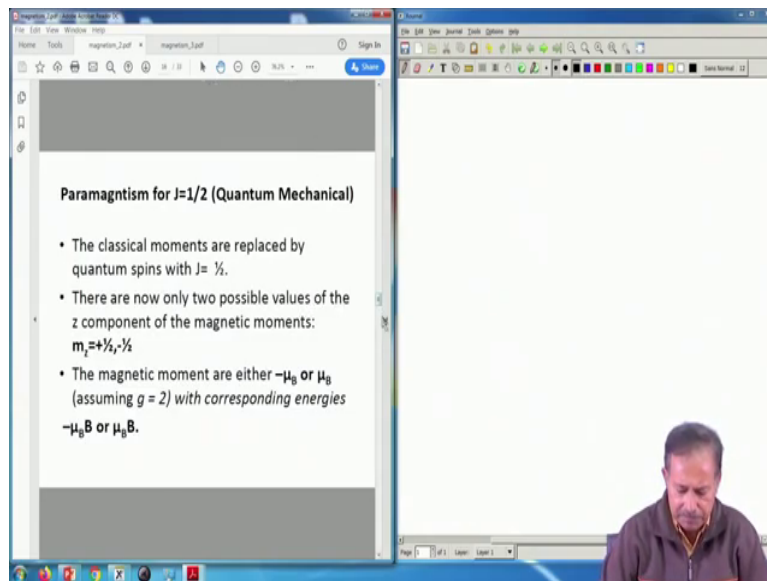**Electronic Theory of Solids**
Prof. Arghya Taraphder
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture – 32
Curie's law for any J, Susceptibility

(Refer Slide Time: 00:26)

We have been discussing the paramagnetism of isolated ions and or atoms with moments. And so, for the for simplicity let us start with the case of J equal to half, that means, there is at every atom or ion that we have in the system we have J equal to half moment sitting, and they are randomly oriented.

And we want to find out at finite temperature, how does the moment order what or if it orders what is the susceptibility like what is the magnetization and so on. So, as I said there are classical descriptions available, which as Bohr-Van Leeuwen theorem, tell us tells us are not kosher, and we will not get into that.

We will just do what we do normally in any quantum description. And since it is at finite temperature, we will do the thing do the calculation using statistical mechanics, because there are large number of moments, and although the moments are all independent. So, you

calculate the partition function for individual moments and multiply n times, so that gives you the partition function of n moments, they are not interacting with each other at this stage.

So, this is the scheme of things that we are following. So, there are only two possible values of the Z-component of J which is written as m sub z plus half and minus half, and the corresponding magnetic moments are either minus mu B or plus mu B and their corresponding energies are mu B into H plus or minus if H is the magnetic field, so, that is the that is what it is.

(Refer Slide Time: 02:26)
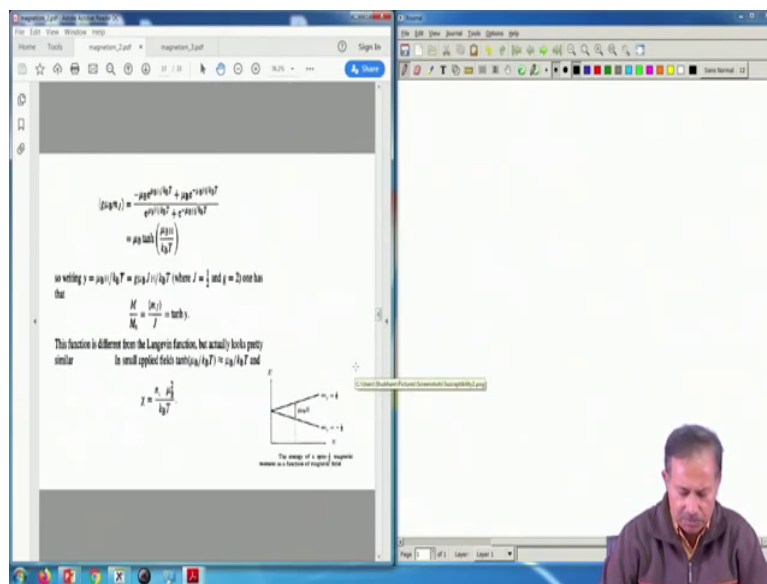
As you can see from this picture the as magnetic field becomes larger and larger. This is these two levels separate out proportional to H and that is I mean you have probably done this in Stern-Gerlach experiment where these two magnetic states are used. So, let us do the calculation as I said one can calculate the expectation value of this quantity as we do in statistical mechanics. So, multiply the that quantity by corresponding Boltzmann factor and then sum, and then at the bottom you sum the probabilities.
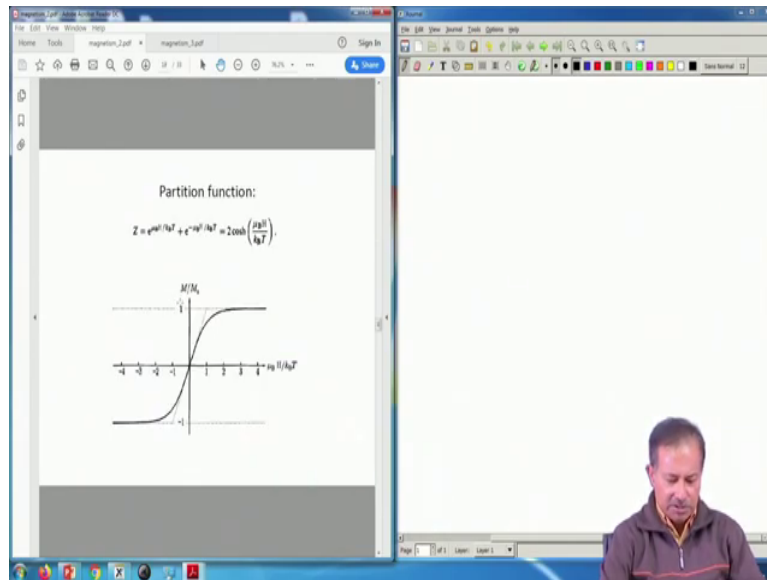
Instead you can also do, so that will give you a result which is m by m sub s, m sub s is when all spins are fully aligned, so that is the magnetization value, so that is where you will get this full m equal to m s. But because of thermalization as I said that if you remember I mentioned that H by T, H is trying to align and T is trying to misalign.

So, T basically is a randomizing effect, and so at any finite temperature these two compete, and so therefore the ratio H by T appears in this these kinds of derivations. We will actually use that fact that the free energy or the partition function is quantity which depends on the ratio H by T rather than individually on H or individually on T.

The partition function is a function of H by T and that is that will be used actually. So, you can write this quantity y mu B H by k B T. Now, this quantity of course, requires some attention, because mu B H typically even for a Tesla field and for J equal to half for example, mu B H is for J equal to half, and that quantity mu B H for an electron is about for 1 Tesla field is about less than a degree of Kelvin point 6.7 degree Kelvin.

And so therefore, that is far less than the temperatures that we usually discuss unless of course, k B T is exceedingly small milli Kelvin or some such number, then this is always less than 1. And so that please bear it in mind, we will be using that as an approach when we do approximations, because the right hand side is tan hyperbolic function and so you can expand

it for y small, and you can just write tan hyperbolic equal X equal to x for small x, and this susceptibility comes out.

Instead of doing this treatment, this is of course, perfectly all right you can also take recourse to the absolutely standard stat mech procedures, where you calculate the partition. And this is a kind of a mechanical way of doing things, but it is perfectly kosher, and it is very useful.

So, just calculate the partition function which is again these two Boltzmann factors corresponding to the two eigen energies basically trace e to the power minus beta z sub n and sum over all energies energy states e n. So, here there are only two states, so that is all two cos hyperbolic mu B H by k B T.

(Refer Slide Time: 06:31)
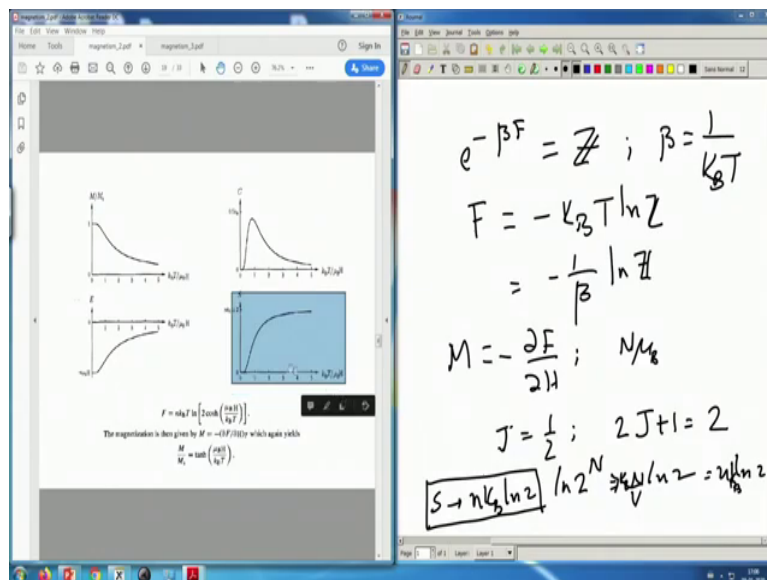
And from that you can calculate the free energy free energy density is n k B T divide by volume log 2 cos hyperbolic. So, basically you use this relation that free energy is e to the power minus beta f Helmholtz free energy is equal to partition function, so that gives you F equal to minus k B T log Z or minus 1 by beta log Z, where beta is 1 by k B T so that is the standards stat-mech relations that I am using.

So, this is how you can calculate. Now you can calculate you know the magnetization is basically one derivative with a minus sign, so that relation minus del F del H is used to calculate the magnetization, which again gives you back the M by M s which is, see M s is

basically all spins giving you mu B times the total number, so that is M s, so that is the same formula we obtained.

You had to get the same formula of course, therefore, then you can plot one way to do is it is just plot. So, M by M s as a function of mu B H by k B T and that is this plot this is the tan hyperbolic function, and as temperature reduces this becomes steeper and steeper ok.

So, at for low temperatures again for high temperatures compared to mu B H, the energies if k B T is much greater than mu B H which is normally the situation, then you can approximate this by just a linear term that is the dotted line that is drawn here, which becomes nearly exact as you approach 0 in the x-axis.

The magnetization of course, you could actually tell how it will behave, because magnetization has to be saturated at low temperature with no thermalization. And it will be starting it will start to decline from its saturation value, and it at large temperatures, of course, it will start towards going it will march towards 0, because thermalization will just make all the moments fluctuate randomly and then the some of these magnetic moments will no longer give you a finite value. It will become start it will just approach 0 as T rises.

So, this is a value starting from 1 to 0, you could actually right you could just predict right from the beginning without doing any calculation actually, of course, the exact curve requires the calculation. The energy of course, again is the same thing that it is minus n times mu B H which is the saturation magnetization times the number of particles divide by number of ions divide by or number of moments divide by volume and energy per volume is energy density is this starts from a large negative value and goes towards 0.

So, then specific heat is interesting specific heat is basically a derivative of energy and with temperature and these kind of curves, you must have seen in many places. There is a specific heat goes to 0, at 0 temperature, and then it rises with a peak and peak is look at the peak it is k B T equal to mu H mu B H.

So, what does that signify? That signify a transition between these two states. So, there is these kind of pictures, these kind of specific heat curves are called Schottky curves. And this Schottky, this is called a Schottky peak and they appear when you have this kind of resonance

between, you have two states for example, where you can excite one to the other one goes to the other as you supply energy. And exactly at mu B H amount of energy when thermal energy matches mu B H, you actually hit the peak.

Then of course, it declines exactly as you can see this derivative is becoming 0. And this is the standard curve for any such two level systems. You can you will encounter it in stat mech in many places. The other thing is that the entropy. Now, entropy of course, is the number of states that you the you can it just the counting of states right and logarithm of that.

So, since we have a J equal to half, the number of values m J values is 2 J plus 1 which is 2 into half plus 1 is 2 ok. So, every site every magnetic moment can take two values. So, then there will be number of possible states at large very high energies will be just 2 to the power n. And if you take a log of that, it will be just N log 2.

So, if you divide this by volume then entropy density will be this small n log 2 and that is exactly what you get times of course, k B you have to multiply by k B, n k B, this log 2 leads to n k B times log 2. So, that is the SOS approaches n k B log 2. This log 2 is a very telltale signature it is a telltale signature that you have a two levels two spins you have two spin states per systems, so spin half and per moment and so that is the J equal to half.

And at high temperature, you have to reach these value as the all the states are now accessed; at low temperature of course, the higher energy state is not accessed. But at very high temperatures temperature is much greater than k B for example, H k B mu B times H which is one beyond that temperature far beyond that temperature you are really at high temperature and the value should be n log 2 n k B log 2. This is a very very important result.

This tells if you do an experiment if you find that your entropy is going towards n k B log 2, then you know that its mostly coming its almost all of it is coming from the moment spins. Remember there are other contributions to specific it as well in a system, electronic contribution, phonon contribution and so on.

But if you find an n k B log two kind of term, then that surely is coming from the spin part if the system has magnetic moments. So that basically tells you the kind of spin you are doing you are dealing with J equal to half for example.

(Refer Slide Time: 14:49)
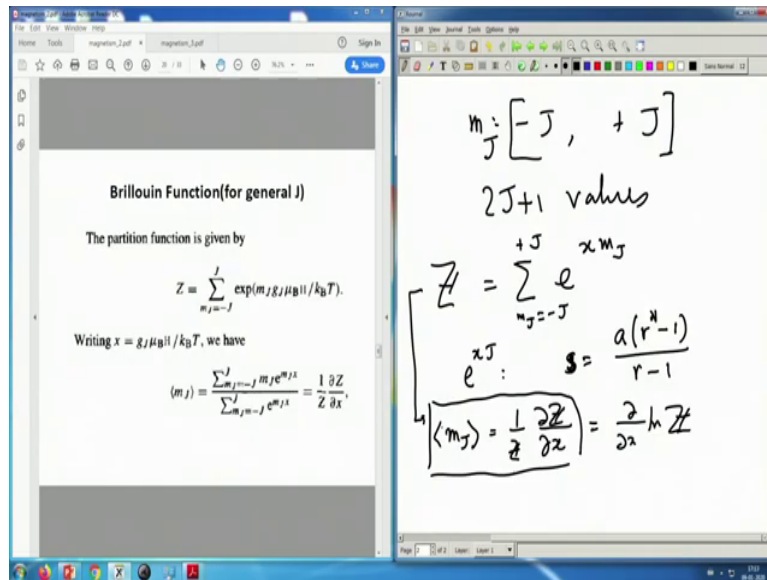
Now, the calculation can be extended. And this, so let me just once more tell you what is happening here for spin half system or J equal to half system which is like l equal to 0, S equal to half. This magnetization goes to 0 at high temperature, and energy is minus n B n mu B H at 0 temperature, and then goes towards 0 at high temperature. And so energy increases, it starts from a large negative value, and it increases towards 0.

Now, specific heat has this peak structure at around mu B k B T equal to mu B into H, and then of course, it declines it goes down as a function of temperature, and so that is the typical specific heat value for this kind of a system. And then of course, this is an important curve. It shows that the entropy at large temperatures high temperatures saturates to a value which is the maximum entropy that you can have out of the systems.

Every spin now is accessing both the states and so you get log 2 out of it. So, there are 2 to the power n states k B log 2 is what you each and each of them supply the entropy amount of entropy. And then n by V will give you the small n. So, that is the entropy.

The other interesting thing is that the entropy as you can see goes down to 0 at 0 temperature this is also consistent with third law of thermodynamics which requires that the entropy has to go down to 0. So, this log 2 behavior does not survive for long at lower temperature, of course, you have to go down to 0 entropy ok.

So, let us now consider a situation where you have the spin is no longer half or the total J is no longer half. So, spin can be half, but l will can contribute. So, the thing is that you have a moment with value J, I mean that is all. As I said we do not bother whether there is an ion or atom or whatever is the species that we are talking about for this calculation we only have moments. So, we consider free independent moments they are in a magnetic field at finite temperature ok.

So, again we start with the partition function, but now this m J value is there are just not two values there is a 2 J plus plus 1 values right. So, this 2 J plus 1 is the number of value. So, you have to go take your m J m sub J; m sub J goes from minus J to plus J right. So, this is the interval over which m J varies.

So, and changes by integer minus J, minus J plus 1, minus J plus 2 and so on up to J. So, there are 2 J plus 1 values, so that is the sum you have to do. But this is if you write this so let me write with this definition z equal to, so this will be e to the power x m J so g J mu B H by k T is written as x, and m J goes from minus J to plus J.

Now, this is basically a g p series and then it is a finite series and you can sum it. And so the common factor is e to the power m J common ratio, because your m e to the power x or e to the power x because m J changes by one at each stage. So, it will be x J, this is your common ratio, and your you can use the formulas for sum. So, let me just write it as double this kind of S and a first term r to the power the number of terms minus 1 divided by r minus 1.

So, then you can straight forward do this calculation, leave it to you to do it. And what you will get is the value formula for J z. That formula is not really important what is important is that you need to calculate m J. So, what you do is that you know the usual procedure. So, m J will be average m J will be from here 1 by Z del Z del x right, so that we will bring down and m J in the front and then e to power x J x m J is the probability remember the previous calculation and sum over all these states, so that is all you are doing.

So, this will give you now this can also be written as del del x of log of Z right that will give you 1 by Z del Z del Z del x. Remember that log of Z if you multiply it by minus k B T

becomes the free energy, so that is the way the connection to free energy is made of the magnetization.

(Refer Slide Time: 21:17)

So, that is exactly what is being done here. So, look at the first line the derivative is now you can just redo the calculation Z is a function of H, so you can del z del x del H del x and so on, but this is straight forward calculation. The essential calculation is this, this is what you have to figure out ok.

So, that is exactly this is the series that r equal to e to the power x, so r, so x every time you change this x here for example, J changes by 1 m this is m j, so m J changes by one. And so your r here is t to the power x ok, so that is what gives you z, and then z will give you the magnetic moment.

And of course, a is e to the power minus. So, let me just write down r is this, and a equal to e to the first term is minus J x. So, with these two you can just these two you plug it in, and you get this sum which is the partition function ok. So, we you can do it.

Now, z is the formula is given here this is what we will land up with. So, there is you have to take some common factors and they will cancel from a numerator and denominator, and that

algebra is fairly straightforward and you can do it. And the net result is that this is what you will end up with ok. This is N. So, N equal to 2 J plus 1 ok.

Once you do that then again then you do a substitution which is write y equal to x times J which again brings you gives you back the factor that we had in the numerator. So, numerator of course, has m J which ran from minus J to plus J. Here this is J itself, so x J.

(Refer Slide Time: 24:17)
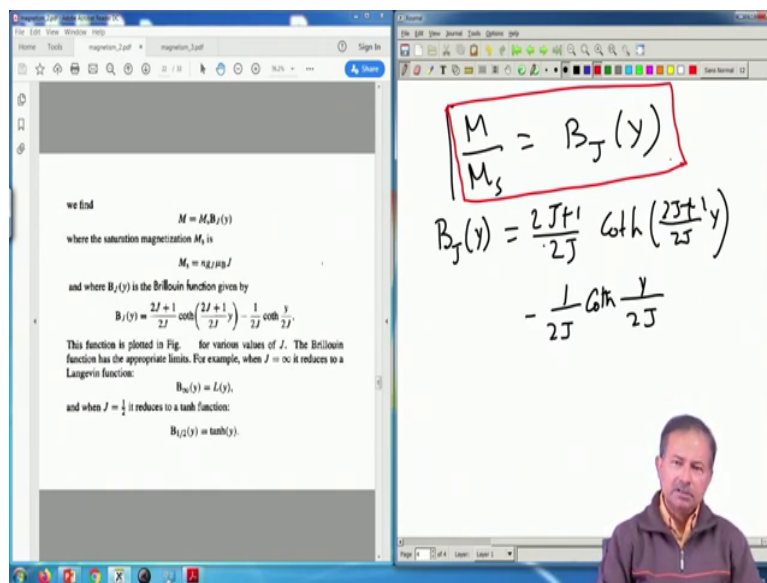
And in terms of x J you can write the factor M, M is basically the magnetic moment. So, M by M s is what we write again and that is equal to something called B J of y. Now, this B J is called a Brillouin function it is the name it is written down here B J of y is basically 2 J plus 1 by 2 J cot hyperbolic 2 J plus 1 by 2 J into y minus 1 by twice J cot hyperbolic y by twice j.

So, this is what you will get once you take the derivative with respect to m. So, that means, M by M s is equal to, so this is my relation that I will have to use from now on. Of course, this has again the same thing we will have to do as we did in the other case that we will find out the range of y that we are interested in the range where y is y what are the ranges where we are interested in temperature, and that in that case we will now again approximate this, and try to find out the magnetization. And from magnetization which we find as a function of H, we will find out the susceptibility.