Electronic Theory of Solids
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Lecture - 07
Statistics Fermi-Dirac distribution and Maxwell-Boltzmann Distribution: comparison and Specific Heat

Hello and welcome. We are discussing the Electronic Properties of Solid, and in that we have so far shown that some of the classical treatments of electronic theory work fairly well, if you are particularly describing transport, thermal conductivity and so on. But then, we also mentioned at some point that it such kind of treatments go horribly wrong when you are measuring quantity which a particularly for example, which require you to find out the amount of energy that a system observes, a gas of electron in a solid observes. And for example, specific heat is one such quantity which is a derivative of the internal energy with respect to temperature and that; obviously, goes wrong in a classical treatment.

Now, as we started doing we were calculating the quantum mechanical description of electron gas, we are still in the free electron gas regime electrons are not interacting with each other. So, in this approximation the spectrum is still p square by twice m. So, it is a free electron like spectrum, e equal to p square by twice m, but we have to now treat this electron's as quantum mechanical objects.

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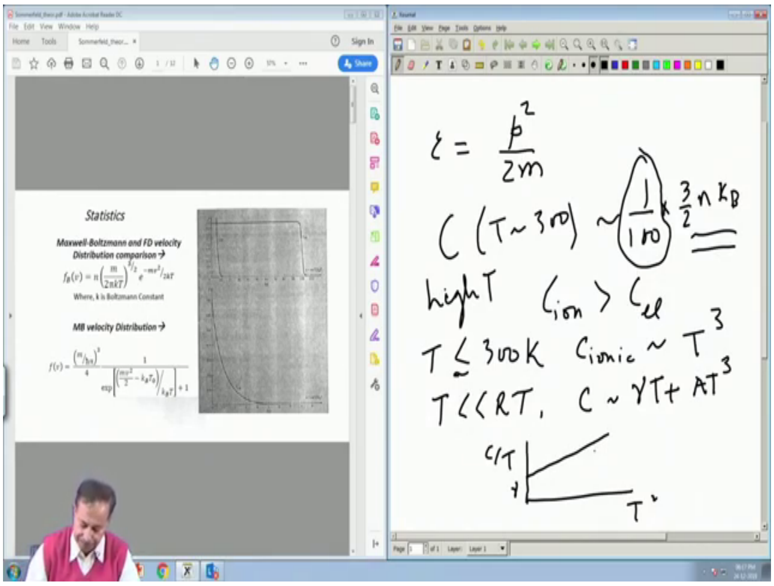

Statistics

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 →

$$f(v) = \frac{\left(m/h\right)^3}{4}\frac{1}{\exp\left[\left(\frac{mv^2}{2} - k_BT_0\right)/k_BT\right] + 1}$$

$$\varepsilon = \frac{p^2}{2m}$$

$$C\,(T \sim 300) \sim \frac{1}{100} \times \frac{3}{2} n k_B$$

high T $\quad C_{ion} > C_{el}$

$T \lesssim 300K \quad C_{ionic} \sim T^3$

$T << RT, \quad C \sim \gamma T + AT^3$

These are quantum particles, so we started doing it, we wrote down the Schrodinger equation we found out the density of states that is allowed to these electronic states. And then we said that once you have that you have to also remember that fermions electrons which are fermions must obey the Fermi-Dirac statistics instead of the Maxwell Boltzmann statistics that we have been using so far.

Now, these are the drastic effect, because if you look at the picture of for example, the distributions; two distributions for example, for the top picture compares Maxwell Boltzmann distribution with velocity distribution with Fermi-Dirac distribution. And if you look at it, see that at low temperature the Maxwell Boltzmann distribution basically shoots up. This is a close up view of it, the Maxwell Boltzmann distribution is basically shooting up, whereas the Fermi-Dirac distribution is always limited by the value 1.

So, for example, this is your Maxwell Boltzmann distribution velocity distribution, have per number of particles within a range of velocity v and v plus dv. So, that goes like this e to the power minus mv square by 2 k B T and whereas, the Fermi-Dirac distribution goes us this is Fermi-Dirac distribution, this picture is the Maxwell Boltzmann distribution whereas the Fermi-Dirac distribution goes like this that it is limited by the value 1. And there is a very sharp drop at the Fermi energy, so this is the E F. So, this is done at a finite temperature, so that you can see there is a slight deviation, it is not exactly a vertical drop there is a slight deviation from vertical drop. We will come to it.

Now, so how did we suspect that we have to use Fermi-Dirac distribution instead of Boltzmann distribution? It came from the fact that the, if you look at the specific heats, the specific heat or heat capacity in a solid at modularity high temperature is actually dominated by the contributions from the ions.

Now, both the ions and electrons do contribute to specific heat; whereas, the ionic contribution at any moderate temperature dominates the value of the electronic contribution. On the other hand, if you go down to low temperatures then there is regime where the electronic contribution to specific heat, we are talking about metals, so, in that the electronic specific heat starts dominating over the ionic contribution.

Now, typically at around 300 degree Kelvin the classical specific heat is typically about 100 of the classical value which is 3 by 2 n k B per unit volume. So, this factor of 1 by 100 was missing in the classical description which gave us this value. And it was quite surprising because even a person like Lorentz who claim that it is extremely surprising that for description of transport and conductions, the conduction of electricity the electronic the classical description of electron gas is working so well the free electron description, whereas for specific heat it is going wrong by typically a factor of 100.

So, this was a mystery at that point and then it was obviously, later on realize that you have to once quantum mechanics came in that you have to use classical, you have to abundant classical statistical mechanics and you use the quantum statistics which is the Fermi-Dirac statistics for this calculation. And that basically, serially restricts the states and the electrons that can accept the certain amount of energy.

Typically, at high T, the ionic contribution to specific heat is dominating over C electronic, ok. And around T less than typically 300 degree Kelvin of course, we know that us ionic contribution goes as T cube. This we will find out later, but experimental one knows that this is how specific heat goes at moderate at around room temperature or slightly below it.

At very low temperature, much much below room temperature the total specific heat has a form like C gamma T plus AT cube. So, typically if this gamma T term dominates at very low temperature over this T cube term which comes from ions. So, one actually experimentally one sees that usual plots are C by T versus T square and it is obviously, linear from this graph with a intercept which is gamma from this you can actually determine the gamma.

The units of specific heat or Joules or calories per mole per degrees, so its C, the unit is joules or calories per mole per degree Kelvin and gamma the unit is one mole T will coming, so this joule or calorie mole inverse degree k to the power minus 2. So, this is what one actually plots, one determines from the plot of C by T versus T square.

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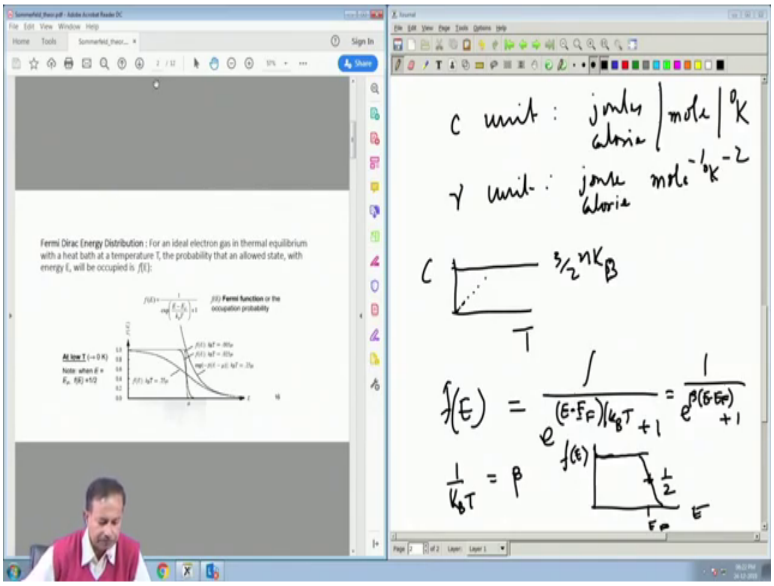

Fermi Dirac Energy Distribution : For an ideal electron gas in thermal equilibrium with a heat bath at a temperature T, the probability that an allowed state, with energy E, will be occupied is $f(E)$:

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

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

At low T (→ 0 K)

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

C unit : joules / calorie | mole | °K

γ unit : joule / calorie mole^{-1} °K^{-2}

$$f(E) = \frac{1}{e^{(E-E_F)/k_BT}+1} = \frac{1}{e^{\beta(E-E_F)}+1}$$

$$\frac{1}{k_BT} = \beta$$

So, as we said in the classical description we will always get this C versus T stuck at 3 by 2 N k, right, N k B. So, this is a value that typically comes from Maxwell Boltzmann, that comes from Maxwell Boltzmann distribution and we calculate half N k B t of energy part degree of freedom and so this is how you get the classical law. It is completely temperature independent as you see whereas the specific heat that we just plotted linear is linear at low temperature.

So, one has to make it and it goes down to 0. So, at T equal goes to 0. So, this is something that one has to figure out and it was Fermi who first figured it out from a very basic argument using the quantum statistics which is the Fermi-Dirac statistics. This of course, his own style it goes by his own name.

So, what he did was to realize simple fact which I will show you. Here for example, so let us this look at the Fermi-Dirac statistics written that itself we will tell us what to look for. So, this is the Fermi-Dirac energy distribution. For an ideal electron gas in thermal equilibrium with a heat bath at temperature T, the probability that an allowed state with energy E will be occupied is f of E and that f of E has this form.

So, it has a form f of E equal to 1 by E to the power E minus for an electron gas E minus E F divided by k B T plus 1. Now, 1 by k B T is sometime is written usually by beta, so you will you will find that this is also written as E to the power beta E minus E F plus 1. So, when T goes to 0, beta goes to infinity.

Now, it immediately tells you that as beta becomes large that is T becomes smaller, this exponential quantity at the denominator for any E greater than E F starts dominating and so that quantity will be much more than 1 soon and then you can neglect it and you get the usual Maxwell Boltzmann formula.

The other interesting thing is that if you look at this status the f E versus f E is plot versus E for example, at E F their value is exactly half. So, at E F this is one at low temperature, very low temperature and then it deviates from the value 1 and, but it is always stuck at the value half; no matter what the temperature is as long as you are at E equal to E F, because then this is 0, 1 by 2 is half. So, that is the in nature.

So, the other interesting thing to notice that the deviation from 1 becomes more and more as you as you go up in temperature; that means, there are states now at this these energies beyond the Fermi level. So chemical potential is the same as Fermi level at E chemical potential is the same as Fermi energy at temperature 0. But, as temperature rises chemical potential also shifts will come to that, but the more important thing is the change in the nature of this curve it becomes the value of f E deviates from 1, goes below 1 here and it and beyond E mu it has a finite value now. While at 0 temperature it has it was just a sharp drop at the chemical potential or same as Fermi energy, ok.

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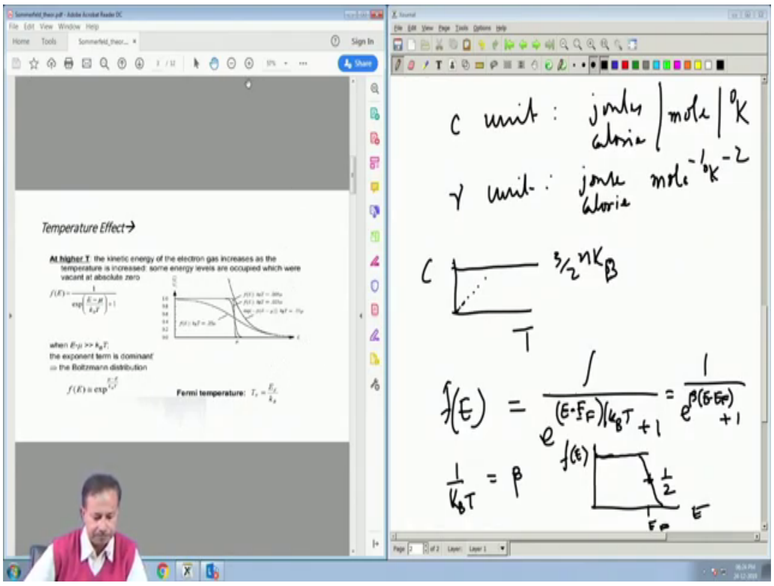

Temperature Effect→

At higher T: the kinetic energy of the electron gas increases as the temperature is increased: some energy levels are occupied which were vacant at absolute zero

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

when $E-\mu >> k_BT$:
the exponent term is dominant
⇒ the Boltzmann distribution

$f(E) \approx \exp^{\frac{\mu-E}{k_BT}}$

Fermi temperature: $T_F = \frac{E_F}{k_B}$

C unit : $\frac{\text{joules}}{\text{calorie}}$ | mole | °K

γ unit : $\frac{\text{joule}}{\text{calorie}}$ $\text{mole}^{-1}\,{}^{\circ}\text{K}^{-2}$

$f(E) = \frac{1}{e^{(E-E_F)/k_BT}+1} = \frac{1}{e^{\beta(E-E_F)}+1}$

$\frac{1}{k_BT} = \beta$

So, at very high temperature as I said as you can see from this curve, this curve gives you the Maxwell Boltzmann distribution as well. You can see that it is still going up and up and up, it is shooting up as you go down in temperature, it goes down in energy whereas, this one the Fermi-Dirac distribution is a line which is going which is it is a curve, which is going below 1 at less than E less than mu and then it is a finite at higher temperature.

And at very high temperature of course, when, sorry at very when E minus mu is much greater than k B T the exponential term is dominant, the Boltzmann distribution is obtained at temp at energies at very high compared to the value of k B T. So, that is exactly what you can see that at large energies the two statistics sort of merge. One can define a Fermi temperature which is just the E F by k B. So, k B T f is equal to Fermi energy that defines the Fermi temperature.

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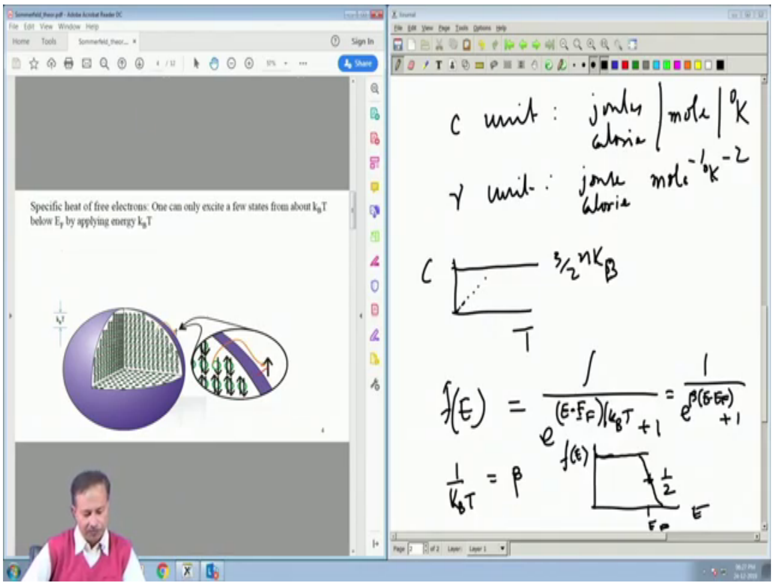

Specific heat of free electrons: One can only excite a few states from about k_BT below E_F by applying energy k_BT

C unit : joules / calorie | mole | ^0K

γ unit : joule / calorie mole^{-1} $^0K^{-2}$

$$f(E) = \frac{1}{e^{(E-E_F)/k_BT}+1} = \frac{1}{e^{\beta(E-E_F)}+1}$$

$$\frac{1}{K_BT} = \beta$$

Now, comes the question as to why statistics is so important to getting that linear in T term and getting a factor of nearly 1 by 100 compare to the classical hello electronics specific heat, ok. So, let us just try to understand physically now what is happening.

Now, as we discussed in the in one of the previous classes that a gas of even free fermions, the gas of fermions is allow it has states to go to in quantum mechanical description. So, these states of filled in by pairs, pair of electron in the up spin and down spin. So, you keep filling from the bottom and as you go up and up and up when you exhausts your electron number the highest level that you feel up is called the Fermi energy.

So, that means, an electron deep below the Fermi energy cannot take an energy and go up because all the states above it or even below it are completely filled up. So, the electron can or cannot take an energy which is which will not take it beyond the Fermi energy. So, if you want to go given electron an energy at the at somewhere below the Fermi level then you have to bring it above the Fermi level below that there is no state, that is allowed these states are all occupied by electrons already and that is what Pauli principle tells us that you cannot occupy a state by more than two electrons with up and down spins.

So, that is the picture on the right hand side shown. So, suppose I want to take one of these electrons from here to anywhere up I can only go above this, above the Fermi level. So that means, when you are giving a thermal energy to this electron gas where all states below Fermi level are filled up to Fermi level are filled up then you can you can of course, give energy the this is the amount of energy you are giving k B times T. But that energy will only we accepted by electrons which are only below k B T from this Fermi level Fermi energy, because any electron below that if it gets k B T amount of energy it has to go somewhere below the Fermi level and that is not allowed because these states are already occupied.

So, only electrons that can take that amount of energy k B T are the once which are within a narrow region just below the Fermi level whose width is basically k B T. So, that is the argument that tells you that the classical description which allowed all these electrons sitting here at the bottom to take the amount of energy k B T and that is how you calculated that 3 by 2 n k B T, this is no longer valid that argument is gone.

So, the so called phase space is serially restricted, the number of electrons that can take the energy, thermal energy is serially restricted compare to the original classical description. In this quantum description, you cannot give energy to a particle which is to an electron which is below the energy k B T of the Fermi level. Ok, so, how much energy do they take? So, that is one can actually do some small back of the envelop kind of calculation, some estimate one can make easily.

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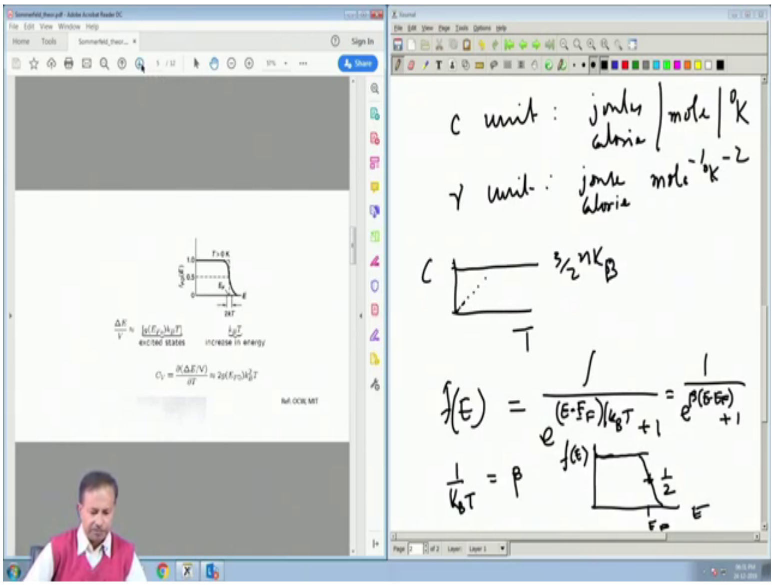

$\frac{\Delta E}{V} \approx [g(E_{F0})k_BT]$ excited states k_BT increase in energy

$C_V = \frac{\partial(\Delta E/V)}{\partial T} \approx 2g(E_{F0})k_B^2T$

Ref: OCW, MIT

C unit : joules / calorie | mole | °K

γ unit : joule / calorie mole^{-1} °K^{-2}

$$f(E) = \frac{1}{e^{(E-E_F)/k_BT}+1} = \frac{1}{e^{\beta(E-E_F)}+1}$$

$$\frac{1}{K_BT} = \beta$$

So, let us see how one makes this as estimate. So, look at this figure there is a region of k B T below the E F which is what the electrons sitting there can electrons which are there can take the energy k B T. So, how many electron how many states are here at the Fermi level this g of E F? So, the number of electrons there is basically twice g of E F, so and each of them is taking an energy k B T. So, the number of electrons is the number of states is g E F, each can occupy two electrons and the width over which you have to count is k B T from the Fermi level.

So, the change in energy per unit volume is basically the density of states at the Fermi level which we assume to be a constant within the range of k B T of the Fermi level. The k B T is 1 more than less than 100s of E F, so within that temperature range the density of states remains almost flat. So, this is the number of excited states, number of electrons, these are the number of states that will be able to accept the energy. The electron sitting in those states will be able to accept the energy. How much energy will they accept? They will each accept k B T. And there are two electrons per each density each state, so or each orbital, so then this is the total number then.

So, one can take, so this is k B T square k B T into g f the derivative of that with respect to temperature will give you this formula. So, it is a evident that this is g of E F into k B square into T. So, this gives me the linear dependence of the specific heat in the electron free electron gas. We are still in free electron gas as I said, but there is a Fermi surface and there is a Fermi energy corresponding to that.

So, that is the argument that first Fermi put forward and said that look at first of all this rectifies to big problems one that at low temperatures the specific heat coming from electrons is of the order of this linearly proportional to T and the second thing is that its value is much much less than the classical value, because E F for example, is inversely proportional to one to E F to sorry, g F E F is inversely proportional to EF. So, this is already k B T into T by E F.

I will come back to it when we do another calculation and show you that this gives us a factor of nearly 1 or 100 or more and that rectifies the problem of the number. And more importantly the linear temperature dependence comes out of this calculation, it goes to 0 at 0 temperature and it solves the experiment the problem that people saw in the experiments in the early 20th centuries, once quantum mechanics came in.

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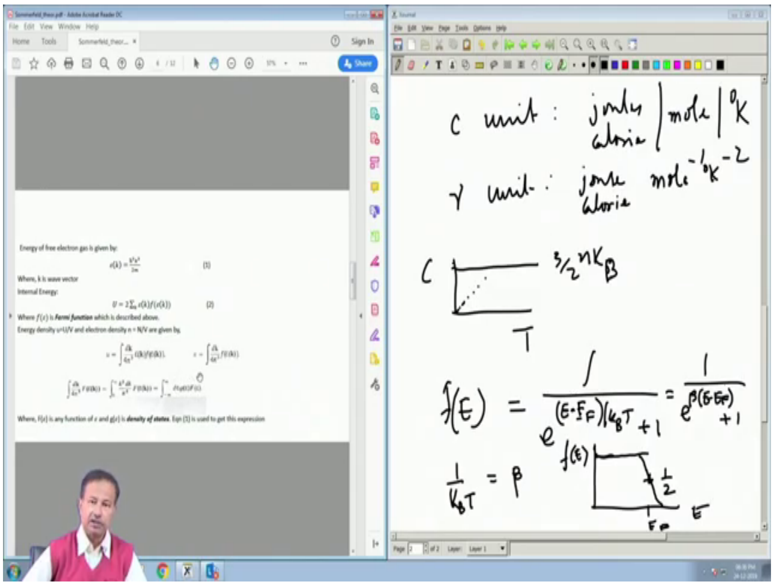

Energy of free electron gas is given by:

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m} \qquad (1)$$

Where, k is wave vector

Internal Energy:

$$U = 2\sum_{k\sigma} \varepsilon(k) f(\varepsilon(k)) \qquad (2)$$

Where $f(\varepsilon)$ is ***Fermi function*** which is described above.

Energy density u=U/V and electron density n = N/V are given by,

$$u = \int \frac{d\mathbf{k}}{4\pi^3}\varepsilon(\mathbf{k}) f(\varepsilon(\mathbf{k})), \qquad n = \int \frac{d\mathbf{k}}{4\pi^3} f(\varepsilon(\mathbf{k}))$$

$$\int \frac{d\mathbf{k}}{4\pi^3} F(\varepsilon(\mathbf{k})) = \int_0^\infty \frac{k^2\,dk}{\pi^2} F(\varepsilon(\mathbf{k})) = \int_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon) F(\varepsilon)$$

Where, $F(\varepsilon)$ is any function of ε and $g(\varepsilon)$ is ***density of states***. Eqn (1) is used to get this expression

C unit : joules / calorie / mole / °K

γ unit : joule / calorie mole^{-1} °K^{-2}

$\frac{3}{2} n K_B$

$$f(E) = \frac{1}{e^{(E-E_F)/K_BT}+1} = \frac{1}{e^{\beta(E-E_F)}+1}$$

$$\frac{1}{K_BT} = \beta$$

So, one can do a more sophisticated calculation and to do that one has to start again from the free electron theory. There are many arguments, many calculations that are given in several books for example, Charles kittel a solid state physics as a back of the envelop kind of simple calculation, but a really thorough calculation was first done by Sommerfeld and that calculation is fairly complicated. It is long, it is not that one has to remember it, but one I just show you how he corrected this result to up to order T square.

So, the linear temperature dependence comes out correctly, the although the pre factors are not exactly the correct once, the then the higher order terms are also not coming and that comes that I will you show you where it comes from. See, basically what happens is that the assumption that we are taking in most of these back of the envelop calculations that the chemical potential is still the same as the Fermi energy. This assumption actually is no longer correct at any finite temperature and as temperature rises the chemical potential deviates from the Fermi level.

So, this factor E minus E F has to be replaced by E minus mu which is a function of temperature, so you have to do the calculation accordingly and that is exactly what

Sommerfeld did. So, let us just look at his calculation. Just for a reference it is not in the required that you have to remember that calculation, but that calculation is important in the context of history of free electron gas and it is a specific heat and corrections using quantum statistics. So, I will just go through it briefly.

Now, just to recap these are the things that we have already done a epsilon k for a free electron gas is given by each particle carries this energy v square by twice m, which is h cross square k square by twice m, where k is a wave vector. Now, internal energy of course, is then epsilon k times the Fermi function, because you have to find out how many particles are occupying that energy state e, so that is f of e k Fermi function. In two comes from this degeneracy it is spin degeneracy, so its sum over all k's.

Now, the energy density is of course, you have to divide by the volume and the electron density n is capital N divide by V and they are also given by these kind of formula. So, u small u is now dk by 4 pi cube, you can convert this k sum to an integral because it is very dense. The intervals of k are extremely small that we have done in one of the previous classes where in we introduce the density of states.

So, you can convert the sum to an integral and remember that look at this integral the right hand side all quantities which are functions of k are actually also functions of energy, this energy e k h cross square k square by twice m. The functional dependence on k enters only through the energy, so this is very crucial. We will just come to it. Similarly, for n you can you just have to some the Fermi function for all k values.

Now, this is where this feature, that in any function capital F for example, if it is a function of k only through epsilon k, now directly depending on k then of course, you can convert this integral. So, now, of course, this is no longer dependent on the angle this function F is function of energy only which is k is the function of k square. So, there is no angle dependence here.

So, you can simply integrate out the angles which is 4 pi, so 4 pi into k square by 4 pi cube so that gives me k square by pi square; dk into F of e k and this is the relation that is important that this summation this integral over k can be converted to integral to an integral over density of states. This we have done in a previous lecture. You can look up your previous notes. So, this makes life much simpler because now you have to do only one integral over the energy.

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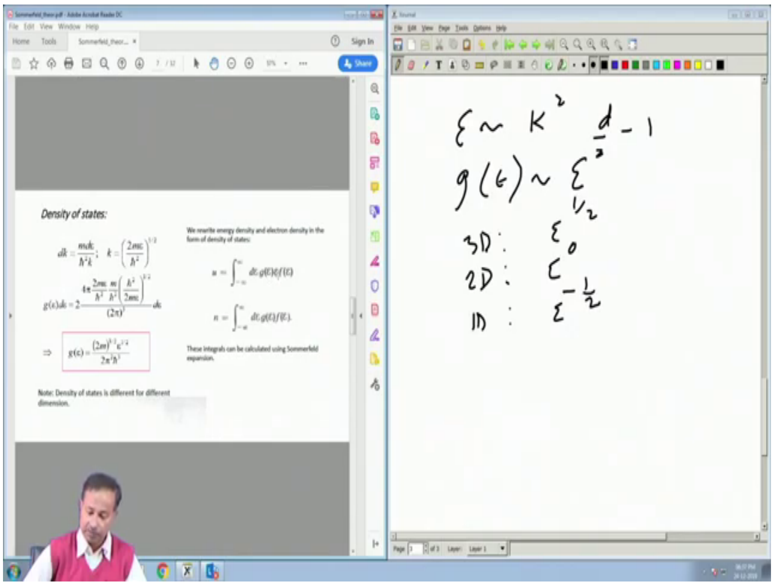

Density of states:

$$d k=\frac{m\,d\varepsilon}{\hbar^2 k};\quad k=\left(\frac{2m\varepsilon}{\hbar^2}\right)^{1/2}$$

$$g(\varepsilon)d\varepsilon=2\,\frac{4\pi\frac{2m\varepsilon}{\hbar^2}\frac{m}{\hbar^2}\left(\frac{\hbar^2}{2m\varepsilon}\right)^{1/2}}{(2\pi)^3}\,d\varepsilon$$

$$\Rightarrow\quad \boxed{g(\varepsilon)=\frac{(2m)^{3/2}\varepsilon^{1/2}}{2\pi^2\hbar^3}}$$

Note: Density of states is different for different dimension.

We rewrite energy density and electron density in the form of density of states:

$$u=\int_{-\infty}^{\infty}d\varepsilon\, g(\varepsilon)\varepsilon f(\varepsilon)$$

$$n=\int_{-\infty}^{\infty}d\varepsilon\, g(\varepsilon)f(\varepsilon).$$

These integrals can be calculated using Sommerfeld expansion.

$\varepsilon \sim k^2$

$g(\varepsilon) \sim \varepsilon^{\frac{d}{2}-1}$

3D : $\varepsilon^{1/2}$

2D : ε^{0}

1D : $\varepsilon^{-\frac{1}{2}}$

Now, the df we will already did all these calculations in the previous class that the density of states for a free electron dispersion which is E goes as k square is for three-dimensional it is like this, in general it is we showed that in any dimension if E goes as k square then the density of states g of E will go as E to the power d by 2 minus 1. So, in 3D it is E to the power half, in 2 D E to the power 0; that means, energy independent and 1 D E to the power minus half. So, this we have done in our in one of the previous classes and showed how these density of states behave, there plots, ok.

Now, so once you have this density of states g of E then of course, this integrals have to be done now. So, these integrals are not so straight forward because as I said the Fermi function contains a chemical potential which is temperature dependent and that is exactly what Sommerfeld did and I will show the calculations in the next class.

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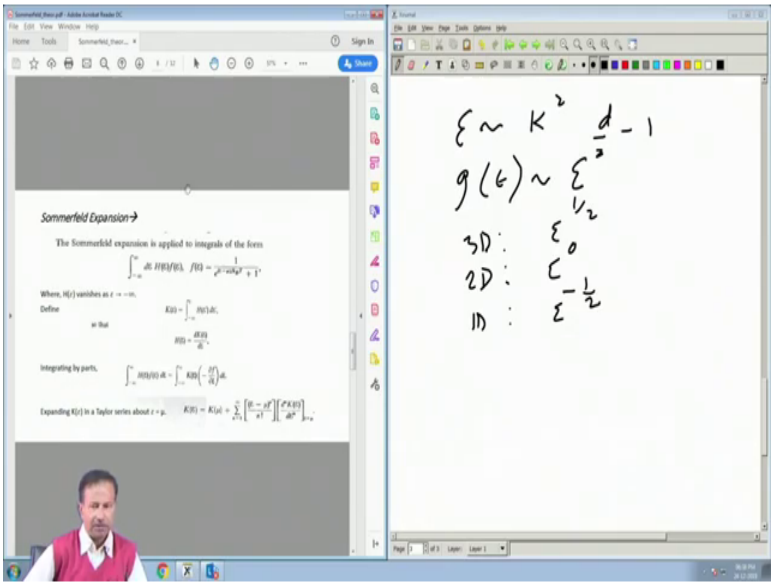

Sommerfeld Expansion→

The Sommerfeld expansion is applied to integrals of the form

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

Where, H(ε) vanishes as ε → −∞.

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(ε) in a Taylor series about ε = μ,

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

$\epsilon \sim k^2$

$g(\epsilon) \sim \epsilon^{\frac{d}{2}-1}$

3D : $\epsilon^{1/2}$

2D : ϵ^{0}

1D : $\epsilon^{-\frac{1}{2}}$

But again, I emphasize that you do not have to remember this, but you have to only realize that these calculations are nontrivial, and they require you to go to show the linear temperature dependence can come out with just hand owing argument as I showed, but the coefficients will not be correct. The other thing that is required is that the chemical potentials dependence on temperature has also to be taken care of and that is something that Sommerfeld did and that is something I will do in the next class.

Again, we do not need to copy it or we do not need to do this calculation yourself, but you just remember the logic behind this calculation and why it was done, and I will show you how it was done, but that is just for a reference. It is an important calculation. It is historically extremely important and it gives results up to a term T square. So, that is what I will do in the next class.

Thank you.