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Lecture – 22 Understanding the electronic contribution to the specific heat of a solid Part-IV

We continue with calculating now the specific heat.

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And, by working through this entire derivation we have reached a point where the specific heat is written in terms of the density of states at the Fermi energy, integrated over this expression where now you have the derivative of the Fermi-Dirac distribution.

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 $C_{v} = g(\varepsilon_{e}) \int_{0}^{\infty} (\varepsilon_{x} - \varepsilon_{e}) df_{0} d\varepsilon_{u} d\varepsilon_{u}$ $f_{D}\left(\underline{x}_{n-\mu}\right) = \frac{1}{1+\rho} \frac{R_{n-\mu}}{\kappa_{0}T}; \quad \xi_{1}$ $\frac{dt_0}{dT} = k_0 \frac{dt_0}{d\xi} = k_0 \frac{d}{d\xi} \left(\frac{1}{1+1} \right)$ Cu = kg g(54) EBT dr= dE =) dr= den =

So, let us look at this expression a bit more closely. The specific heat is the density of states at the Fermi energy it is expected as I have already discussed, that only the states which are very close to the Fermi energy are the ones which get; electrons in these states are the ones which are going to get excited around the Fermi energy and go to unoccupied states as you are supply a temperature T. And that is how the energy of the system will rise and so, they will contribute to the specific heat. So, these states are contributing to the specific heat integral 0 to infinity E k minus E f d f D by dT d E k.

And now let us evaluate this expression the Fermi-Dirac distribution f D E k minus mu is 1 over is to E k minus mu E k minus mu by k B T. So, therefore, d f D by dT ok, here before we continue further let us make a substitution that you have a quantity which is let us say let us call it as zeta which is equal to k B T. Then d f D by dT is k B into d f D by d zeta, is this is nothing else, but k B T, so, I have to multiply it by k B T.

So, this is k B into taking the derivative of d by d zeta of this expression 1 by 1 plus E raised to E k minus mu by zeta and this would give me a term k B into E k minus mu by zeta square times E raised to E k minus mu by zeta divided by 1 plus E raised to E k minus mu by zeta the whole square. You can just check it. It is very easy to take the derivative of this, you will get this will be the derivative of this expression and then if you take the derivative of this you will get this term.

So, you can now write and we will take the integration now. So, now, we can put it back into the integral if we substitute all of this here C v is equal to k B into density of states at the Fermi energy integral 0 to infinity E k minus E F by zeta the whole square into E raised to E k minus mu divided by zeta divided by 1 plus E raised to E k minus mu by zeta the whole square d E k. So, we have this expression.

And, now mu is of course, the chemical potential at finite temperature and now we can make a substitution of this x equal to E k minus E f by zeta which implies that dx is equal to d E k by zeta which implies that k B T into dx is equal to d E k because this zeta is k B T. Now, let us look at this expression a bit longer and what you see is that here is the chemical potential mu.

(Refer Slide Time: 05:24)



And, if you recall that the chemical potential at any finite temperature T is defined by the density by the counting and that is $g \to k \neq D \to k$ minus mu dE k, 0 to infinity, and if you actually calculate it again we have calculated it for fine 0 temperature which is this counting has to be equal to 0 to infinity $g \to k \neq D \to k$ minus mu at 0 temperature dE k. This is at a finite temperature T not equal to 0 and this is equal to 1 for energies which are less than or equal to $E \neq f$ and is equal to 0 for energies greater than $E \neq f$. So, by integrating this expression at 0 temperature which is equal to the density we get the expression for the Fermi energy.

However, if you do not do this if you just consider this then you can calculate the chemical potential at a finite temperature and that chemical potential at a finite temperature is equal to the chemical potential at 0 temperature; if you do this detailed calculation which I will not do here. You can show that by solving this expression again similar almost along the lines with a little bit more involved calculations. You can show that the chemical potential at a finite temperature is the chemical potential at 0 temperature is the chemical potential at 0 temperature plus a term which is of the order of T by T F the whole square.

So, the chemical potential mu T is equal to the Fermi energy plus a term which is of the order of T by T F the whole square. Now, if you recall that the Fermi temperature of the material is like 10 raised to 4 Kelvin and the temperature of the material can be of the order of say 10 raised to 2 Kelvin that, is considering it that you have really heated up the system to about 100 Kelvin or so or 300 Kelvin and so on.

Even then the T by T F is just 10 raised to minus 2 of course, there are higher order corrections, but this is the leading order term. You will get T by T F the whole square and then there are higher order corrections, but just the first correction to the chemical potential at a finite temperature is T by T F which is minus 2. And so, therefore, this term at a finite temperature is E f the Fermi energy which is the chemical potential at 0 temperature plus a term which is like of the order of 10 raise to minus 4 because, it is T by T F the whole square and then you will have of course, much much smaller terms. So, already you have a correction which is very small compared to the Fermi energy.

(Refer Slide Time: 08:36)



And, so, although the chemical potential because at 0 temperature if you look at the Fermi-Dirac distribution as a function of energy it is like this so, this is Fermi energy. But, if you look at the Fermi-Dirac distribution at a finite temperature then the distribution changes and the particles start leaving lower energy states and going up to higher energy states.

So, although the Fermi energy will be sitting at somewhere at E F, this is the Fermi energy which is the original location of the chemical potential at 0 temperature, the actual chemical potential will be slightly higher. This is the chemical potential at finite temperature and this chemical potential at finite temperature is the chemical potential at 0 temperature plus a term which is of the order of 10 raise to minus 4 and higher order corrections. But, you can see I have exaggerated the shift in the chemical potential with respect to 0 temperature. This is at a finite temperature and this is the 0 temperature, this is the chemical potential at 0 temperature at a Fermi energy.

So, while this was the original location when it was at 0 temperature because of a redistribution of particles around the Fermi energy the chemical potential just moves around a little bit and this is the amount of motion. So, for all practical purposes you can assume that the mu T is of the order of Fermi energy. So, in our calculation to simplify the calculations a bit further when we are looking at the specific heat; if you go back to this expression this chemical potential which is occurring here, this chemical potential

which is occurring here we will replace this with the Fermi energy. We will approximate these with the Fermi energy.

And therefore, we can rewrite this expression as equal to if you go back to this expression then we will rewrite this expression as k B g E f integral 0 to infinity E k minus E f by zeta the whole square E raised to E k minus E F by zeta divided by 1 plus E raise to E k minus E F by zeta the whole squared d E k. And, now x is E k minus E F by zeta you replace this by this d E k will be equal to k B into T dx which I have already shown you. Furthermore now you have the limits of integration if E k equal to 0, x is equal to minus E F by zeta for E k equal to infinity x is equal to tends to infinity.

So, the specific heat can now be written as k B square into T the density of states at the Fermi energy integral of minus E F by zeta to infinity, x square E raised to x divided by 1 plus E raised to x the whole square dx. So, now, we are coming to some point where we can now have an integral, and this if you look at the lower limit of integral it is going from a minus value to a plus value and what is important to see out here is that this negative value if you take it to minus infinity it does not change things too much.



(Refer Slide Time: 12:42)

Because, E F by zeta is of the order of E F by k B T which is of the order of T by T F this is the Fermi temperature divided by the temperature ok, this is far far greater than 1. So, e raised to x by 1 plus e raised to x the whole square for minus E F by zeta this is a very large value. So, the minus value of this would all approximately be of the order of 1 plus

a very small number the whole square where this number is much much less than 1 which is of the order of E raised to x. So, therefore, your and this itself tends to 0.

So, already this number is very large minus E F by zeta the lower limit of integration is already a very large number and it is almost making the contribution from this integral. So, therefore, if you take x square into e raised to x by 1 plus e raised to x the whole square this term goes to 0 as x tends to minus E F by zeta because E F by zeta is E F by k B T which is of the order of T F by T which is much much greater than 1, it is of the order of in fact, this term is of the order of 10 raised to plus 2. And so, if you go to a minus value of this these exponential terms become very small and tend to 0 and so, this term tends to 0 if you are going towards the negative limit.

So, already this term is 0 so, instead of going to this value if I take it to minus infinity, I do not make any this lower limit which is E F by zeta, if I take it towards minus infinity the lower limit by taking it to minus infinity I do not do any error in this integral. So, instead of keeping the limits of integration from minus E F to zeta I will change it to minus infinity and I do not make any errors by doing that because I already see that at minus E F by zeta the integral is already contributing to only zeros.

And, so, if I take it to minus infinity even larger values it will make it even for the zeros. So, in this negative direction I can take it to minus infinity. So, k B T into g E F integral minus infinity to plus infinity x square e raised to x divided by 1 plus e raised to x the whole square dx and it turns out that this is a standard integral whose value is pi square by 3. This is a standard integral in mathematics were integral from minus infinity to plus infinity x square e raised to x divided by 1 plus e raised to x the whole square dx. This definite integral has a well defined value which is pi square by 3.

(Refer Slide Time: 16:10)



And so, now, my specific heat of the electron gas finally, starts appearing which is pi square by 3 g E F the density of states at the Fermi into k B square T. This is my expression for the density of states of the electron gas; this is my expression for the specific heat of the electron gas. This is my expression for the specific heat of electron gas as obtained from Sommerfeld's model.

The first things, that you see from this is that the specific heat C v is proportional to temperature. Just as it was expected and was seen in the experiments that at very low temperatures when you remove the contributions which are coming from the vibrating ionic lattice what remains is only the specific heat of the electrons and if you look at the behaviour temperature dependence of the specific heat of the electrons they are linearly dependent on temperature and that comes out directly from the Sommerfeld's model. So, this is one of the major successes of the Sommerfeld's model.

The second success is that if I look at this expression a little bit more carefully if you recall that g of E k was equal to 3 by 2 n by E F divided by E by E F raised to half, because the density of states goes as this. And, now if I look at the density at E k equal to E F the density of states is at the Fermi energy is 3 by 2 n by E F because this becomes equal to 1. So, the density of states at the Fermi energy is nothing else, but 3 by 2 n by E F and if I now replace this in this expression if I replace the behaviour of the density of states at the Fermi energy I will get the specific heat as equal to pi square by 3 into 3 by

2 n k B into k B T by E F I am only rearranging terms. This is the expression 3 by 2 n k B where 1 k B I have taken and joined it with this and this is k B T by E F.

Now, this is nothing else, but pi square by 3 3 by 2 N k B by V; N is the number of electrons and V is the volume k B T by E F. What is this? This is nothing else, but 3 by 2 R the specific heat of the electron gas per unit volume from kinetic theory. This is the specific heat of the electron gas per unit volume from Drude's model or which uses the electron gas model as kinetic theory. We are using the kinetic theory of gases you know that it is going to be 3 by 2 R for n electrons in this gas it will be 3 by 2 R.

So, you see that that expression has returned back, but the specific heat of the electron gas is not 3 by 2 R it has that term, but it is smaller than 3 by 2 R by an amount which is this.

(Refer Slide Time: 20:59)

So, the specific heat of the electron gas is pi square by 3 into 3 by 2 R by V k B T divided by k B T F as the Fermi energy is written as k B times the Fermi temperature and T by T F is of the order of 10 raise to minus 2, if you look at pi square by 3 into if you put in numbers. For example, for copper if you put in the temperature and you calculate the Fermi temperature which we have calculated earlier, this is about 80000 for copper and temperature you take it as about 300 Kelvin and if you put in pi square by 3 you will find that the specific heat of the electron gas is compared to the value which is obtained

from kinetic theory this ratio into pi square by 3 is of the order of 0.01. It will bring down the value by 0 point 0 one compared to the kinetic theory of gases.

So, from the kinetic theory of gases, if you just were to measure the specific heat of the electron gas that value would be 3 by 2 R at some temperature T. However, if you were to measure the specific heat of the electron gas it would be linearly temperature dependent and at this temperature the actual specific heat would be 0.01 times the 3 by 2 R value. This is a hypothetical value or a theoretical value which is obtained by considering the gas classical having a Maxwell Boltzmann distribution and it will give you 3 by 2 R. But, if you use the Sommerfeld's model and consider the gas as quantum mechanical then it shows that it is far more lower than 3 by 2 R at this temperature, ok.

So, there is a significant suppression with respect to the classical theory because of using the quantum mechanical nature of the electron gas. So, this was a very major success of the Sommerfeld's model because now you could explain why is the specific heat of the electron gas so much lower than compared to what you know from kinetic theory and also you get the temperature dependence very neatly. Thus C v you can write it as pi square by 3 density of states at the Fermi energy k B square T, ok. This is your specific heat.



(Refer Slide Time: 24:30)

And, this term this constant C v can be written as gamma times T the specific heat of the electron gas can be written as some constant into gamma times T where gamma is called

as the Sommerfeld's constant. Gamma is the Sommerfeld's constant, where gamma is pi square by 3 density of states at the Fermi energy into k B square. This has a very specific value and this of course, you can write it as pi square by 3 into 3 by 2 density divided by the Fermi energy into k B square.

This Fermi energy you know is h cross square by 2m into 3 pi square n raised to 2 by 3. We have already seen this as the expression for the Fermi energy. So, if you put that all of that in here then you will get term which is this term Sommerfeld's constant will be given as pi square k B square n raised to 1 by 3 divided by h cross square 3 pi square raised to 2 by 3 into m, where m is the mass of the electron in the solid.

So, the Sommerfeld's constant depends on the density as well as the mass of the electrons inside the solid. This is a function of the density and mass of electrons in the solid.

(Refer Slide Time: 26:45)



So, what you can do is that you can actually calculate the Sommerfeld's constant, ok. You can find out how much is the value of the Sommerfeld's constant for different metals, because you know that gamma is some function of the density of electrons and the mass of the electrons. And, for mass you just use the bare mass of electrons whatever is the bare mass of the free electrons you can use that to calculate the Sommerfeld's constant. And, so, for different materials you can find out the value of the Sommerfeld's constant milli joules per mole per degree Kelvin square, in these units if you find out the Sommerfeld's constant you can determine it and calculate it for different materials. For sodium the value which you measure is 1.38. So, as I had said if you go to low temperature and you measure the specific heat as a function of temperature then at very low temperature there is a linear dependence of the specific heat.

So, if you are very far away from the room temperature at very low temperatures you will get this linear temperature dependence of the specific heat which comes from the electrons inside the solid and from the slope of this the slope is equal to the Sommerfeld's constant gamma. So, you can not only calculate, this is the calculated value by putting in the density of electrons which you can of course, measure using the hall if you recall that the hall coefficient R h is equal to plus minus 1 by n e. So, you can measure if you measure the hall effect through the hall effect, if you measure the hall coefficient you can determine the density or there is also the expression for the density and you put in the mass of the electron which is the bare mass of the electron you will calculate the Sommerfeld's constant and you can derive it you can get it for all these different metals.

From an experiment you can also determine the Sommerfeld's constant. So, this is theoretically calculated and the experimentally obtained value is 1.094. So, there is reasonably good match. Next if you go to copper it is about theoretically calculated value is 0.695, the experimental value is 0.505 slightly different ok. If you go to gold 0.29 729 and 0.642, roughly they are similar. Aluminium 1.35 is the value you should theoretically get, if you experimentally measure it you will get a value of 0.912.

This is now starting to become significantly different. There are materials like lithium where one it is 1.63 and it is 0.749 more than 50 percent difference. There is a significant difference as you between the theoretical value and the experimentally measured value. strontium 3.6 and it is 1.790. If you recall that the Sommerfeld's constant is some constant n raised to 1 over 3 into m it is some constant.

So, if you take the ratio of observed value, which you are getting from an experiment to the theoretical value assuming that n is the same, the density is the same whether you are using it for an experiment or for theoretical calculation the density is not different. The

difference between the observed and theoretical value is the mass of the electron which is actually present inside the solid divided by the actual free electron mass. The free electron mass, the mass of an individual electron is m e that is what you are using in theory.

So the ratio of the observed value to the theoretical value; so, if you take the ratio of this to this you will get the ratio of the observed to the gamma theory which is nothing else, but the actual mass of the electron divided by the mass of the free electron and that value for sodium is about 1.26, it is about 1.38, so, 1.14, 1.48, 2.18, 2.0. So, you can see that certain materials the as if the electron inside the solid the electron inside the solid becomes heavy because the mass of the actual mass of the electron is approximately twice the mass of the free electron.

So, compared to the mass of the free electron it looks like the m actual which is what you get in an experiment is almost twice in some metals is almost twice that of the mass of the free electron. So, this is an unusual thing which comes up the moment you start understanding where from is a specific heat of the electrons coming up it leads to another new issue you see that the mass of the electron is no longer that of a free electron mass, but sometimes it is higher. And, these are some of the drawbacks which are not explained by the Sommerfeld's theory.

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In fact, there are certain class of materials in which are certain class of compounds which are compounds like uranium based compounds, cerium aluminium compounds or celicates like Ce Cu 2 Si 2. In this if you do the same experiment of measuring the specific heat and from the slope measure the Sommerfeld's constant and take the ratio of theory observed to the theory you can show that the actual mass of the electron in these metals can be as large as 1000 times the mass of the free electron.

So, here the electron really has become heavy. Compared to the free electron mass the actual electron inside the solid has become as if it is a very heavy particle, ok. The electron inside the solid is no longer behaving like a free electron moving around freely with a mass m e, but it is mass has increased, its inertia has increased and these go by a very famous name which are called as heavy fermions. These are not explained within the Sommerfeld's model. So, this is something which is outside the purview of the Sommerfeld's model, but yet the Sommerfeld's model actually lends away to discover such materials and these new phenomenas where actually the electron seems to be much heavier than what it would be if it was free.

So, we will discuss next a few of these drawbacks which come out from the Sommerfeld's model. Although the Sommerfeld's model has been very successful in explaining the behaviour of the specific heat which comes out from the theory of the quantum mechanical nature of the electrons it has its drawbacks. And, this is one of the drawbacks that the electron mass does not behave like a the electron does not behave really like a free electron. Its mass is very different could be very different from that of a free electron and sometimes in some materials they can be orders of magnitude larger than the free electrons.

We will continue this in the next lecture.