Electronic Theory of Solids

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Lecture - 08
Sommerfeld Expansion & Band Formation: Temperature dependent densities, Chemical Potential, Specific Heat

Hello and welcome. We have been discussing the effects of quantum mechanics on the gas of electrons in solid typically a metal is what we are considering now. Now, the important thing that we mentioned is that, although for transport electrons behaving as a free classical particle kind of theory give a reasonably good agreement with experiments for thermodynamic quantities like specific heat or heat capacity, the discrepancy between the classical theory and the experimental results was considerable, it is about a factor of 100 or more.

Now, the question is where does it come from. Such a huge discrepancy and in one case there in transport electrons electronic theory based on classical physics gave us reasonably good results whereas, only for thermodynamic quantities it did not. So, the discrepancy was actually sorted out when people realize that, these electrons are quantum particles and you have to use quantum mechanics and which came only after 1925.

So, the early confusion was sorted out when one started using the Fermi statistics, Fermi Dirac statistics for electron gas and Pauli Exclusion Principle they are off.

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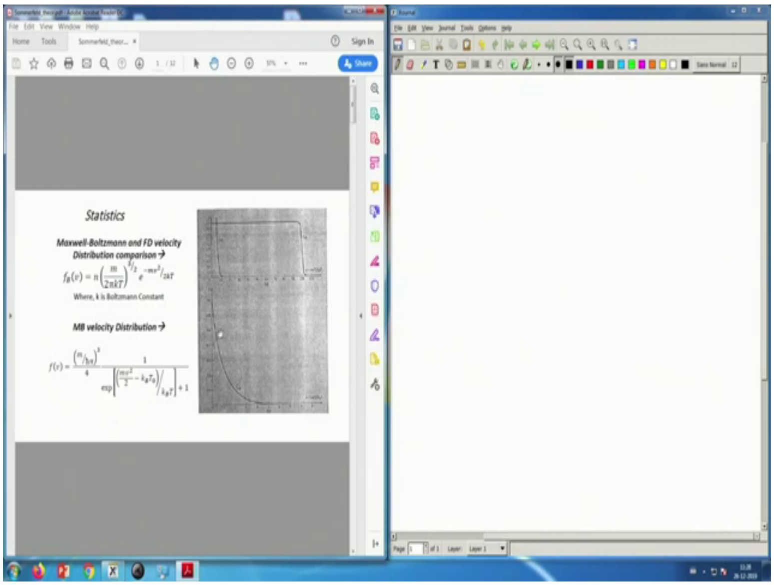

Statistics

Maxwell-Boltzmann and FD velocity Distribution comparison →

$$f_B(v) = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}$$

Where, k is Boltzmann Constant

MB velocity Distribution →

$$f(v) = \frac{\left(m/h\pi\right)^3}{4}\frac{1}{\exp\left[\left(\frac{mv^2}{2} - k_B T_0\right)\Big/ k_B T\right] + 1}$$

Now, the again to just recap what I said in the previous class what we did we said that the discrepancy is primarily because of the fact that the Boltzmann statistics the for example, velocity distribution runs very high at low temperatures, at low energies. And, these corrections are much, I mean these are the things that take care of this huge factor that comes in the specific heat.

Look at the Fermi Dirac distribution which is cut off by 1 it is always 1 here and it has a small almost vertical drop at the at around k f or e energy e f. Whereas, the Maxwell Boltzmann distribution is very large at very low energies and then it falls off exponentially. So, the low energy specific heat will using Maxwell Boltzmann statistics is going to be wrong. It is going to be off by a factor of 100 or more. The other interesting thing is that this classical statistics will not give you a linear in temperature dependence which I said is what people found at low temperatures for a gas of electrons.

When the ionic contributions are negligible, you only have electronic contributions to specific heat and at that point at low energy low temperatures, you should experimentally people found out that it is linear in temperature. So, that linear in temperature dependence will never come out of classical theory because it’s a classical theory gives you just a constant independent of temperature.

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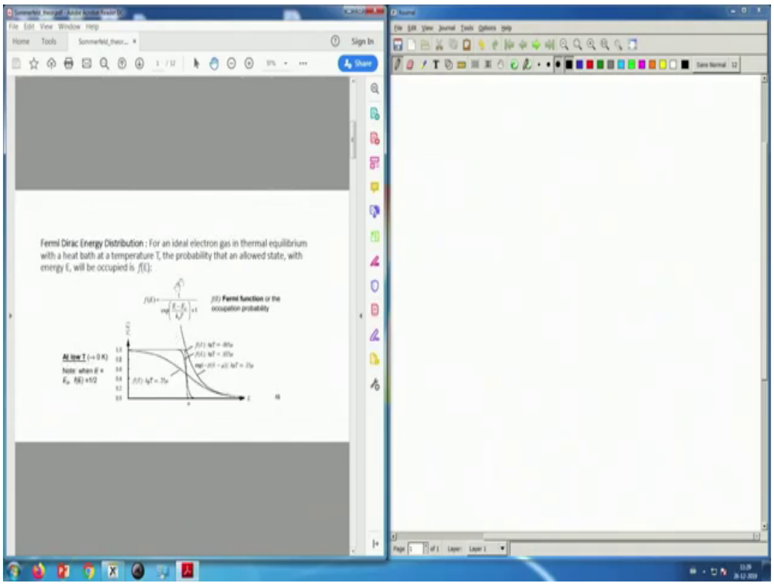

Fermi Dirac Energy Distribution : For an ideal electron gas in thermal equilibrium with a heat bath at a temperature T, the probability that an allowed state, with energy E, will be occupied is $f(E)$:

$$f(E)=\frac{1}{\exp\left(\frac{E-E_F}{kT}\right)+1}$$

$f(E)$ **Fermi function** or the occupation probability

At low T (→ 0 K)

Note: when $E = E_F$, $f(E) = 1/2$

Now, the in the when you apply quantum theory you have to be alerted by the fact that the Fermi Dirac distribution has a form which is at 0 temperature, it is just a box kind of structure, it goes all the way up to a Fermi a particular energy and then drops off vertically. And, as temperature rises that vertical drop of sort of becomes smeared and it is the drop becomes less vertical; it has a finite slope and so on. But it is interesting that if you just look at this nature of this function at E equal to E F it will always pass through half.

But now, what will happen at finite temperature is that some states from here will be lost and they will come beyond the E F. This is shown at different temperatures for example, in this graph. Then that has a, that is what causes the specific heat of a degenerate electron gas, that there are excited states beyond E F at finite energy finite temperatures.

So, and one another thing I mentioned is that the at very large energy is of course, the Boltzmann statistics and Fermi energy and the Fermi Dirac statistics almost merge which is very clear from this expression, when the exponent dominant exponential factor dominates you can neglect the one and then you get back your Boltzmann statistics.

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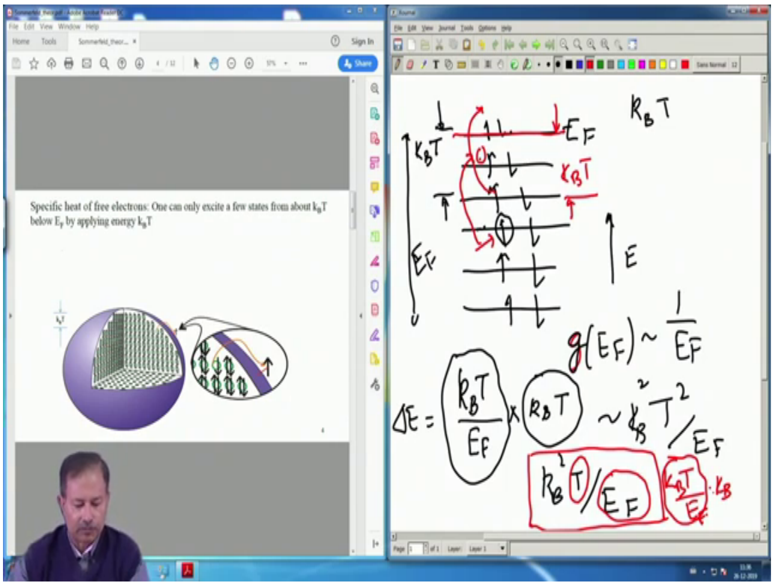
Specific heat of free electrons: One can only excite a few states from about k_BT below E_F by applying energy k_BT

Now, this is what we argued that if you have a. So, let me just give a recap of the argument, the electronic states are filled up to say. Suppose these are your electronic states as shown in this picture, these are the states all of them are filled up to a certain energy. So, that energy is E F. Now, as I said if you now want to give supply some heat energy to this system, suppose all of these are filled up to at 0 temperature just filled up to; all these are filled up to Fermi energy and you are supplying an energy k B T.

Now, the point is that suppose this is the k B T. This is the k B T amount of energy that you are supplying, this is my energy axis. So, how many electrons can take the energy? The electron which is here if it if you if one gives it k B T amount of energy this electron for example, will rise up to probably here, but there are no states here. So, these are all these are states where these electrons just cannot go. I cannot take it up here because these states are all filled up. So, the only electrons that I can take out are within the distance of k B T, they can accept this energy to get excited and they will be excited beyond E F. So, this electron for example, can go here.

So, if this k B T is slightly more than these distance this energy difference. So, the electrons which can go these are; so, up to this is forbidden basically, you cannot excite and only once which are excited are within k B T. So, they are the ones which can accept the energy k B T now how many of them are there? I mean typically the number of states here is g at E F. So, g at E F the density of states which is almost I can write it as 1 over E F proportional to. Now remember it is 3 by 2 n by E F. So, it is inversely proportional to E F in the free electron theory. So, so the proper number of electrons that takes this energy is proportional to k B T f k B T by E F right this ratio of these two energies.

So, this is all the way from here to out of all these states which is E F a fraction of states which is k B T by E F, these number of states can take can accept the this energy and how much energy can they accept? They will each accept k B T. So, electrons lying within this range of these this fraction of total electrons this fraction of total electrons will take that energy and how much energy each takes? This is the energy. So, it is proportional to T square k B square into T square.

Now, if this is the energy change in energy then of course, the derivative with respect to temperature will give you a k B square into T factor divided by E F. Now, this division by E F this denominator is extremely important. Because, remember we needed a factor of 100 or more and if you look at the temperature typical temperatures are say 300 degree Kelvin and typical a E F is like 50,000 degree Kelvin right.

So, this immediately gives me this huge factor of more than 100 to 500 and so on. So, that is that basically resolves this problem of finding a specific heat which is linear in temperature first of all. So, this linearity and the facts factor the T by k B T by E F. So, this I can write as into k B k B. So, this factor gives me the 100 that way I was looking for we were looking for to match experiments ok.

So, the both the problems are resolved by this argument of Pauli using Pauli principle; that means, quantum statistics. So, one can make it more formal and that is what I am going to do now. So, let us just do a treatment which is somewhat for a more formal than what I have just said in words ok.

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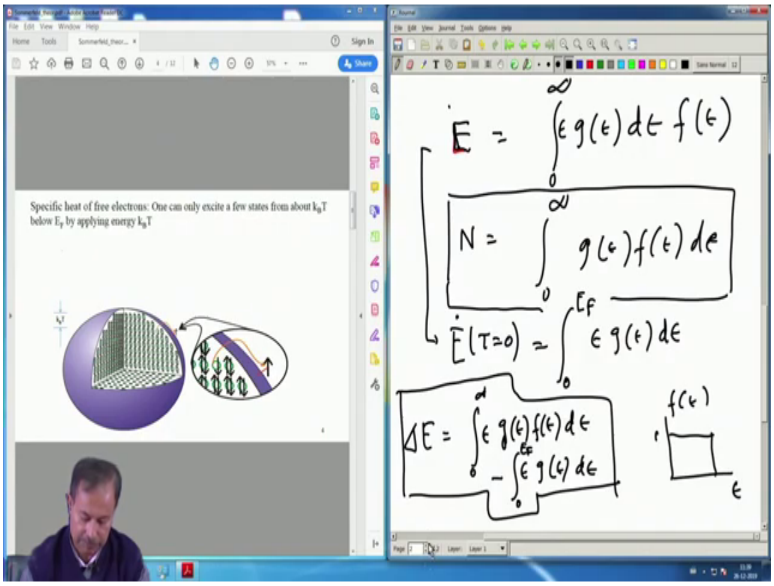

Specific heat of free electrons: One can only excite a few states from about k_BT below E_F by applying energy k_BT

$$E = \int_0^\infty \epsilon\, g(\epsilon)\, d\epsilon\, f(\epsilon)$$

$$\boxed{N = \int_0^\infty g(\epsilon) f(\epsilon)\, d\epsilon}$$

$$E(T=0) = \int_0^{E_F} \epsilon\, g(\epsilon)\, d\epsilon$$

$$\boxed{\Delta E = \int_0^\infty \epsilon\, g(\epsilon) f(\epsilon)\, d\epsilon - \int_0^{E_F} \epsilon\, g(\epsilon)\, d\epsilon}$$

So, the energy E is basically as I said in the previous day that I can convert the k integral into a energy into an energy integral using the density of states g E then E d E 0 to infinity ok. So, this is my energy of the system, but then this is not exactly correct because at finite temperature, you have to multiply this by the Fermi function. So, this is the energy of the system similarly the number total number of particles is of course, again due to infinity g E f E d E.

So, these are the two equations that I am going to use. So, at 0 temperature for example, the E at T equal to 0 is basically the same integral, but there are two things are important that f E the remember that f E is just one at 0 temperature this is one f E versus E. So, this integral at 0 temperature will become from g from 0 to E F because if the f E is 0 beyond that epsilon g epsilon d E ok. So, this subtraction of this from this will give me the change in energy at a finite temperature. So, it is E; so, epsilon g E f E d E 0 to infinity minus epsilon g E d E 0 to E F.

So, that is the change in energy at a finite temperature. So, let us just also write the N equation which is so, that equation is already here. So, I will use these two equations.

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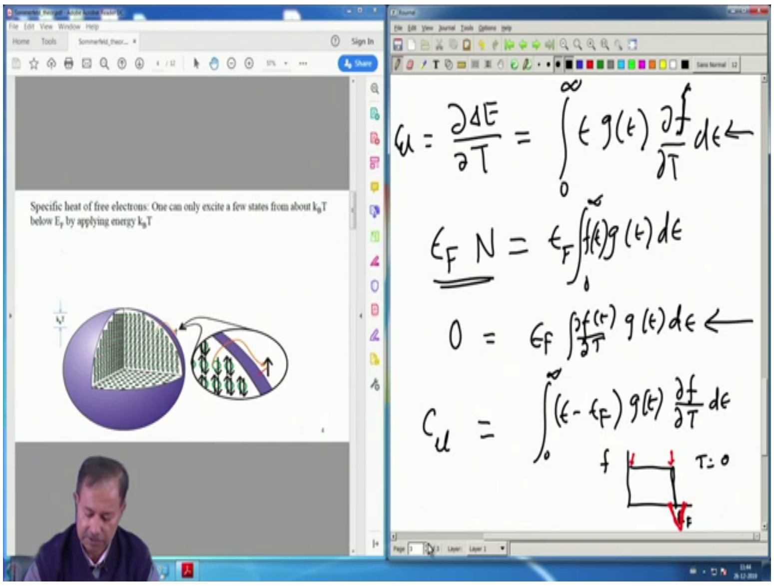

Specific heat of free electrons: One can only excite a few states from about k_BT below E_F by applying energy k_BT

$$C_{el} = \frac{\partial \Delta E}{\partial T} = \int_0^\infty \epsilon\, g(\epsilon) \frac{\partial f}{\partial T} d\epsilon \leftarrow$$

$$\underline{\underline{\epsilon_F N}} = \epsilon_F \int_0^\infty f(\epsilon) g(\epsilon) d\epsilon$$

$$0 = \epsilon_F \int \frac{\partial f(\epsilon)}{\partial T} g(\epsilon) d\epsilon \leftarrow$$

$$C_{el} = \int_0^\infty (\epsilon - \epsilon_F)\, g(\epsilon) \frac{\partial f}{\partial T} d\epsilon$$

So, what I do is that I do two things del E by del T that is equal to epsilon g E del f del T d E 0 to infinity. So, this is, see, because the other terms are constant in temperature. So, they follow they are just they cancelled out. So, I do not have to bother about those terms. So, this is basically my electronic specific heat C electron let me use write it C electronic specific heat.

Now, I multiply that previous equation for N by E F; so, E F into N equal to just E F into to infinity g E d E into f E ok. Now, this left hand side both the, both these are constant numbers. So, if I take a derivative with respect to T this will just give me 0. So, this will be 0 E F f del f del T g E d E. So, if I now subtract this one from this one then what I will get is C electronic equal to e minus E F g E del f del T d E right 0 to infinity.

Now, this is the this is so, far we have not done any approximations, but this is the point where we can make some approximations and the level of approximation tells you at what degree of correctness you will get your results. For example, the Fermi function as I said is a it is like the box like function, there is a vertical drop here at 0 temperature T equal to 0.

So, if you take a derivative of Fermi function then it you will get 0 all the way from here from here to here you will get 0, but except at this point E F where you will get a value because it drops its like a discontinuity at this point. So, you will get a function which is the derivative function will be like this.

So, it is like a delta function in the negative direction. So, this minus del f del T is actually a delta is behaves like a delta functions at 0 temperature. But, the moment you deviate from 0 temperature of course, this will this delta function picture will not work, but you have to then take their exact derivative of the Fermi function and then of course, you have to the calculation cannot be done. See if you do the calculation using the Fermi function, then you have to do the whole calculation in the sense you have to integrate the equation and that integration is not easy to do.

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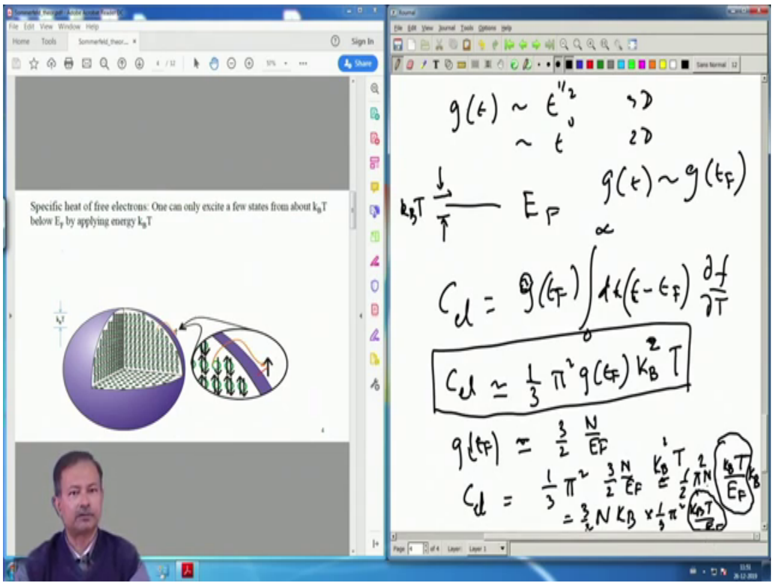

Specific heat of free electrons: One can only excite a few states from about k_BT below E_F by applying energy k_BT

$g(E) \sim E^{1/2}$ 3D

$\sim E^{0}$ 2D

k_BT — E_F $\quad g(E) \sim g(E_F)$

$\propto$

$C_{el} = g(E_F) \int_0 dE\,(E - E_F)\,\frac{\partial f}{\partial T}$

$$\boxed{C_{el} \simeq \frac{1}{3}\pi^2 g(E_F)\, k_B^2\, T}$$

$g(E_F) \simeq \frac{3}{2}\frac{N}{E_F}$

$C_{el} = \frac{1}{3}\pi^2 \frac{3}{2}\frac{N}{E_F} k_B^2 T \simeq \frac{1}{2}\pi^2 N \left(\frac{k_BT}{E_F}\right) k_B$

$= \frac{3}{2} N k_B \times \frac{1}{3}\pi^2 \left(\frac{k_BT}{E_F}\right)$

Nevertheless what one can make an some kind of an approximation is that you assume that your g of E which is which in three dimensions. For example, goes as E to the power half and in two dimension goes as it E goes as E to the power 0, you can assume that this the regime of energies that we are talking about is about around E F there is a small energy range 100 or even less than the value of E F of with k B T.

So, within that range of temperature, we can assume that the g of f can be replaced by its value at the Fermi level. So, if you do that then of course, your C of electronic is you can pull it out the g of E F can be pulled out of the integral and then the rest of the integral remains d

E E minus E F. Just a second d of E E minus E F then del f del T. So, this integral has to be evaluated. Now this is this of course, you can calculate del f del t because you know the no E F as a function of temperature also. So, all that can be done and you can put those values in and if you do that an approximate calculation leads to the value which is about one-third pi square g E F into k B square T.

So, this is kind of a back of the envelope calculation valid up to the order more or less valid up to the order T; it does not take care of the shift of chemical potential change of chemical potential due to the thermal effects. Because, we are working at finite temperatures, we should have used that, but this approximation still gives us the linear in T dependence and the factor one-third pi square.

Now, if you remember g of E F for a free electron gas was 3 by 2 N by E F then your C of electron in this theory is one third pi square and g of E F is 3 by 2 N by E F into k B square into T. So, these 3 cancels it will be half pi square equal to this will give me half pi square N k B square T by E F. So, this k b square T I can write as k B T into k B. So, I put a k B here N then a k B here. Now look at this, this is pi square. So, half pi square into n k B T by f.

Remember it was 3 by 2 N k B only in the in the classical theory here you have a factor k B T by E F and a numerical factor of about one third to do that. So, this factor k B T by E F gives you a factor of 100 or low or even less and the linear in temperature dependence comes out of this kind of a back of the envelope calculation. I mean it is a very simple approximate calculation one can even do better I mean that is the whole exercise that Sommerfeld it took.

What he did was that he wanted to correct his calculus he wanted to make first of all write down a general calculation, where this kind of integrals appear where you have to sum over the these degenerate states and their energies and so on to get physical quantities. So, so far what we have done actually pulls out the physics correctly. Remember the physics involved two things; we required a factor of about 100 less than the classical value which this one is right.

So, if you compare this one for example, with 3 by 2 N k B then you can see that you are only if factor of one-third pi you are down by a factor of pi square k B T by E F. So, that k B T by

E F gives me a factor of 100 less than the this see one-third pi square is like 3 or something close to 3.

So, that is not important a factor of 3 would be alright, but there is this factor of 100 and this factor of 100, 1 by 100 gives me the correct ballpark figures for the specific heat, besides it also gives this very important factor that the specific heat of electrons which is visible at very low temperatures; when ionic specific it is already down. And, this specific heat electronic specific heat for a gas of electrons in a metal is proportional to temperature.

So, these are the two major achievements of this kind this particular calculation which was first undertook by Fermi and its as you can see it is a simple back of the envelope calculation approximate calculation gives you the correct result to order T. The question of course, is can I do better than that and that involves the so, called Sommerfeld corrections, Sommerfeld did these calculations are correct up to order T square.

Now, these that calculation I will just show briefly as to how to do it is not to be remembered and it is some its a fairly complicated long calculation. And, if you ever need corrections up to order T square, then of course, you have to look at these calculations. So, as I said the main corrections will come from the change in chemical potential.

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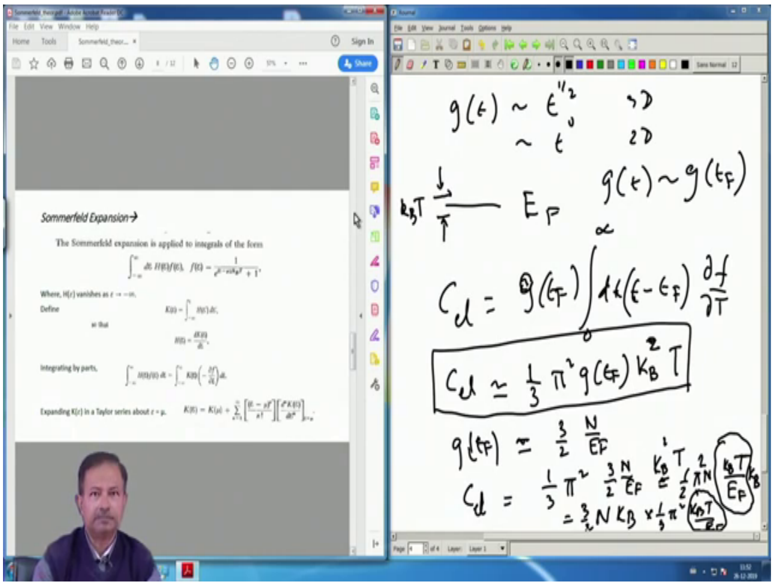

Sommerfeld Expansion→

The Sommerfeld expansion is applied to integrals of the form

$$\int_{-\infty}^{\infty} d\epsilon\, H(\epsilon) f(\epsilon), \quad f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_BT}+1},$$

Where, $H(\epsilon)$ vanishes as $\epsilon \to -\infty$.

Define

$$K(\epsilon) = \int_{-\infty}^{\epsilon} H(\epsilon')\, d\epsilon',$$

so that

$$H(\epsilon) = \frac{dK(\epsilon)}{d\epsilon}.$$

Integrating by parts,

$$\int_{-\infty}^{\infty} H(\epsilon) f(\epsilon)\, d\epsilon = \int_{-\infty}^{\infty} K(\epsilon)\left(-\frac{\partial f}{\partial \epsilon}\right) d\epsilon.$$

Expanding $K(\epsilon)$ in a Taylor series about $\epsilon = \mu$,

$$K(\epsilon) = K(\mu) + \sum_{n=1}^{\infty}\left[\frac{(\epsilon-\mu)^n}{n!}\right]\left[\frac{d^n K(\epsilon)}{d\epsilon^n}\right]_{\epsilon=\mu}.$$

$$g(\epsilon) \sim \epsilon^{1/2} \quad 3D$$

$$\sim \epsilon^{0} \quad 2D$$

$$k_BT \quad E_F \qquad g(\epsilon) \sim g(\epsilon_F)$$

$$C_{el} = g(\epsilon_F)\int_0^{\infty} d\epsilon\,(\epsilon-\epsilon_F)\frac{\partial f}{\partial T}$$

$$\boxed{C_{el} \simeq \frac{1}{3}\pi^2 g(\epsilon_F) k_B^2 T}$$

$$g(\epsilon_F) \simeq \frac{3}{2}\frac{N}{E_F}$$

$$C_{el} = \frac{1}{3}\pi^2 \frac{3}{2}\frac{N}{E_F} k_B^2 T = \frac{1}{2}\pi^2 N \left(\frac{k_BT}{E_F}\right) k_B$$

$$= \frac{3}{2} N k_B \times \frac{1}{3}\pi^2 \left(\frac{k_BT}{E_F}\right)$$

So, let us see what Sommerfeld did ok. So, this is what we will start right now.

Thank you.