Statistical Mechanics

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Lecture - 26
N Non-Interacting spins in Constant Magnetic Field

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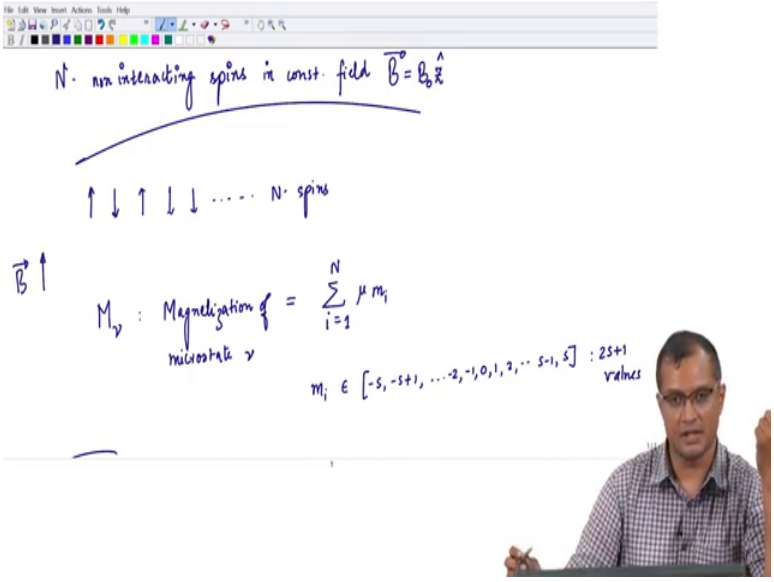

N non interacting spins in const. field $\vec{B} = B_0 \hat{z}$

$\uparrow \downarrow \uparrow \downarrow \downarrow \cdots\cdots$ N spins

$\vec{B} \uparrow$

M_ν : Magnetization of microstate ν $= \sum_{i=1}^{N} \mu m_i$

$m_i \in [-s, -s+1, \ldots -2, -1, 0, 1, 2, \cdots s-1, s]$: 2s+1 values

Good afternoon students, today we will do a worked example of a N Non-Interacting spins in a Constant External Magnetic Field. Now, this is going to be a demonstration of how we compute a physical properties of interest using statistical mechanics and a working example that I have shown as spins in a magnetic field.

So, we could think of these spins that are up and down, in a magnetic field that is uniform and pointing allowed some direction let us say the z axis. I can choose z axis to be anywhere, but I am just showing the magnetic field to be along this direction that is my z axis, and this is like constant magnitude in the direction of z axis.

So, you can take N such spins and for this system we can compute the magnetization of any given realization ok.

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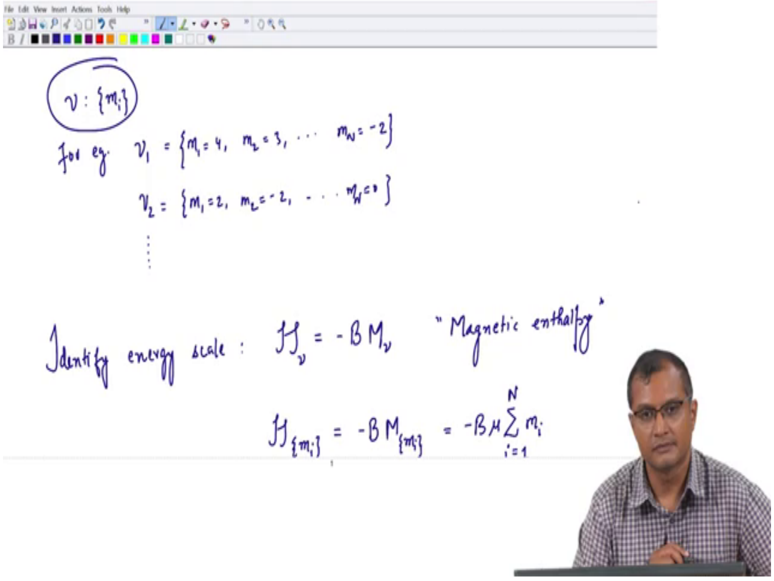

$\boxed{\nu : \{m_i\}}$

For eg. $\nu_1 = \{m_1 = 4,\ m_2 = 3, \cdots\ m_N = -2\}$

$\nu_2 = \{m_1 = 2,\ m_2 = -2, \cdots\ m_N = 0\}$

$\vdots$

Identify energy scale : $\mathcal{H}_\nu = -BM_\nu$ "Magnetic enthalpy"

$$\mathcal{H}_{\{m_i\}} = -BM_{\{m_i\}} = -B\mu\sum_{i=1}^{N} m_i$$

As I am going to say that let us take a microstate nu and if you want to write down the magnetization under constant temperature and constant field, this is nothing but just summation overall these spins, the individual magnetic moment. So, I am going to take nu as some magnetic moment per spin into the excitation of that spin.

Now, this is going to be a system where the values of excitation can take anything between minus s 2 plus s. These are basically 2 s plus 1 values. So, this is not s equal to half or spin half system where you can only take a minus 1 and plus 1 for the m i's. Here s could be 3 by 2 5 by 2 or any you know large number and this essentially gives your excitation values of minus s 2 plus s ok. So, it is not restricted to spin half system I can take it the spin to be s and so, if this is for a spin s system and I have taken n such spins ok.

So, the m i's that is the excitation of each spin can assume values between minus s 2 plus s total 2 s plus 1 values and what I have written here is nothing, but the magnetization of the some nu th microstate ok. So, you can call it as the of magnetization of some microstate nu which is a label of a microstate. Now what is meant by a microstate here as you already know microstate is nothing, but specified values of these excitations ok. For example, you can take one microstate can be specified as m 1 equal to 4, m 2 equal to 3 and so, on and so, forth and m N equal to some minus 2 whatever. So, this is one microstate you can specify another set of values.

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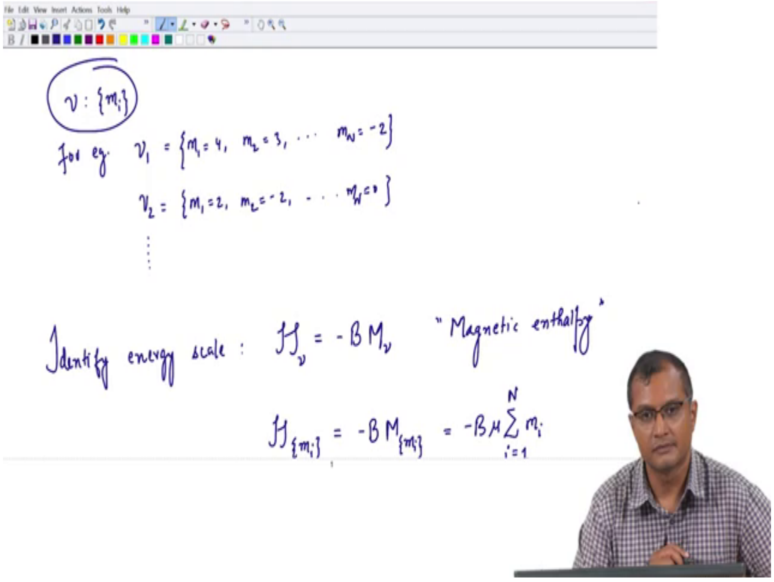

$\boxed{\nu : \{m_i\}}$

For eg. $\nu_1 = \{m_1 = 4, \; m_2 = 3, \; \cdots \; m_N = -2\}$

$\nu_2 = \{m_1 = 2, \; m_2 = -2, \; \cdots \; m_N = 0\}$

$\vdots$

Identify energy scale : $\mathcal{H}_\nu = -B M_\nu$ "Magnetic enthalpy"

$$\mathcal{H}_{\{m_i\}} = -B M_{\{m_i\}} = -B\mu \sum_{i=1}^{N} m_i$$

So, this way you can set up a large number of microstates each one of them is nothing, but the set of particular values of m i which means I can also call my microstate as nothing, but a set of m i's this is my label microstate ok. Having said that I can identify the energy scale of the problem, which is the first thing to do. If you want to setup statistical mechanics you have to set up the energy scale and the energy scale is basically the Hamiltonian or the total energy scale and since these spins are non interacting, there is no internal Hamiltonian of the system there is no interaction nearest neighbour interaction between the spins, all this spins have is basically a coupling to the external magnetic field. So, the total energy scale is nothing, but the magnetic enthalpy of the system that is my energy scale.

So, I am just going to write down the magnetic enthalpy as minus B M ok. So, if this is the Hamiltonian of the nu th microstate then it is just minus B times M nu also called as the magnetic enthalpy. There is no other scale in the problem this spins are non interacting. I think I have already mentioned is yes spins are non interacting. So, you do not take an I seeing like model where spins have a nearest neighbour interaction that is given by a coupling constant j, there is no such j this spins can only talk to an external magnetic field and can align parallel or anti parallel to the field.

So, the energy scale are the problem is nothing, but the magnetic enthalpy which is this. If I want to write down explicitly you can say my nu is nothing, but the set of excitation.

So, that is the Hamiltonian of this particular microstate given as minus B times the instantaneous magnetization which is nothing, but the set of values of in our new notation ok. And this is nothing, but minus B times I have already written what is the magnetization which is summation overall degrees of freedom nu times mi. So, I am going to pull out mu because it is a constant and so, mu here is nothing, but magnetic moment per spin ok.

So, you some over all this spins along with their excitations you get the total magnetic moment. So, this is just summation over i going from 1 to N the total degrees of freedom in your problem of a spin excitation this is my magnetization of the of certain microstate. So, the mis that I take here in the summation are the mis that are fixed by the microstate like I have shown here fine.

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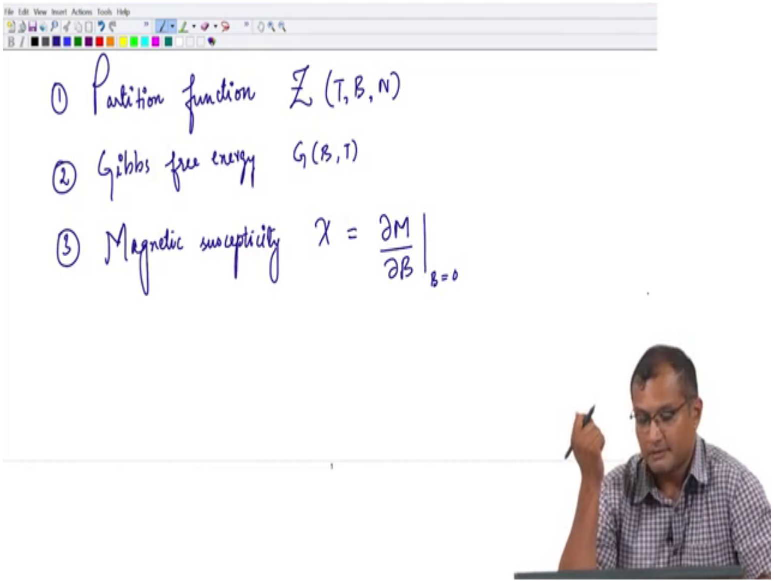

① Partition function $Z(T,B,N)$

② Gibbs free energy $G(B,T)$

③ Magnetic susceptibility $\chi = \frac{\partial M}{\partial B}\Big|_{B=0}$

Once the energy scale has been specified in this case it is the magnetic enthalpy I can ask meaningful questions, I can ask questions as to what would be the partition function of the system. The first important object that you construct on any physical system in statistical mechanics is the partition function because once you have the partition function your hand, you can ask you can do a lot of things.

For example, if you have the partition function, I will call it as the Gibbs canonical partition function at constant temperature in magnetic field, you can also called constant number of spins.

Now, with this if you compute the partition function, you can compute for example, Gibbs free energy of the system. So, this is now development of thermodynamics. So, you can compute Gibbs free energy of the system as a function of B and T now then with the Gibbs free energy, you can compute very interesting properties you can for example, compute what is the magnetic susceptibility of the system. This is a quantity that will depend on the system whether it is close to a phase transition or not, and near to the phase transition there will be large values of magnetic susceptibility, it will sort of diverge indicating a second order phase transition.

So, magnetic susceptibility is in important in quantity that one often constructs for magnetic systems. So, chi which is defined as the rate of change of magnetization as a function of applied field for very small values of field. This should be like if you want to expand magnetization and powers of the field, then the leading term of that expansion will be the susceptibility the Taylor expansion of magnetization.

So, to linear order the rate of change of magnetization as applied field for very small values of field gives you the susceptibility of the system. And you can show that this susceptibility is of measure of fluctuations in magnetization. See we are not controlling magnetization in the system we are controlling magnetic field temperature in number of spins. Now the only way you can do it is to allow for magnetization to fluctuate. So, you can also you know connect this susceptibility to fluctuations in magnetization.

It is like saying that in a canonical ensemble when you had a gas in contact with the thermal reservoir you kept number of particles volume and temperature to be fixed. You could only kept, you could only keep temperature fixed by allowing in exchange of energy with the reservoir. So, the fluctuations of energy with the reservoir was a direct was directly shown to be related to the heat capacity at constant volume. So, the in some sense our susceptibility is also measure of you know fluctuations in the magnetic field, and it will be nice to compute this quantity.

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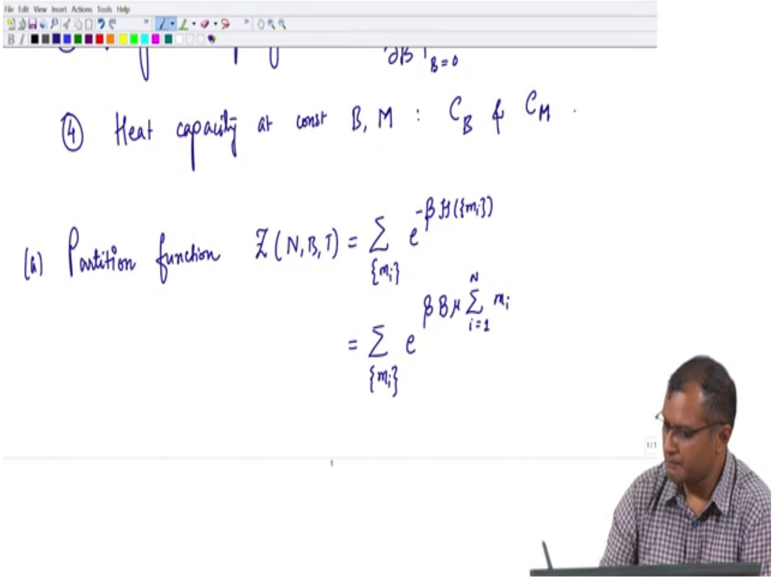

④ Heat capacity at const B, M : C_B & C_M .

(a) Partition function $\mathcal{Z}(N,B,T) = \sum_{\{m_i\}} e^{-\beta \mathcal{H}(\{m_i\})}$

$$= \sum_{\{m_i\}} e^{\beta B \mu \sum_{i=1}^{N} m_i}$$

Another quantity that you can compute is basically the heat capacity at constant field and magnetization which means I would like to compute what is heat capacity at constant magnetic field and heat capacity at constant M right. So, now, we will compute the partition function first and then compute the remaining physical properties. So, let us start with the partition function. So, the partition function here is nothing, but the summation over all degrees of freedom you can also call it as a trace and the Boltzmann factor which is e raise to minus beta into the energy scale of the problem.

So, I have taken the energy scale which depends on the microstate and I know this energy scale which is basically e to the power minus which now becomes e to the power minus beta and energy scale itself is minus b m. So, the 2 minus multiply to a plus and you get nothing, but summation i going from 1 to n mi. The mi is here are picked up from the specified microstate in the summation ok. You have to sum over all microstates and for each microstate whatever m i's you pick up you have to use that in that summation ok.

And then add up to a next exponent and so, on and so, forth sum it over all microstates you have the partition function ready ok.

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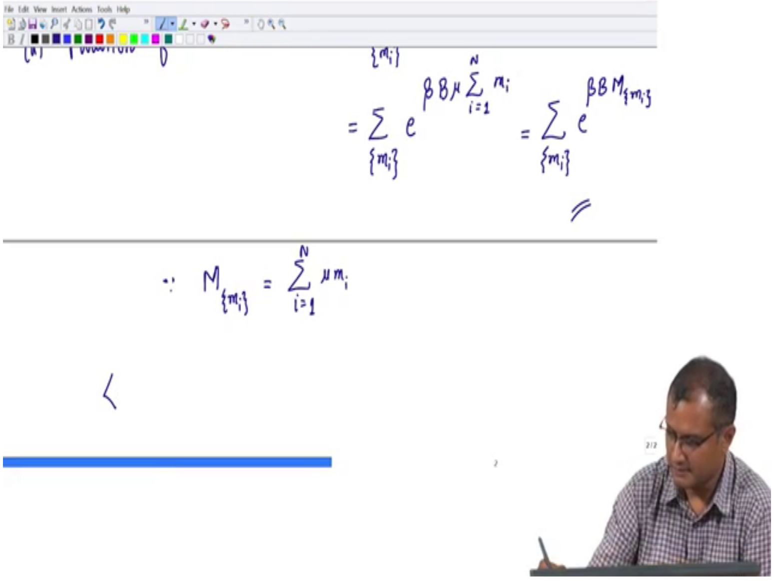

$$= \sum_{\{m_i\}} e^{\beta B \mu \sum_{i=1}^{N} m_i} = \sum_{\{m_i\}} e^{\beta B M_{\{m_i\}}}$$

$$\because \; M_{\{m_i\}} = \sum_{i=1}^{N} \mu m_i$$

$\langle$

So, I can also write this as just summation over all microstates e to the power beta B into magnetization of the microstate and this is because the magnetization of a particular microstate is nothing, but summation over all degrees of freedom mu times mi ok. So, the preceding equation which is this allows us to write down the average magnetization.

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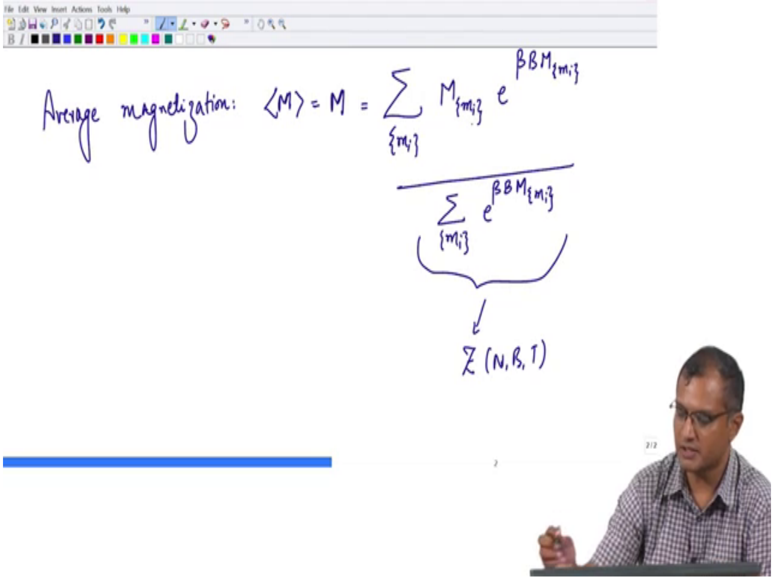

Average magnetization: $\langle M \rangle = M = \dfrac{\sum_{\{m_i\}} M_{\{m_i\}} e^{\beta B M_{\{m_i\}}}}{\underbrace{\sum_{\{m_i\}} e^{\beta B M_{\{m_i\}}}}_{\downarrow \; Z(N,B,T)}}$

I can or write down the average magnetization which is nothing, but M or you can just call it as M we or with an angular brackets up to you it is nothing, but summation over all the microstates magnetization of the microstate that is being summed over e to the power minus beta into the energy scale and I know this energy scale is already been written as beta B into mu magnetization of the mu th microstate which is set of m i's divided by our partition function ok.

Because this is the normalization of the probability that is all the denominator is nothing, but our Gibbs canonical partition function ok.

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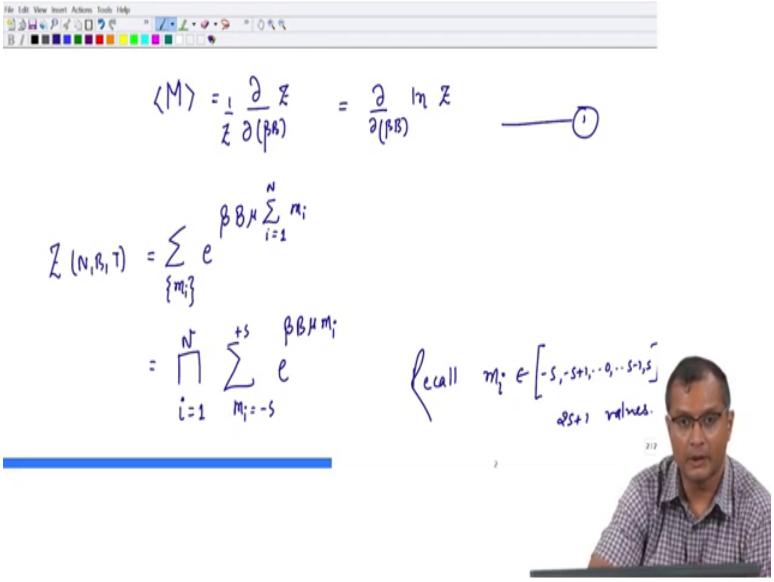

$$\langle M \rangle = \frac{1}{Z}\frac{\partial Z}{\partial(\beta B)} = \frac{\partial}{\partial(\beta B)}\ln Z \quad \text{———} ①$$

$$Z(N,B,T) = \sum_{\{m_i\}} e^{\beta B \mu \sum_{i=1}^{N} m_i}$$

$$= \prod_{i=1}^{N} \sum_{m_i=-s}^{+s} e^{\beta B \mu m_i}$$

Recall $m_i \in [-s, -s+1, \ldots 0, \ldots s-1, s]$

$2s+1$ values.

So, I can write this as you know just to extract the magnetization here in the numerator I can write down the average magnetization as nothing, but d over d beta B of the partition function divided by the partition function z which is my denominator and this is nothing, but d over d beta B of the logarithm of the natural logarithm of the partition function ok.

So, just keep this result handy. So, I am just going to sort of call this as equation 1. Once we have the partition function with us we can compute magnetization also which is not on the cuts by then it is a by product you can use it ok. So, let us continue with our partition function. So, our partition function at constant field in temperature was already computed up to this step ok. So, I am just going to copy this here, we had already computed pre computed. So, let us just bring it down here ok.

So, I can now split up these summations because there are they are summations over the degrees of freedom the microstates, I can write rearrange this in the form that simply the exponents that are added up become now products ok. And for the each I that I have taken out side I can take my m i’s to go from minus s to plus s I will sum up overall these exponents there is a recall that our excitations are from the set minus s 2 s 2 s plus 1 values ok.

Now, we can see this summation that is inside, for each i that is fixed by the product outside you take the same values of mi minus s to plus s and compute the sum; which means I can simply compute it for one value of I and raise everything to the power n ok.

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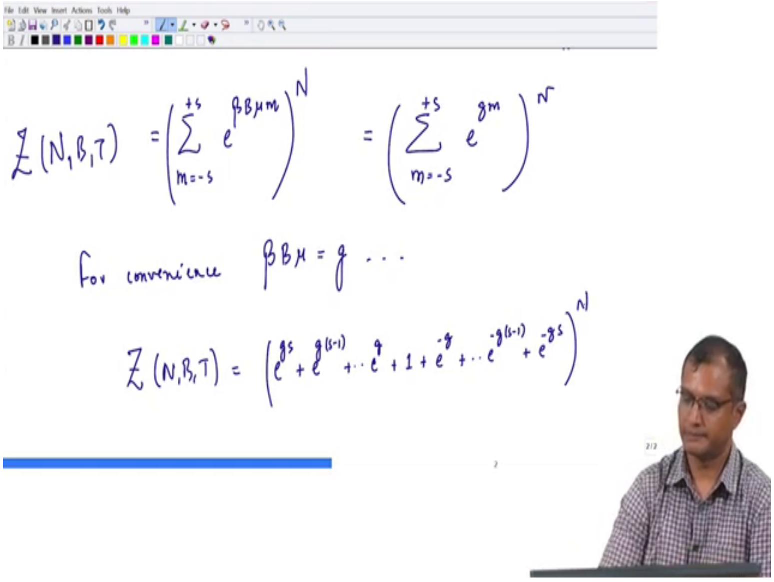

$$Z(N,B,T) = \left(\sum_{m=-s}^{+s} e^{\beta B \mu m}\right)^N = \left(\sum_{m=-s}^{+s} e^{gm}\right)^N$$

For convenience $\beta B \mu = g \ldots$

$$Z(N,B,T) = \left(e^{gs} + e^{g(s-1)} + \cdots e^{g} + 1 + e^{-g} + \cdots e^{-g(s-1)} + e^{-gs}\right)^N$$

So, this is now a simple task of just taking some variable m going from minus s to plus s e raise to beta B mu m and you simply raise the entire thing to N because you do it repetitively for each i the same task which is like doing it for one i and raising the entire thing to power n ok. And we can for the sake of convenience I can take the factor beta B mu as sum g because I do not want to write 3 symbols every time.

So, this is nothing, but summation m going from minus s to plus s e to the power g m the whole thing raise to n this is my partition function that I am going to compute is that ok. So, then I can write down my partition function as nothing, but if I expand it, I will get terms I will write down a few terms here. So, let me write down the terms here I will be getting e to the power g s plus e to the power g s minus 1 all the way to e to the power g plus m equal to 0 will give me 1 plus e to the power minus g plus e to the power ok. So, I am need some space here. So, let me write down in a you know conserving space.

So, suppose the first term I will write down from the positive side is becomes e to the power g s plus e to the power s minus 1 all the way to e to the power g plus 1 plus e to the power minus g plus fine and the entire thing is raise to the power n ok.

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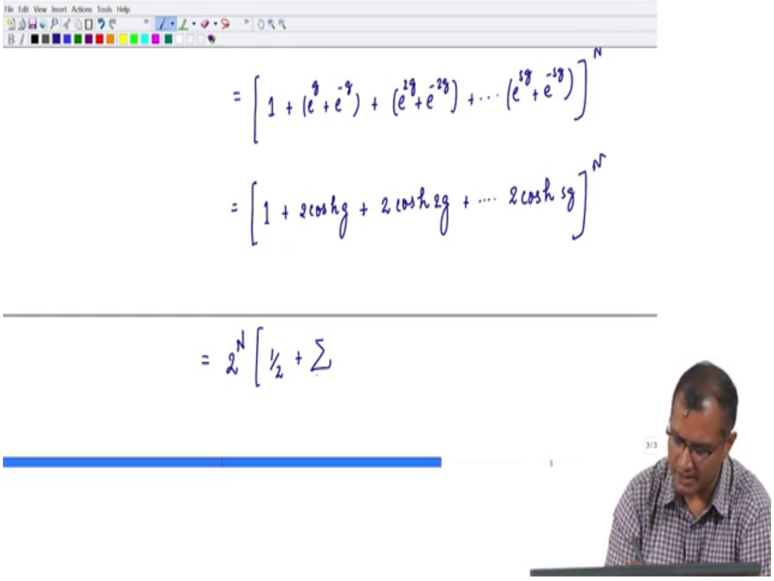

$$= \left[1 + (e^{g} + e^{-g}) + (e^{2g} + e^{-2g}) + \cdots (e^{sg} + e^{-sg})\right]^{N}$$

$$= \left[1 + 2\cosh g + 2\cosh 2g + \cdots 2\cosh sg\right]^{N}$$

$$= 2^{N}\left[\tfrac{1}{2} + \sum\right.$$

So, you can now look at we can club this term and that term, we can club this term and this term we can club this term and this term you will be left out with just one. So, you can write this as 1 plus. So, I am going to write 1 first e to the power g club these 2; then you can write down e to the power twice g 2 g all the way to that would be the last term ok.

So, then you can call this entire thing as 1 plus twice cosine hyperbolic g plus twice cosine hyperbolic 2 g all the way to twice cosine hyperbolic s g entire thing raise to N by using the formula for cosine hyperbolic. And I am going to take a factor of 2 outside. So, this will make me 2 raise to N into 1 by 2 plus summation sum you can take some variable let us take.

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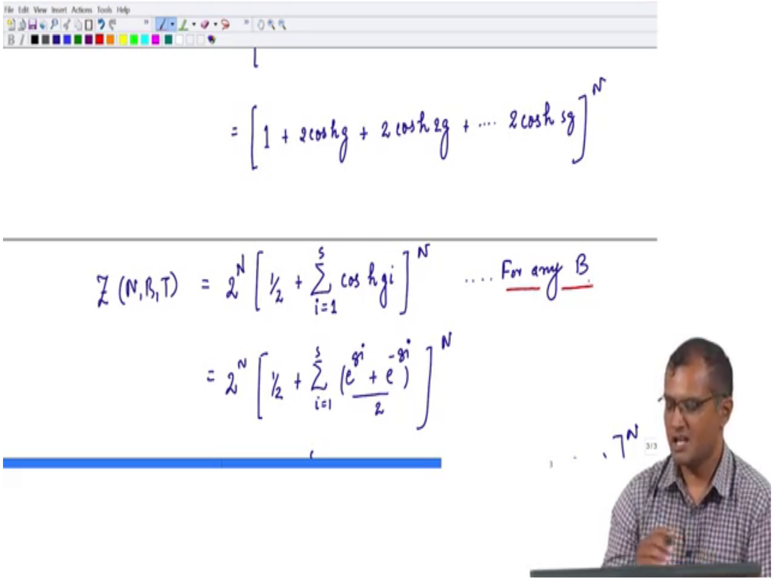

$$= \left[1 + 2\cosh g + 2\cosh 2g + \dots 2\cosh sg\right]^N$$

$$Z(N,B,T) = 2^N \left[\frac{1}{2} + \sum_{i=1}^{s} \cosh gi\right]^N \quad \dots \text{For any } B$$

$$= 2^N \left[\frac{1}{2} + \sum_{i=1}^{s} \frac{(e^{gi} + e^{-gi})}{2}\right]^N$$

Let us take i going from 1 to s cosine hyperbolic g i, the entire thing to the power N, this is my partition function for constant field in temperature ok. We can do some simplification here itself let see if we can simplify this further.

Yes we can. So, we can write down this cosine hyperbolic hypered I have simplified it there itself, but ok. So, I can write cosine hyperbolic gi as a e to the power gi plus e to the power minus gi over 2 ok. What I am trying to do here is because I do not thing we need the entire summation up to s ok. So, I am going to approximate the partition function if you want to call it you know if you want to call this is in approximation.

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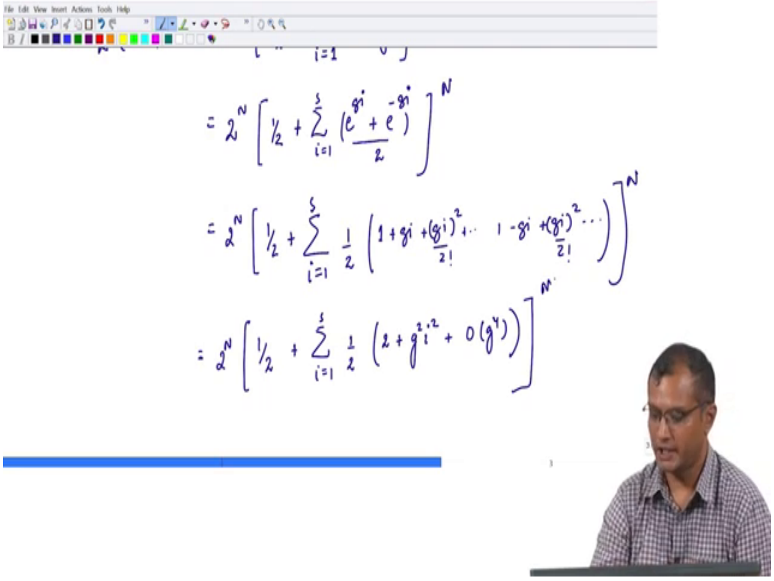

$$= 2^N \left[\frac{1}{2} + \sum_{i=1}^{s} \frac{(e^{g_i} + e^{-g_i})}{2} \right]^N$$

$$= 2^N \left[\frac{1}{2} + \sum_{i=1}^{s} \frac{1}{2} \left(1 + g_i + \frac{(g_i)^2}{2!} + \dots \quad 1 - g_i + \frac{(g_i)^2}{2!} \dots \right) \right]^N$$

$$= 2^N \left[\frac{1}{2} + \sum_{i=1}^{s} \frac{1}{2} \left(2 + g^2 i^2 + O(g^4)\right) \right]^N$$

So, let us approximate this that will not entire sum of to s. So, certainly I can do this approximation the limit of small fields which is what is required right which is what is mentioned. So, we are taking a field which is small enough and before the small enough fields, I want all these quantities to be computed partition function g susceptibility and heat capacity ok. So, let us try to compute this partition function the limit of small field otherwise I have to retain all terms in the summation by let us say if the field is small, then we can certainly do better.

So, let us see if we can. So, this can be written as. So, e to the power gi plus e to the power minus gi by 2 can be written as. So, I will take the 1 by 2 outside, and write down this as 1 plus gi plus gi the whole square by factorial 2, and for the minus gi I will write down 1 minus gi plus gi the whole square by factorial 2. So, I can easily see that all the odd terms will cancel and the even terms will add up.

So, if I do not add terms beyond order g 4, then I get this. This is 2 do not confuse it for anything else. So, I am going to add 1 and 1 that is going to give me 2 plus I am going to add gi square. So, that is going to give me g square i square because there is a factorial 2 in the denominator and so, what I get here is basically the next term would be order g 4 that I am going to drop ok.

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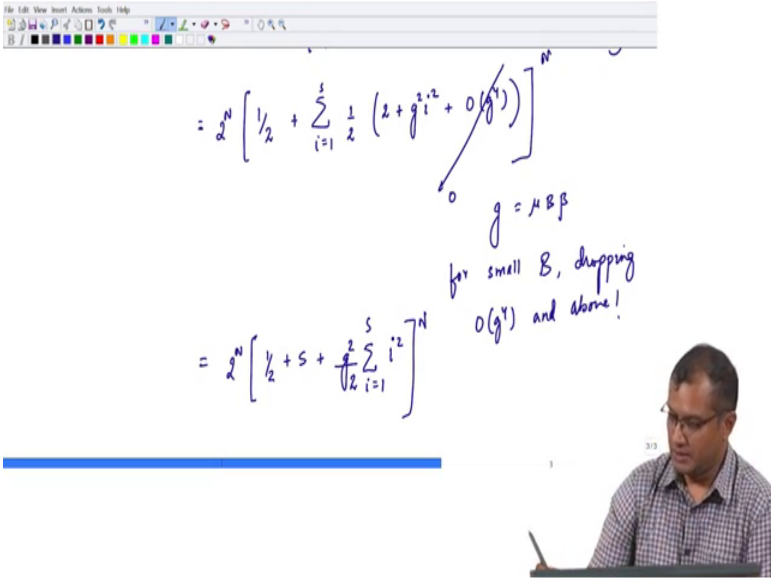

$$= 2^N \left[\frac{1}{2} + \sum_{i=1}^{s} \frac{1}{2} \left(2 + g^2 i^2 + \underset{0}{\cancel{O(g^4)}} \right) \right]^N$$

$g = \mu B \beta$

for small B, dropping $O(g^4)$ and above!

$$= 2^N \left[\frac{1}{2} + s + \frac{g^2}{2} \sum_{i=1}^{s} i^2 \right]^N$$

Now, I am going to drop terms of the order g 4 and above, because g if you recall is mu B beta and this goes to 0 I am going to write down that for small B or small values of field g square g 4 I am going to write down that we are dropping terms of the order g 4 and above ok. Small field approximation like I said I want to do something I want to drop the summation it is not drop the yet, but we will drop it in another step.

So, you can drop the terms of the order ith and 4, and then this summation becomes 1 by 2. So, half into 2 is 1 and you are summing it s time. So, it is just s plus I will take one half outside and call this as summation i going from 1 to s. In fact, I will take g also outside g square also outside.

So, g square by 2 I will take outside and what I will get is basically summation i going from 1 to s i square in the entire thing is raised to the power n fine ok. Now sum of first s squares is already known you know that the sum of first n numbers is n into n plus 1 by 2 sum of first n squares is n into 2 s plus 1 into s plus 1 by 6.

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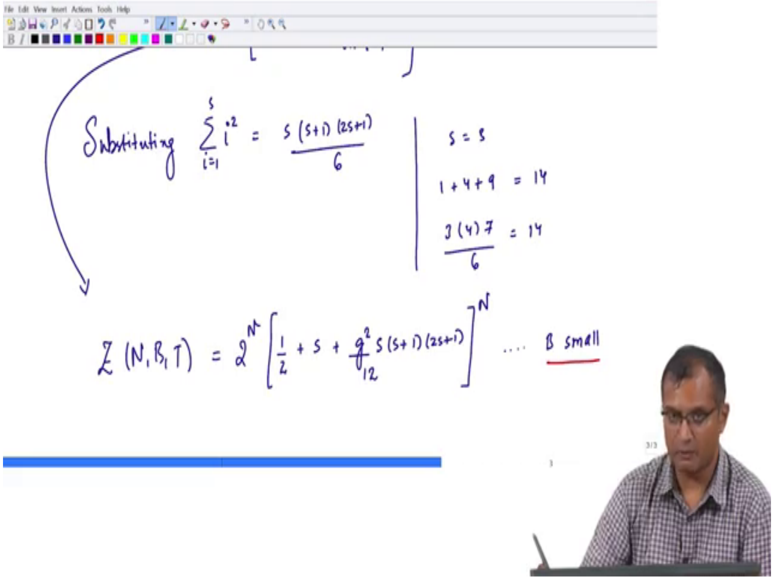

Substituting $\sum_{i=1}^{s} i^2 = \frac{s(s+1)(2s+1)}{6}$

$s = 3$

$1 + 4 + 9 = 14$

$\frac{3(4)7}{6} = 14$

$$Z(N,B,T) = 2^N \left[\frac{1}{2} + s + \frac{g^2}{12} s(s+1)(2s+1) \right]^N \quad \ldots \quad \underline{B \text{ small}}$$

So, simply substituting the known result of the sum of first s squares it is nothing, but s into s plus 1 into 2 s plus 1 over 6 ok. So, we can try and you can check suppose you take s equal to 3. So, what you have for the sum is basically 1 plus 4 plus 9 which is 14 and what is your right hand side? It is 3 into 4 into 7 by 6 which is also 14 ok. So, our formula is correct just verified.

So, let us call that this is a rough work and let us come back to our partition function. So, our partition function is now. So, we are doing all this hard work because I want to write down approximate formula for partition function it small field; plus s plus g square by 2 into what I have just cooked s into s plus 1 into 2 s plus 1 by 6. So, 6 into 2 is 12.

So, this is g square by 12 fine entire thing raise to the power n and this is the partition function for in this small field otherwise you have to take this full partition function which is here ok. So, if you have to write down the partition function for any field then this is your expression, you cannot use their approximation that I have used, but you say my magnetic field is small then this is the approximation.

So, now you can use this approximation and compute the value of your various thermodynamic properties ok. So, for example, the first thing that you can compute is the Gibbs free energy ok.

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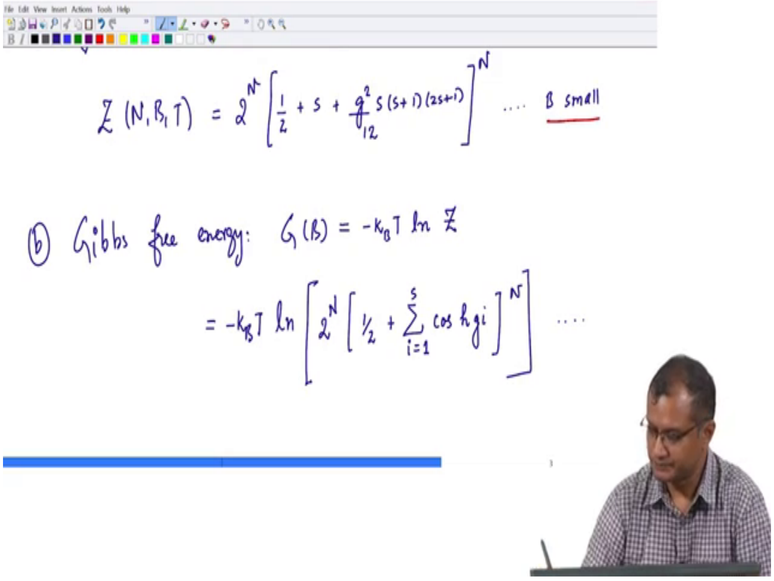

$$Z(N,B,T) = 2^N\left[\frac{1}{2} + s + \frac{g^2}{12}s(s+1)(2s+1)\right]^N \quad \ldots \quad \underline{B \text{ small}}$$

ⓑ Gibbs free energy: $G(B) = -k_BT \ln Z$

$$= -k_BT \ln\left[2^N\left[\frac{1}{2} + \sum_{i=1}^{s} \cosh gi\right]^N\right] \quad \ldots$$

So, the Gibbs free energy as we know will now be a function of the field and we know from the statistical mechanics discussions, there is a bridge between microscopic world and the macroscopic observations and that bridge gives us the bridge that gives us the value of the Gibbs free energy is minus k T lon our partition function now we will do it again for arbitrary field and small field.

So, for the Gibbs free energy, I can simply use this value of our general partition function and this is the value of the partition function here yeah 2 raise to N into 1 by 2 plus summation cosine hyperbolic gi. So, I am just going to copy ok. This is a partition function; you have to take a negative k T lon of your partition function ok. So, let us do that its very simple.

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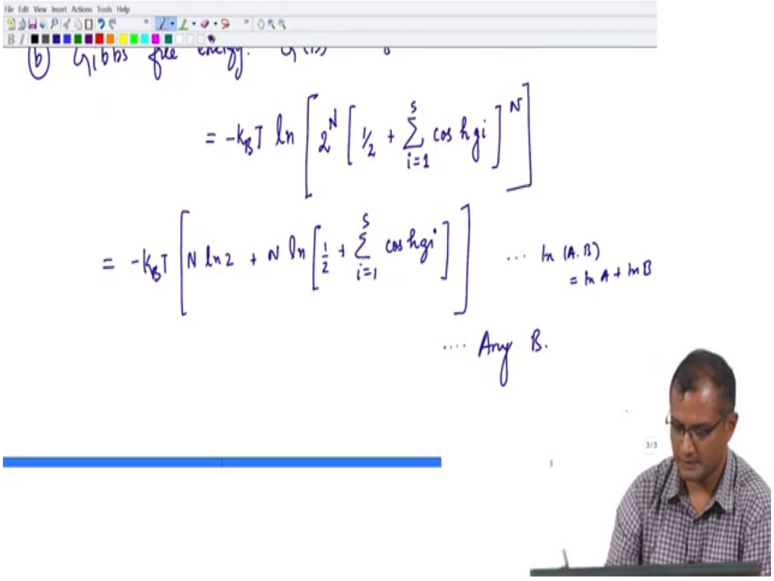
Ⓑ Gibbs free energy

$$= -k_BT \ln\left[2^N\left[\frac{1}{2}+\sum_{i=1}^{s}\cosh g_i\right]^N\right]$$

$$= -k_BT\left[N\ln 2 + N\ln\left[\frac{1}{2}+\sum_{i=1}^{s}\cosh g_i\right]\right] \quad \dots \ln(A.B) = \ln A + \ln B$$

…. Any B.

So, what you can do here is nothing, but minus k T and you can simply take lon of A into B as lon A plus lon B. So, what you get here is just N lon 2 plus N lon half plus summation i going from 1 to s cosine hyperbolic gi fine what I have done here is nothing, but used the fact that lon A into B is lon A plus B. So, now, you can already do a few things we can now use the approximation for the Gibbs free energy that we have worked out of the approximation the partition function that we have worked out ok. So, for small b; so, this was for any field ok.

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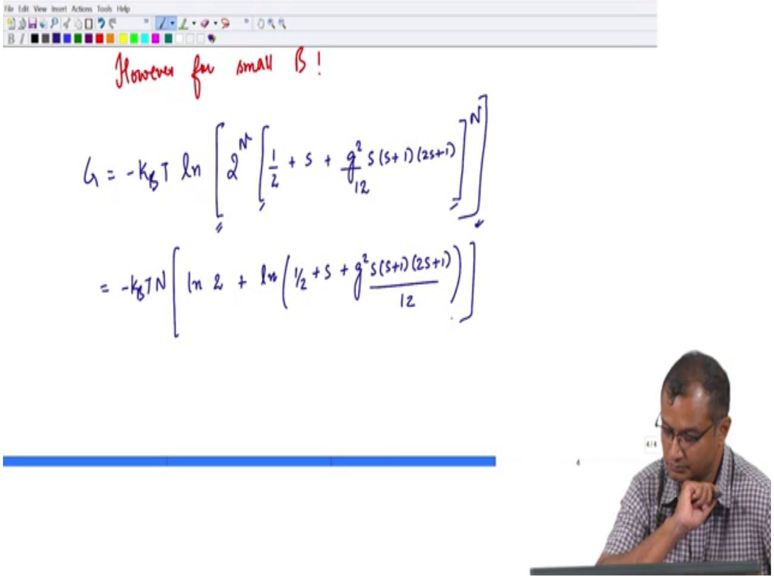
However for small B!

$$G = -k_BT\ln\left[2^N\left[\frac{1}{2}+s+\frac{g^2}{12}s(s+1)(2s+1)\right]^N\right]$$

$$= -k_BTN\left[\ln 2 + \ln\left(\frac{1}{2}+s+g^2\frac{s(s+1)(2s+1)}{12}\right)\right]$$

So, in this small b approximation so we can write down; however, for small B we have a readymade approximation for the partition function. So, we can use that approximation and compute the Gibbs free energy. So, I can write down my g as negative k BT of the and the logarithm of the partition function that is already precomputed here for the small field approximation which is I am just going to since I am lazy I am going to copy this entire expression, and simply paste it here minus k T lon of my z.

So,. So, this bracket here is corresponding to this bracket and this bracket here is for this bracket ok. So, let us do this calculation and. So, what you can do here is the following. So, we can take minus k BT and logarithm of this 2 will give you a common pre factor of outside because both these terms that are multiplying r raise to n. So, I can write down this is and now I can write down inside the bracket as a lon 2 plus lon of half plus s plus g square s into s plus 1 into 2 s plus 1 over 12 is it.

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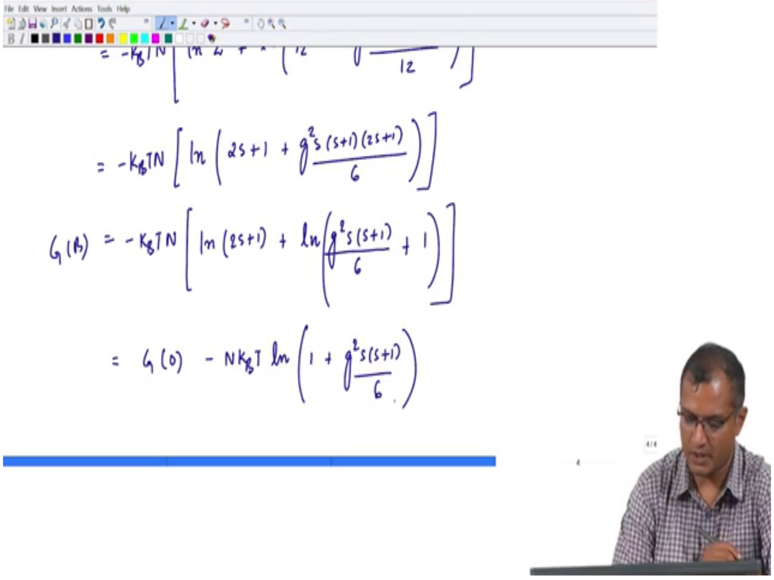

$$= -k_BTN\left[\ln\left(2s+1+g^2\frac{s(s+1)(2s+1)}{6}\right)\right]$$

$$G(B) = -k_BTN\left[\ln(2s+1)+\ln\left(g^2\frac{s(s+1)}{6}+1\right)\right]$$

$$= G(0) - Nk_BT\ln\left(1+g^2\frac{s(s+1)}{6}\right)$$

And now what I am going to do is yeah let us combine these 2 logs see what we can do ? So, I can get log of and then. So, I have just multiplied 2 throughout and what I am going to do is basically take 2 s plus 1 also common. So, these becomes minus k BT N and write it as a; so, just 2 s plus 1 if I take out.

So, what I get is basically lon of 2 s plus 1 plus lon of g square s into s plus 1 over 6, and this will be yeah there will be a factor of 1 that I have missed. So, this will be ok. So, let us see if I multiply this I am getting that second term first and then I am getting the first term also all right.

Now, we can sort of give some name to these terms ok. So, what I can what I can call here is basically. So, this is my G at some magnetic field ok. So, the first term here has no magnetic field dependence. So, I am going to call this as a g at 0 magnetic field without magnetic field plus or minus NK BT lon of I am going to write it as 1 plus g square s into s plus 1 over 6 is it ok.

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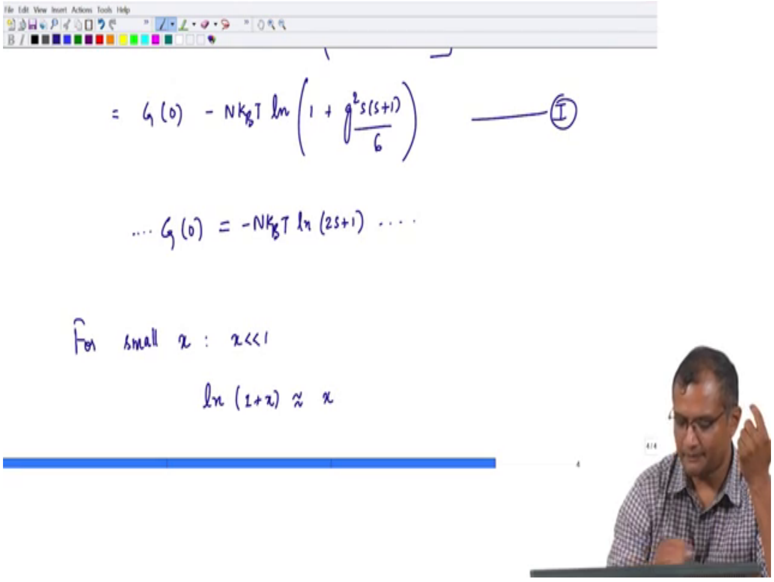

$$= G(0) - Nk_BT \ln\left(1 + g^2\frac{s(s+1)}{6}\right) \quad \text{——} \; \text{(I)}$$

$$\ldots\; G(0) = -Nk_BT \ln(2s+1) \;\ldots$$

For small x : $x \ll 1$

$$\ln(1+x) \approx x$$

Where I have just use this nomenclature that the free energy at 0 field would be just minus n k BT lon of 2 s plus 1. I am allowed to do this because just that is the first term is field dependence. So, I am just calling it as g 0 some arbitrary reference of the free energy its a state function. So, its references arbitrary, I am calling this as the arbitrary reference. The next term which depends on field through this factor called g is called as the field dependent part ok. So, if you take the difference of G B and G 0 that would be the field dependent part of the free energy.

Let us call this as the some equation number let us call this as 1 and noting that you know for small x by small x I mean when x is much much smaller than 1, I can always write down lon of 1 plus x has just x actually the correct expansion here of lon 1 plus x is.

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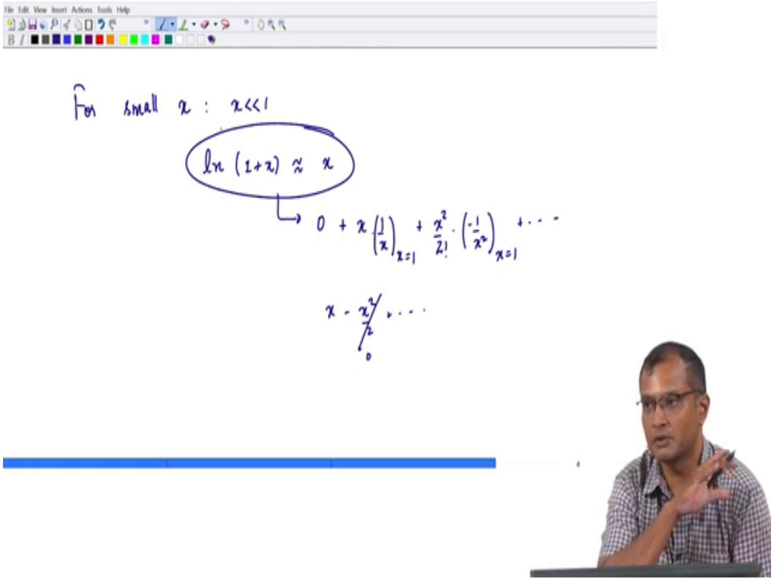

For small x : $x \ll 1$

$$\boxed{\ln(1+x) \approx x}$$

$$\to 0 + x\left(\frac{1}{x}\right)_{x=1} + \frac{x^2}{2!}\cdot\left(\frac{-1}{x^2}\right)_{x=1} + \cdots$$

$$x - \cancel{\frac{x^2}{2}} + \cdots$$

$$0$$

For small x I know that the leading term will be definitely lon 1 which is 0 because your expanding around 1. So, f x is 0 lon 1 plus x is lon 1 plus x times the derivative of lon x which is 1 upon x at x equals to 1 plus x square by 2 factorial 2 into derivative of 1 by x which is minus 1 by x square at x equals to 1 and so, on. So, what you get here is nothing, but x minus x square by 2 and so, on.

Now, I have taken the limit x to be much less than 1. So, I am going to drop this to 0 and simply say that lon 1 plus x is very close to x not a bad approximation. So, this term here can be just written as g square into s into s plus 1 by 6 ok.

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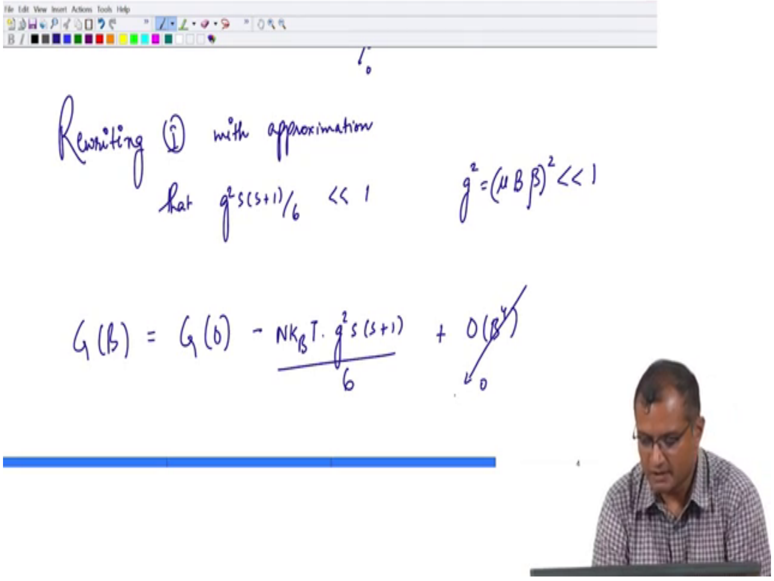

Rewriting ⓘ with approximation that $g^2 s(s+1)/6 << 1$ $g^2=(\mu B\beta)^2<<1$

$$G(B) = G(0) - Nk_BT.\frac{g^2 s(s+1)}{6} + \underset{\swarrow 0}{\cancel{O(B^4)}}$$

So, I am going to rewriting 1. So, rewriting 1 with the approximation that g square into s into s plus 1 by 6 is much much smaller than 1 because have a g is already you know which is the magnetic field if you take square of that it is much much smaller than 1 ok. So, definitely g square into s by 6 into s plus 1 is also much smaller than 1 .

So, I can write down this entire equation has nothing, but g at field is equal to g is 0 minus N K T into g square into s into s plus 1 over 6 is that and definitely here I have dropped terms of the order b to the power 4 and above. So, this is my approximate Gibbs free energy in the limit of small fields. Of course, this approximation is valid only valid field is small if you take fields to be large then you have to take the entire series. So, this is the Gibbs free energy that we have computed.

Now, we can compute important object such as magnetization. So, let me see what is of the agenda. So, we have to compute the next topic is to compute magnetic susceptibility chi.

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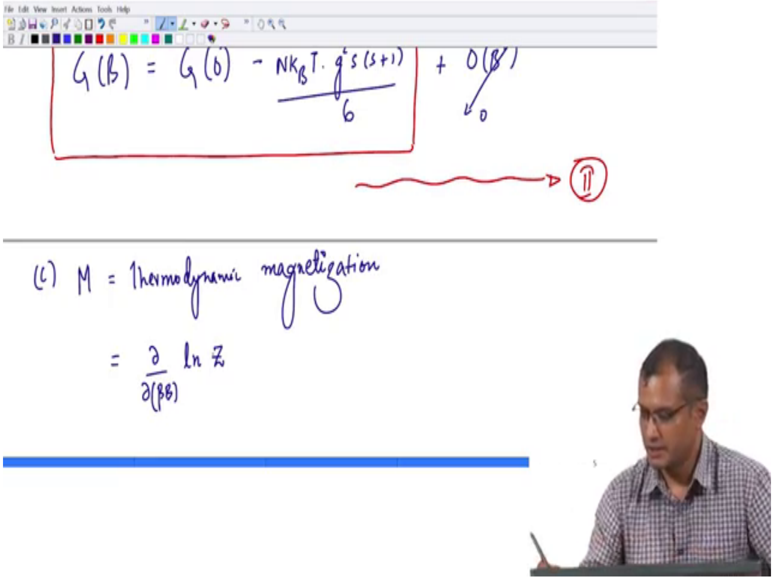

$$\boxed{G(B) = G(0) - \frac{NK_BT \cdot g^2 s(s+1)}{6}} + \underset{\swarrow 0}{O(B)}$$

$\rightsquigarrow$ (II)

(c) M = Thermodynamic magnetization

$$= \frac{\partial}{\partial(\beta B)} \ln Z$$

So, the magnetic susceptibility can now be computed by looking at this expression a very important expression that I have derived ok. So, I am going to call this as a equation 2 ok. So, this is the value of the Gibbs free energy and the magnetization the thermodynamic magnetization this is thermodynamic in nature, this is not the instantaneous magnetization.

So, you can compute this from appropriate derivatives of the Gibbs free energy and we have already shown that this average magnetization is nothing, but d over d beta B of lon partition function ok. You can go upstairs and refer to the discussion yeah look at the equation 1 here ok.

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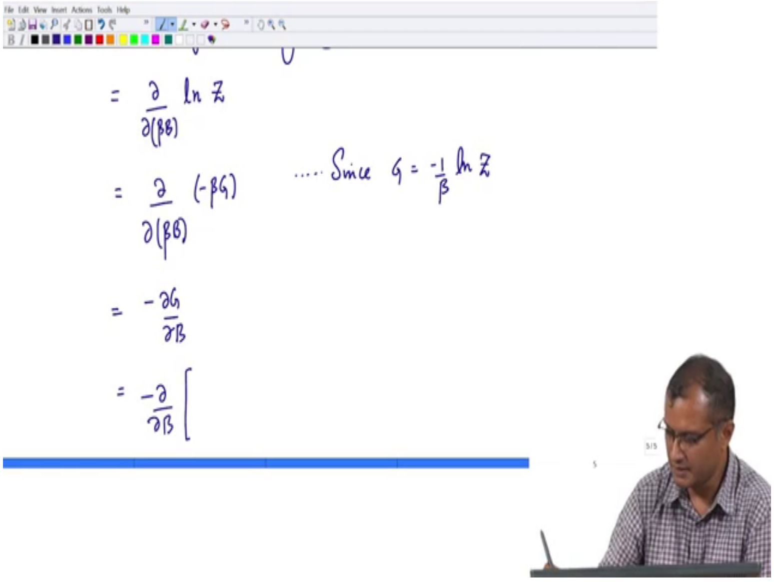

$$= \frac{\partial}{\partial(\beta B)} \ln Z$$

$$= \frac{\partial}{\partial(\beta B)} (-\beta G) \quad \ldots\ldots \text{Since } G = \frac{-1}{\beta} \ln Z$$

$$= -\frac{\partial G}{\partial B}$$

$$= \frac{-\partial}{\partial B} \Big[$$

So, it can be very easily computed I know that my logarithm of the partition function is already related to the Gibbs free energy ok. So, this is already equal to minus beta into the Gibbs free energy because of that bridge between microscopic world and the macroscopic observations. So, I know already that minus 1 over beta lon partition function is related to the Gibbs free energy.

So, I have simply substituted that here, I can knock off beta. So, this is just minus d G over d B this is my magnetization and we have use the value of the Gibbs free energy that is just computed for small fields ok. So, I just computed for the small field like in the substitute for reading term is no dependence on the magnetic field dependence comes only from g square.

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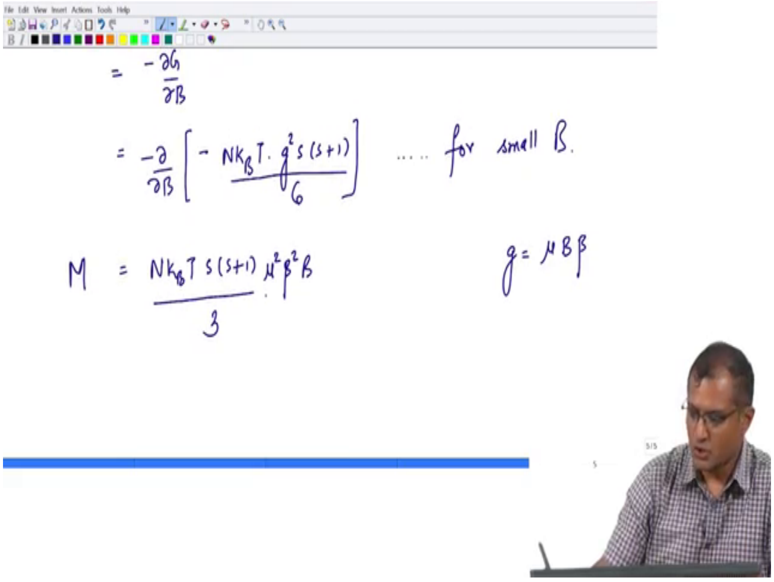

$$= -\frac{\partial G}{\partial B}$$

$$= \frac{-\partial}{\partial B}\left[- N k_B T \cdot \frac{g^2 s(s+1)}{6} \right] \quad \ldots\ldots \text{ for small } B.$$

$$M = \frac{N k_B T\, s(s+1)\, \mu^2 \beta^2 B}{3} \qquad g = \mu B \beta$$

So, I will substitute that here for g and remind all of you that we are using this we can only use this for small B as B goes to 0 our approximation of g is applicable only in the small B which means the magnetization that I am going to construct is also for small B because I have use that value of g here. So, we can knock off these 2 minus signs and put sorry yes of course, I think I were supposed to copy it, but left it upstairs.

So, a lot of things can come out NK BT into s into s plus 1 divided by 6 and of course, our g is a mu B beta. So, mu square beta square will also come out and B square is differentiated to twice B. So, you can knock this off with the 3 here in fact, you can write down just as a B by 3 is a factor.

So, this is the value of the magnetization thermodynamic magnetization. So, we can see the larger the field larger is the magnetization. In the prefactor which is which is essentially constant and also another thing you see here is that magnetization has to be an extensive property and it is because it has an n inside it.

So, it is a both extensive as well as it scales with the magnetic field that is applied externally. So, the next object that we can determine is the susceptibility I believe which was on the cards lets go up and check yes. So, next object is a susceptibility and as I said susceptibility is basically 2 first order it is the derivative of magnetization with respect to the external field as the field is taken to very small values ok.

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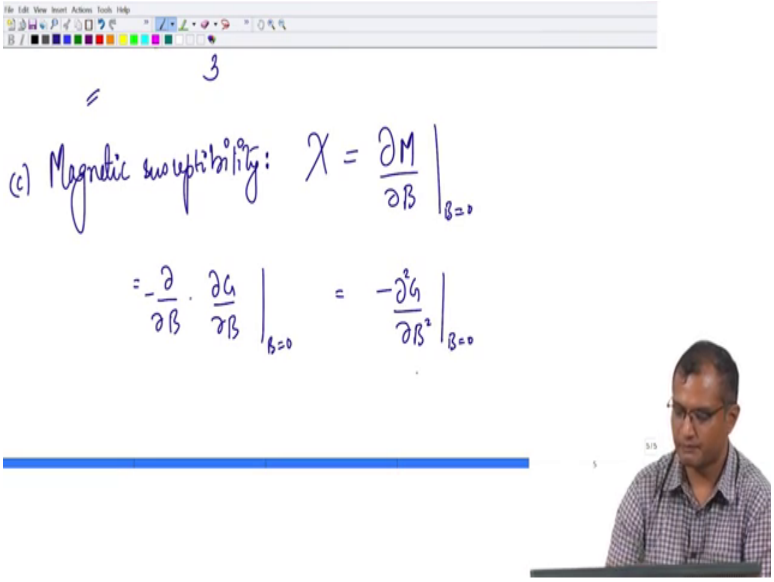

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(c) Magnetic susceptibility: $\chi = \frac{\partial M}{\partial B}\Big|_{B=0}$

$= -\frac{\partial}{\partial B}\cdot\frac{\partial G}{\partial B}\Big|_{B=0} = -\frac{\partial^2 G}{\partial B^2}\Big|_{B=0}$

So, the third object is the magnetic susceptibility of our n spin system. So, it is defined as the derivative of the magnetization over field at small values of field. So, we can compute this, since we have already have m over here I can simply take its derivative at small values of field and get the value of susceptibility ok. So, or what I can do here is take the not take this approximated value of m, and compute m from the Gibbs free energy.

So, I can write this as d over d B and m itself is minus d G over d B at B equals to 0. So, basically what I am going to do is nothing, but minus second derivative of free energy with respect to field at B equals to 0 ok.

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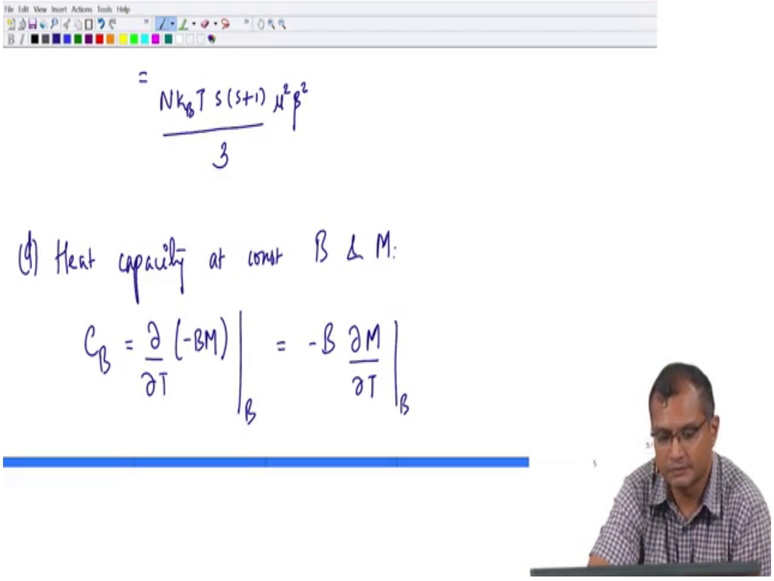

$$= \frac{N k_B T\, s(s+1)\, \mu^2 \beta^2}{3}$$

(9) Heat capacity at const B & M:

$$C_B = \frac{\partial}{\partial T}(-BM)\Big|_B = -B\,\frac{\partial M}{\partial T}\Big|_B$$

Either way you will get the same result. So, you take the derivative here. So, that is the value of the susceptibility as the field goes to 0 and finally, we can compute what is called as the heat capacity at constant field ok. So, you can compute the heat capacity at constant field magnetic field by simply taking the temperature derivative with respect to since we are taking a constant field derivative, it has to be a partial derivative of the energy scale in the problem at constant field ok.

So, the energy scale in the problem we just the magnetic enthalpy which is minus BM ok. So, it is straight forward you can take the field outside because it is held a constant and this is just the temperature derivative of the magnetization which has already been computed for your ease over here ok. So, if you look at this temperature derivative what you get here is nothing, but ok.

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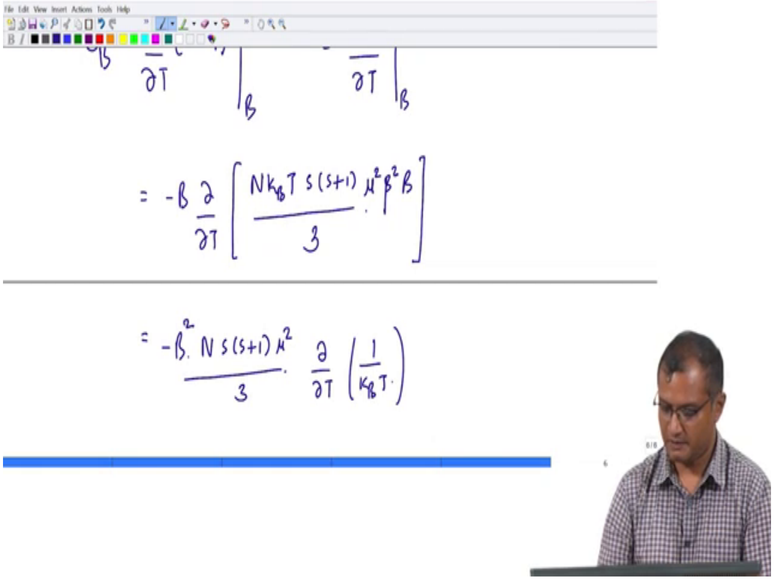

$$\partial T \Big|_B \qquad \partial T \Big|_B$$

$$= -B\frac{\partial}{\partial T}\left[\frac{N k_B T\, s(s+1)}{3}\mu^2\beta^2 B\right]$$

$$= -\frac{B^2 N s(s+1)\mu^2}{3}\frac{\partial}{\partial T}\left(\frac{1}{k_B T}\right)$$

So, if you take the temperature derivative here I am going to just write as minus B d over d T of. So, the quantity notice that there is a beta square here ok. So, what you are going to do here is, either you can convert temperature derivative into beta or we can do it with respect to temperature both are fine. So, what I am going to do here is see that I have a 1 upon k T here ok. So, this simply becomes minus B, I will take all the terms that are constants N I will take out all the constants first N into s into s plus 1 mu square this becomes B square over 3 and d by d T of 1 upon k BT is it.

B becomes B square k T into beta square is just 1 upon k T and s into s plus 1 comes outside.

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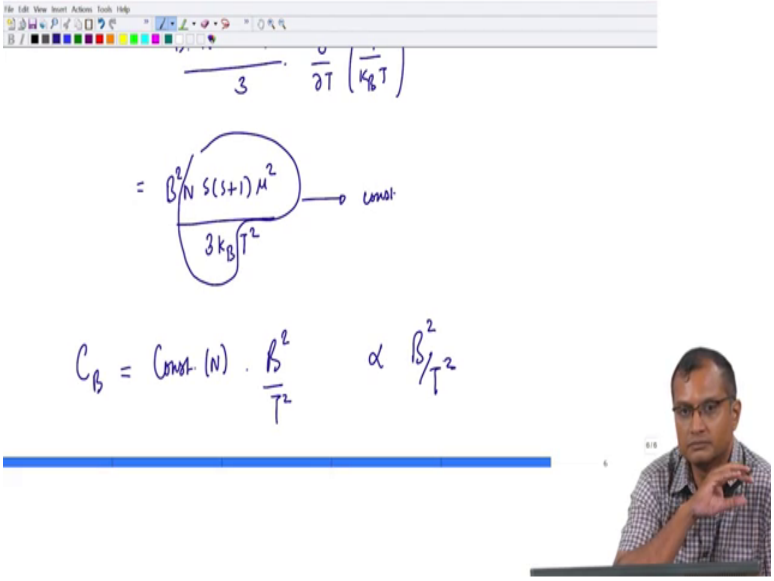

$$= \frac{B^2 N S(S+1)\mu^2}{3 k_B T^2} \longrightarrow \text{const.}$$

$$C_B = \text{Const.}(N) \cdot \frac{B^2}{T^2} \quad \propto B^2/T^2$$

So, what I will get now is basically B square N s into s plus 1 mu square over 3 k BT square ok. So, I can now sort of call all this things a some kind of a constant which does not depend on temperature or the magnetic field it is a constant which is only extensive with nature, it scales with only system size or n. So, I will say that my heat capacity at constant magnetic field is basically some constant which is a system size dependent constant into B square by T square or it is proportional to B square by T square ok.

So, it is an extensive constant, but it is proportional to B square divided by T square. And how about heat capacity at constant magnetic field?

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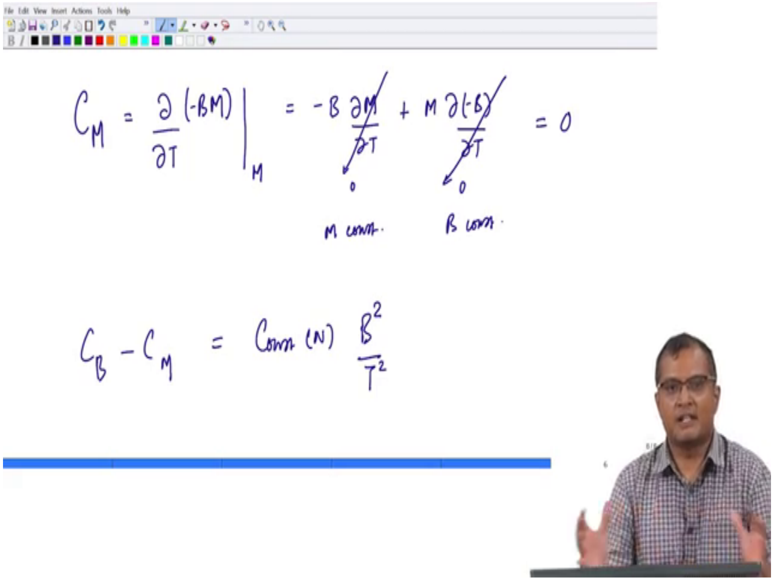

$$C_M = \frac{\partial(-BM)}{\partial T}\Big|_M = -B\underset{0}{\cancel{\frac{\partial M}{\partial T}}} + M\underset{0}{\cancel{\frac{\partial(-B)}{\partial T}}} = 0$$

M const. B const.

$$C_B - C_M = \text{Const}(N)\,\frac{B^2}{T^2}$$

Again we can do the same logic, we can take the partial derivative of the energy scale there is only 1 energy scale in a problem that is the magnetic enthalpy at constant magnetization ok. Now this is interesting. If you do this derivative you can you know of course, the magnetic field is held constant. So, when you do the chain rule, you can write it as minus B into d M by d T and that is 0 because we cannot change magnetic magnetization you want to do this derivative at constant M.

And plus M into d of minus B by d T which is also 0 because B is held constant ok. So, because M is constant, the first term goes to 0 and B is the constant applied magnetic field. So, this is 0. So, you cannot you cannot hold magnetization constant in the system and hence the heat capacity at constant temperature is 0, that would mean what is the energy required to change the temperature of the system keep in magnetization constant.

You will say that this is 0 because it is slightest amount of energy is applied magnetization changes. So, I can now write down that heat capacity difference in the same where as the C B minus C V of ideal gas we now have C B minus C M which is nothing, but C B which is just some constant system size dependent into b square by t square ok.

So, this is where we end our discussion, we have computed the partition function then we forget it to Gibbs free energy and from the Gibbs free energy we computed various thermodynamic properties such as susceptibility which I have already told is related to the fluctuations of magnetization, I leave that as an exercise how to compute susceptibility from fluctuations please do that. And heat capacities at both constant field constant magnetization for our target system which is N non-interacting spins in a constant magnetic field.