon}{\hbar^2} \frac{m}{\hbar^2 \sqrt{2m\varepsilon/\hbar^2}} d\varepsilon f(\varepsilon) = \int \frac{m}{\pi^2 \hbar^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}} f(\varepsilon) d\varepsilon$$

So, what we have done is that? We have converted this integral right which was an integral over a space to an integral over energy.

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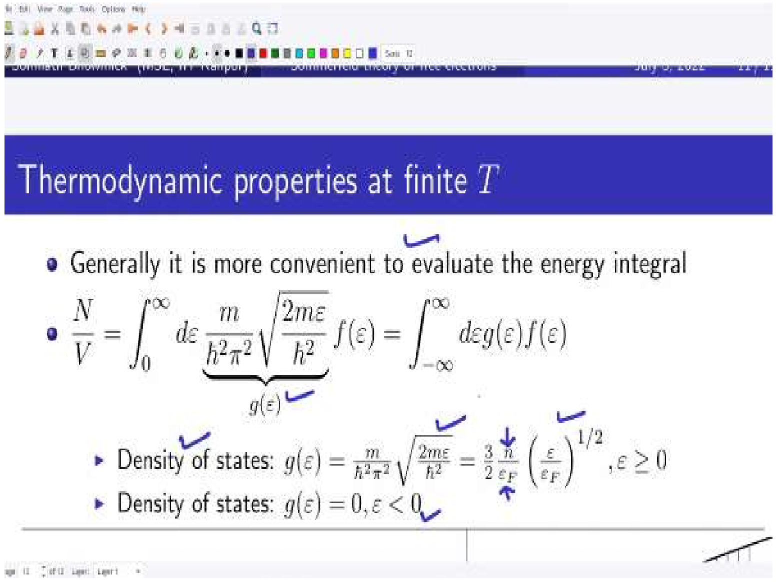


Generally, it is more convenient to evaluate the energy integral that is why we have converted the case space integral to energy integral. Now, let us introduce our new term g of E and we call it density of states let us try to understand what is density of states? First let us look at this equation right density of states it goes as square root of E and then we can further express it in terms of the electron density as well as the Fermi energy in this form. And note that g of E = 0 when energy is less than 0.

And that is why we have converted this integral from 0 to infinity to minus infinity to plus infinity because whenever it is less than 0 the energy is less than 0 g of E goes to 0.

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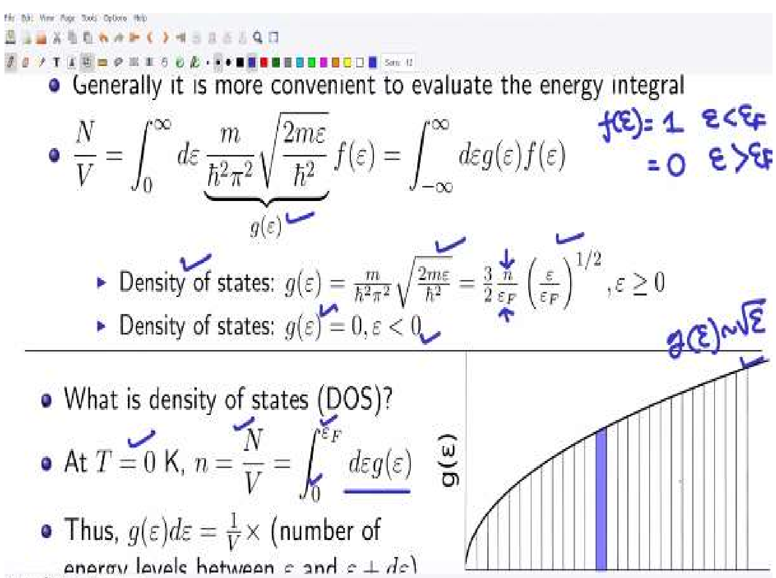

Now, let us come back to the question that what is density of states? To understand let us go back to T = 0 Kelvin. So, what we know that at T = 0 Kelvin, Fermi function is equal to 1 when energy is less than the Fermi energy and this is equal to 0 when energy is greater than Fermi energy. So, in that case N by V, we can write it as dE gE and then you see that E F = 1 when E is less than the Fermi energy. Otherwise, if this is 0, so, that means Fermi function is equal to 1 and the upper limit of the integral changes to E F because beyond the F Fermi function is 0.

Similarly, the lower limit changes to 0 because below 0 density of states is equals to 0. So, that does at T = 0 Kelvin, we can write the electron density is integral 0 to E F dE gE. And then we see that this integral this gives us the electron density; remember that an integral means area under the curve. Thus, we have the star g of E and we divide the total area in small, small bands of width d.

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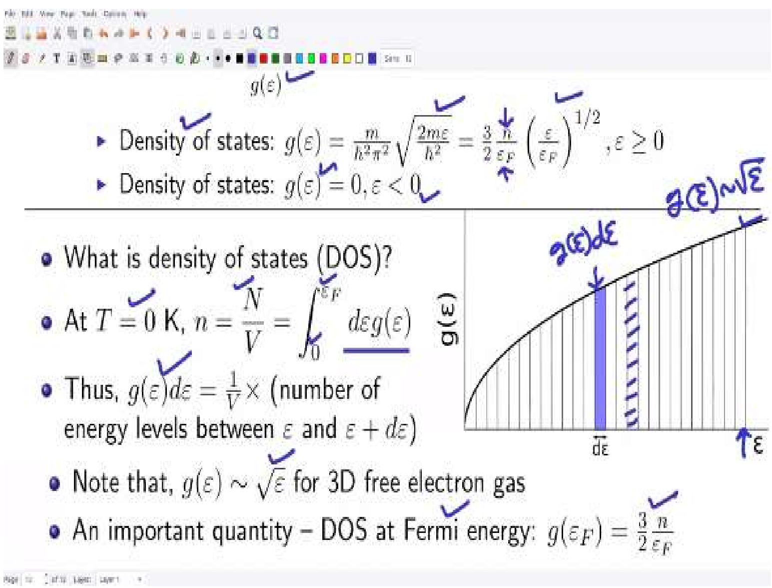


For example, we know that if we calculate the next assume that this is the Fermi energy. So, if n is given by the integral the area under this curve the total area under this curve, now, what we are doing is that the total area we are dividing in small, small bands like this. Now, what we have to do to get the total area we have to add up all the bands. And then, when we add up all the bands, that is equal to the total number of states that means, each band here if you see it, we will look at the each band. So, this area or this area correct.

Each band like and then this area is equal to what this area is gE times dE correct. So, what is this area this must be related to the number of states within this width of dE. So, that means g of E d of E we can write it as number of energy levels between E and E + dE and we multiply with 1 by V. So, that is what is the meaning of density of states. Note that in case of 3D free electron gas g of E goes as square root of E in case of 2D and 1D, it will have some other dependence.

We also define an important quantity density of states at the Fermi energy to do that what we can do is we can just put E equal to EF such that g of EF = 3 by 2 n divided by EF where n is the electron density and EF is the Fermi energy.

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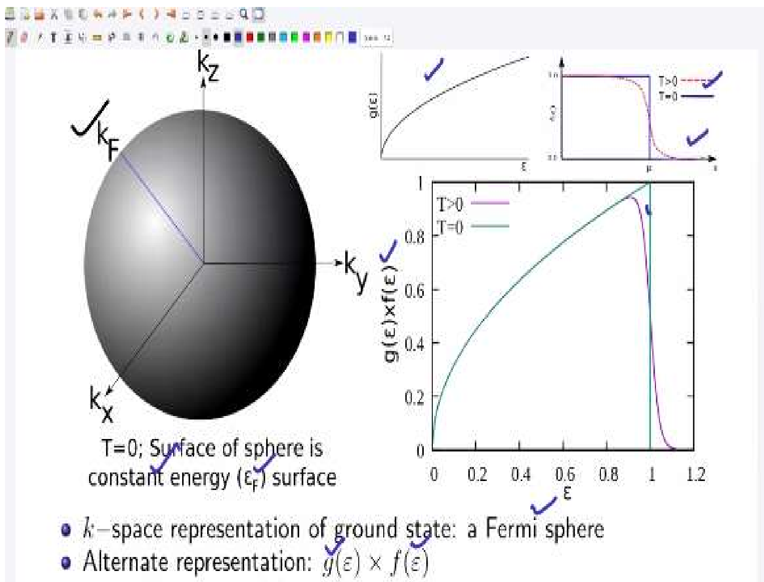


We already have learned how does the ground state of free electrons looks like in the kth space it is spherical with radius k F. So, you see this is the sphere with radius of k F and this is known as the Fermi sphere all the states inside the Fermi sphere are full and there are 2 electrons per state and all the other states outside the Fermi sphere are empty the surface of the Fermi sphere is a constant energy surface and we call this energy as the Fermi energy.

Now, let us look at some alternate representation. For example, we already have learned about the density of states as well as the Fermi function. So, let us see that whether we can develop some alternative representation based on the density of states and Fermi function for a 3D free electron gas, the density of states looks like this, this is square root of E. Similarly, the Fermi function looks like this, this is a step function at temperature T = 0, and this is a smooth function at temperature T greater than 0 shown by this dotted line.

Now, if we multiply this g of E, and f of E like the density of states and Fermi function, then at T = 0, the combined function looks like this, this is shown by the green line.

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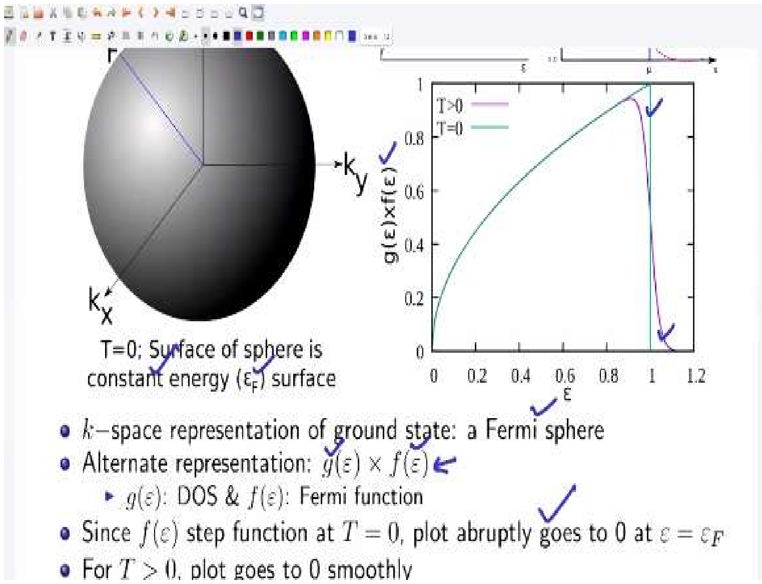


And at T greater than 0, the function looks like this, shown by the purple line. Since Fermi function is a step function at T = 0, the plot of this gE times fE, this will abruptly go to 0 at E = EF, the green line. And since that T greater than 0, the Fermi function goes to 0 smoothly, and the plot of g times fE shown by the purple line that also goes to 0 smoothly. Thus, you see in this figure, that if we represent the ground state and excited state by a function, which is combination of density of states and the Fermi energy.

Then this is how the green line shows that how it looks like at T = 0. So, that is the ground state representation. And the purple line shows that how it looks like at some temperature, which is T greater than 0, and that is the excited state representation.

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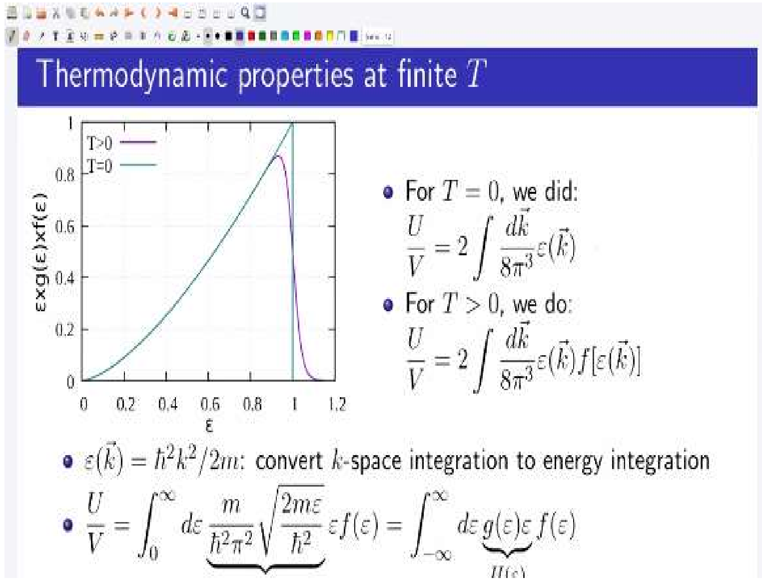


Let us calculate internal energy as a function of temperature. For T = 0, we already have done this, and we calculated this integral within the pharmacy. So, this is some integral over that k space.

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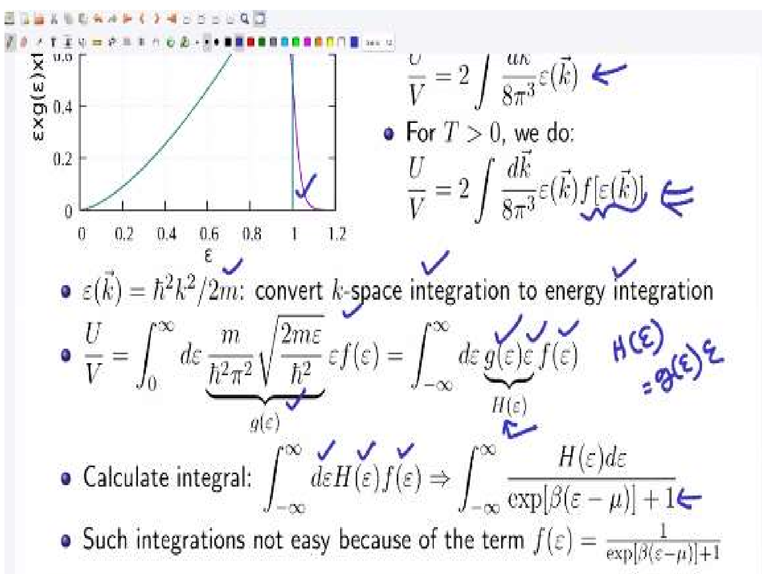


And now, for T greater than 0, we will do again the same thing, but this time to take into account the effect of temperature, we have to multiply this with the Fermi function. Now, again, you see that this integral is an integral over the k space. Now, as we did before we convert the k space integration to energy integration by using this relation energy is equals to h cross square k square by 2m. So, using this, we convert this and then we can write the energy density U by V. So, this integral and then as we did before we just define this done as the density of states.

And then the energy density that is the energy per unit volume that can be written as integral minus infinity to plus infinity dE. And then this is the density of states times the energy times the Fermi function. Now, if you look at this function, the g of E times E times f of E, this is shown in this plot. So, we just multiply energy with a density of states and do it Fermi function and then this is how it looks like at T = 0. The green line and the purple line show how does it, look like at finite temperature.

Now, if you look at this equation, then we just define g of E times E correct as some new function H of E. So, what is H of E? H of V = g of E times E and then this integral right this can be rewritten as integral over dE H of E times the Fermi function and if we just write the Fermi function in its form, then this is the integral that we have to evaluate. Now, such integrals are not very easy to evaluate, because of this term because of the Fermi function. So, let us see that what we can do?

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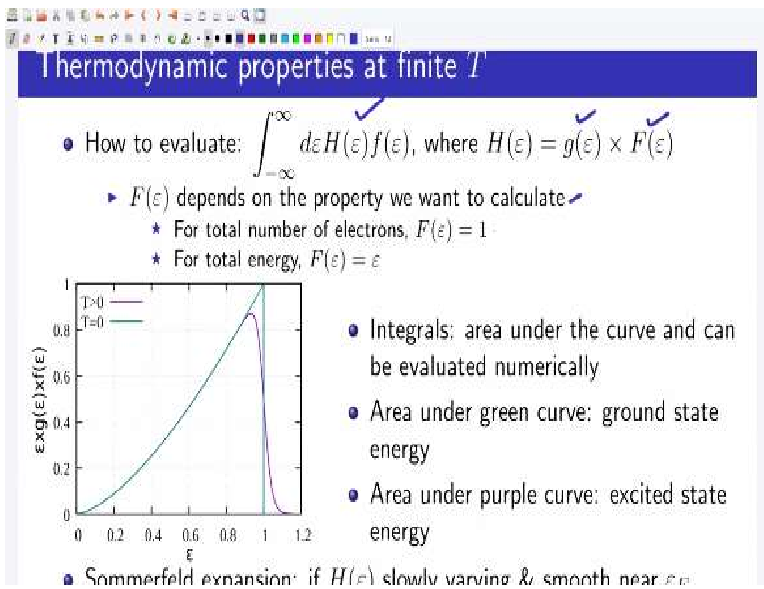


Thus, to find some property at finite temperature, in general, we have to evaluate the integrals of this form dE H of E times the Fermi function where H of E is the density of states times some function of energy and this function f of E it depends on the property we want to calculate. For example, if we want to calculate the total number of electrons F of E is just equal to 1 and if we want to calculate the total energy then F of E will be equal to energy.

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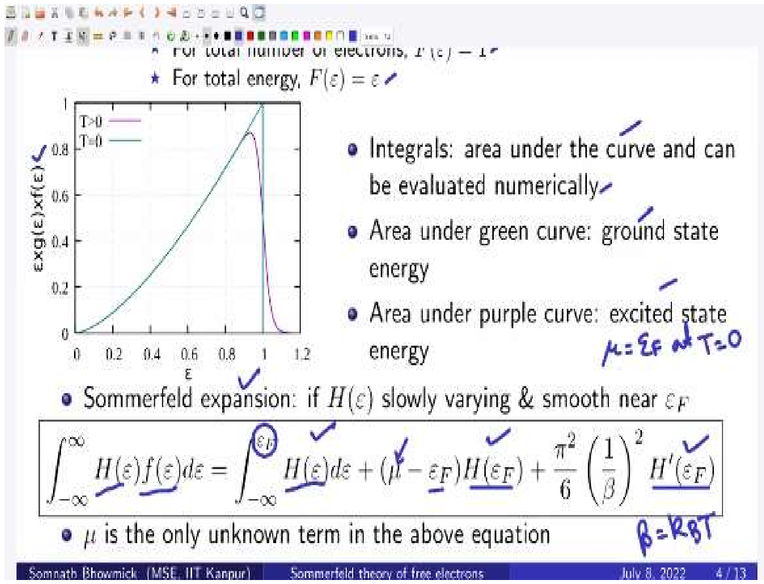


Now, this is the plot of E times g of E times f of E. So, one thing that we can do to evaluate these integrals is we know that the integrals are like area under the curve and we can of course, do numerical integration to evaluate the area under the curve for example, the area under the curve for the area under the green curve is ground state energy area under the purple curve is excited state energy and so on. Thus one way of getting the property at 0 Kelvin or at finite temperature is to numerical, evaluate the area under the curve.

Is there any other way of doing it? Yes, there is another way and that has been given by Sommerfeld and this is known as the Sommerfeld expansion and Sommerfeld expansion is the following. So, if we have to evaluate the integral of some function of energy times the Fermi function, then what we have to do is we just write it in this form. So, this is like minus infinity to EF HE dE + mu - EF H of EF that is the value of the function at the Fermi energy plus pi square by 6 1 by beta whole square.

Where beta = k B T times the derivative of the function at the Fermi energy note that in this equation, the Fermi energy is known the function is given to us H of E and again the Fermi energy is known and we know the value of the function at Fermi energy, we know the temperature and we also know the derivative of the function at Fermi energy. And then the only term that we do not know is this term mu, mu is the chemical potential all we know is that mu = E F at T = 0, but we do not know what is mu that finite temperature. So, we have to somehow evaluate mu at finite temperature.

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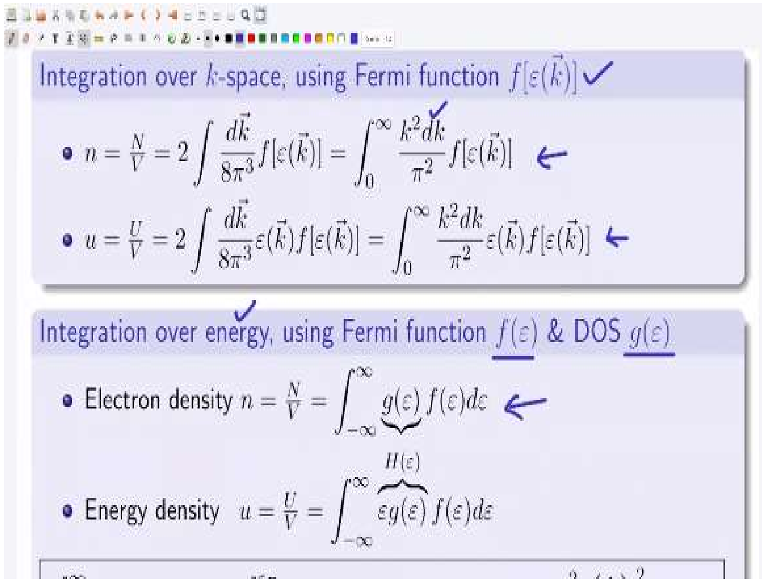


Let me quickly summarize what we have done so far. So, if we want to calculate some property, there are 2 ways of doing it. The first one is integration over k space using Fermi function f of Ek for example, if we want to calculate the total number of electrons or the electron density, then we have to evaluate this integral and note that this integral is over the k space if we want to evaluate the energy density then we have to evaluate this integral epsilon there is an alternate way this is given by the integration over energy.

And here we have used the Fermi function as well as density of states. In this case the electron density is given by this and the energy density is given by this.

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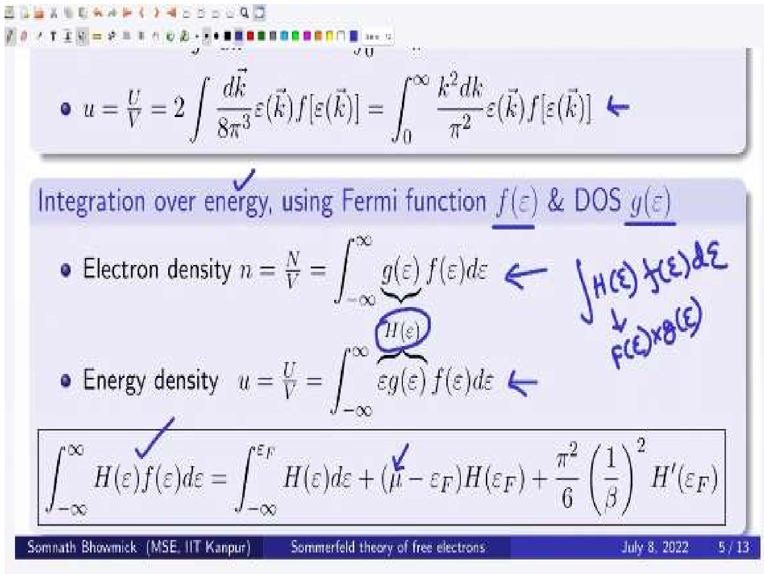


And note that we have some function of energy in general we just write it as H of E. So, that means these integrals if we want to evaluate we have to evaluate the integral of H of E times f of E. So, these integrals can be written in some general form as H of E f of E what is H of E? That depends on what we want to calculate for example, so, H of E will be some function of E times density of states were the function of E that depends on what we want to calculate.

Now, if you want to calculate such integrals, we can use of course, we can use numerical integration, but there is an alternate way we can use something called Sommerfeld expansion which is given by this and as I mentioned in the previous slide, the only term that we do not know in Sommerfeld expansion is what is mu at finite temperature we know what is mu at T = 0? At T = 0 mu is given by mu = E F but we have to find out what is mu at finite temperature.

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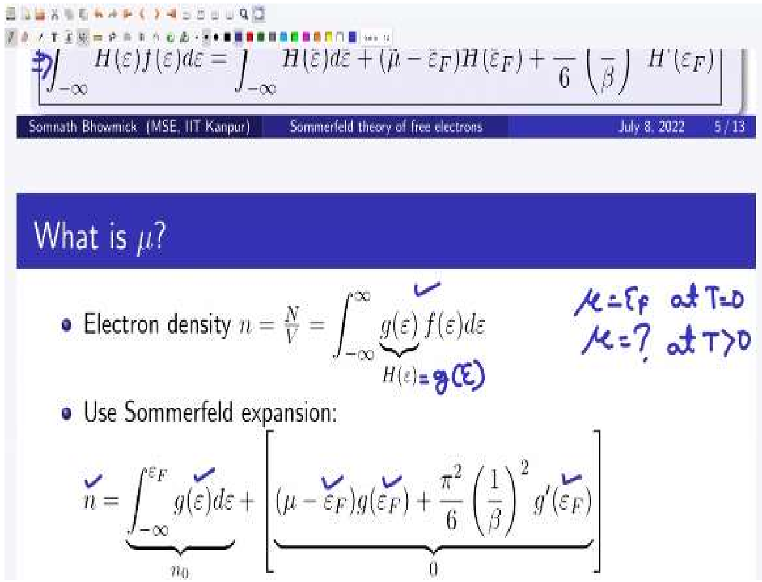


Now, let us try to find the answer that what is mu? So, what we know mu = E F at T = 0 and what we are asking for is mu is what when T is greater than 0? So, to find the answer, let us go back to the calculation of electron density at finite temperature and this time we use the Sommerfeld expansion. So, the electron density at finite temperature is given by this. So, this is an integral over g of E times f of E this is the Fermi function times dE. Thus, in the sommerfeld expansion H of E = g of E.

So, now, let us just put in Sommerfeld expansion that is in this equation, we just put h of E = g of E and then rewrite it here. So, that is the electron density is equals to integral of minus infinity to EF and in case of H of E, we just put g of E, g of E dE plus and then we put this term mu - EF so, this is like mu - EF and in place of h of EF we just put g of EF + pi square by 6 1 by beta whole squared and in place of H dash EF, we just put g dash EF so, this is the electron density at some finite temperature according to sommerfeld expansion.

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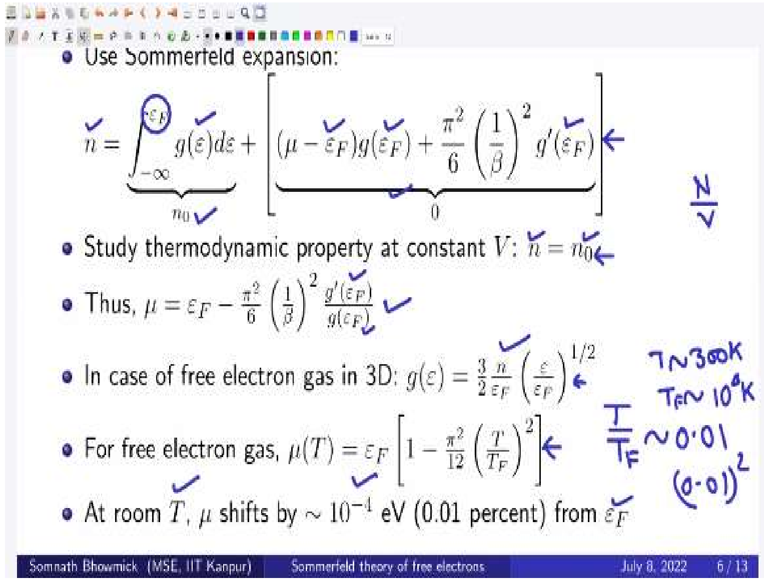


Now, let us consider a constant volume process. So, that means, electron density at 0 temperature will be equal to the electron density at finite temperature. So, electron density is what this is like number per unit volume correct number of electrons per unit volume and if I fix the volume then at the electron density at finite temperature will be same as electron density at 0 temperature which is written as n 0. Now, look at the sommerfeld expansion, so, the first term right minus infinity to EF, so, we are integrating up to the Fermi energy.

We are integrating density of states up to the Fermi energy and then that will give me n naught the 0 temperature electron density and then that means, next term is supposed to give me the change of electron density at finite temperature. And now, since we are considering a constant volume process such that the electron density does not change that means, the next term it should be equal to 0 this part of the integral is 0 because the electron density is not changing because of this constant volume process.

So, that means, we can just equate the entire term that is written inside this bracket, we can equate it to 0 and if we do that, then this is what we get. So, mu = EF - pi squared by 6 1 by beta squared and then this is like g dash EF. So, this is the first derivative of a density of states at the Fermi energy and divided by g EF that is the density of states at the Fermi energy. Note that in case of free electron gas in 3D the density of states is given by this.

And then you can take so, we can get the value of density of states at Fermi energy by putting E equal to EF in this equation. And we can also calculate the first derivative and again put E equals EF and then we can get this term and if we do all that thing, then what we know is that or then what we can derive is mu this is now a function of T is equals to EF 1 - pi square by 12 T by T F whole square. And then remember that T by T F right if T is of the order of room temperature.

So, T is of the order of 300 Kelvin and then we know that T F is the order of 10 power 4 Kelvin. So, that means T by T F is roughly of the order of 0.01 and then this is like T by T F square so, that means, this will be like 0.01 whole square that term in the inside the bracket. So, that means at room temperature mu shifts by only 10 power -4 electron volt that is just 0.01% from EF So, that means, for free electron gas is we see that the yes mu is not same as EF but this is very close to EF even at room temperature.

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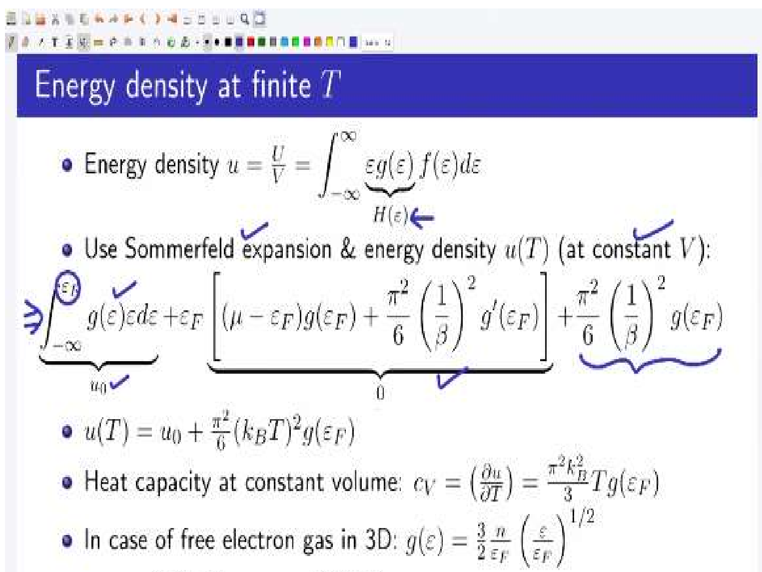


Let us now calculate energy density at finite temperature. So, in case of energy density, we have to evaluate this integral E times g of E times f of E dE where E times g of E we just assume this to be a function H of E and then we can use sommerfeld expansion and again we are calculating energy density remember that we are doing it at constant volume and then you have this big expression written here and then note that this part minus infinity to EF gE E dE what we are doing is that we are just evaluating this integral from up to the Fermi energy.

So, that means, that will give me that u naught the temperature at 0 Kelvin the ground state energy. So, this part is the ground state energy and then you have this part and then we have pi squared by 6 1 by k B T whole square g of EF. And in the previous slide, we just have found that the term inside the bracket is equal to o if we are considering a constant volume process.

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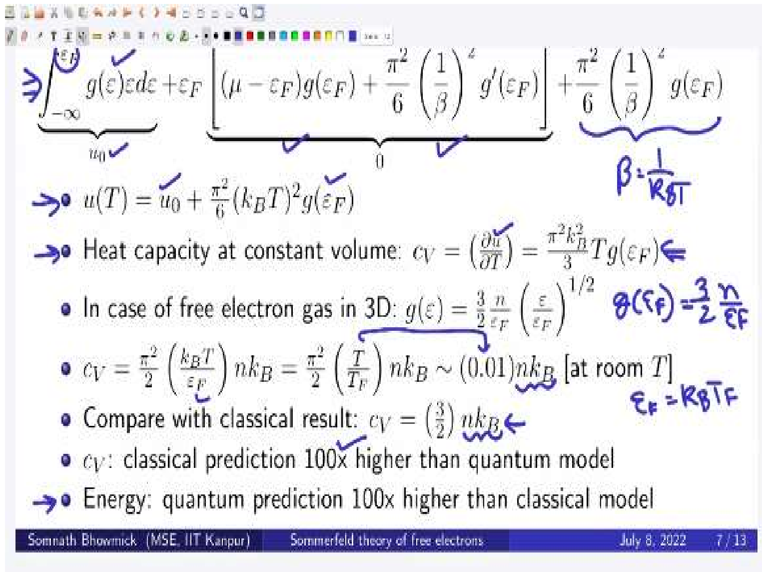


So, in that case, we can just write energy density as a function of temperature in this form u of T is equal to u 0 is the ground state energy plus pi square by 6 and beta is equal to 1 by k B T. So, we just replace that so, pi square by 6 k B T whole square and this is the g of EF that is the density of states at the Fermi energy we can also calculate the heat capacity at constant volume by just calculating the temperature derivative of energy density and then that turns out to be this and we know that for the free electron gas in 3D, we have this is the form of density of state.

So, that means g of EF we can just write it as 3 by 2 n by EF So, if we replace g of EF in this equation, then we can just write gE is equals to pi square by 2 k B T by EF n times K B. And remember that what we can do is that we can just write express this EF as some temperature scale by writing EF is equals to k B times T F correct. So, if we just replace it here, then the heat capacity can be written as pi square by 2 T by EF n k B and then we know that this T by T F this is of the order of 0.01 at room temperature.

So, that means at room temperature CV is 0.01 times n times k B. Now, compare it with the classical result, classically, C V is given by 3 by 2 and k B correct. So, that means, this n can be done is common for both, but then we have a pre factor in case of classical we have a k B factor which is of the order of one whereas in case of one term we have a pre factor which is of the order of 0.01. So, that is what we can conclude is that the C V the classical prediction is 100 times higher than the quantum model.

And remember that if we calculate energy this we already have discussed previously, if we calculate energy this then this is exactly the opposite. The Quantum prediction is 100 times higher than the classical model.