Introduction to Statistical Mechanics
Girish S Setlur
Department of Physics
Indian Institute of Technology – Guwahati

Lecture - 22
Tutorial - IV

Okay so continuing with the tutorial problems, so I want to today discuss something called Curie susceptibility. So, Curie susceptibility involves the interaction of spins which are quantized so that means quantum spins in a magnetic field. So, the point is that now instead of thinking of spin 1/2 or spin 1 or anything specific, so we make it general but then it remains quantized.

So, in other words we consider a general spin s. So, that means the projection of the spin vector in any direction is going to be either - s $\hbar$ or (- s + 1)$\hbar$ all the way up to s$\hbar$.

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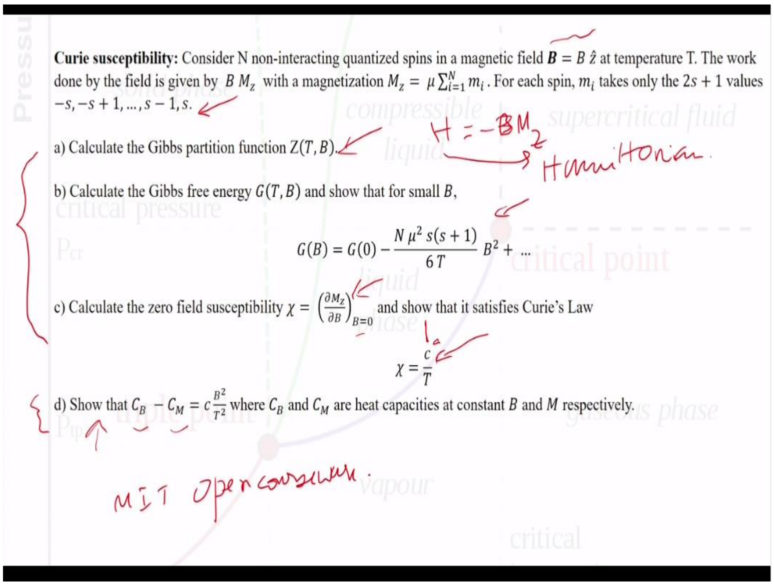

So, if you look at this sentence, so it is, so you see that the spin's projections are quantized in this manner, s is the spin quantum number which can be integer like 0 is uninteresting, so it can be 1 and 1, 2, 3, 4 or it can be 1/2 integer like 1/2, 3/2 like that. Now, this when it is in contact with a magnetic field, so when this, where there is a uniform magnetic field, the Hamiltonian is going to be - s, basically Hamiltonian is going to be – BM_z.

So, this is the Hamiltonian. So, the idea is to calculate the partition function and then expand in powers of B and then because of this you will be able to calculate the, well independent of this you can calculate the magnetization and calculate the linear susceptibility and then show that the susceptibility obeys Curie's law which is basically constant divided by temperature.

And that goal is to also find this constant in terms of the other parameters in the problem and then and this is for this is these are fairly trivial but what is interesting is the last question here. So, by the way, these questions like I told you are from MIT OpenCourseware, so because I wanted to introduce some challenging interesting questions which MIT OpenCourseWare has a number of them which are very interesting and challenging and important.

So, it is worthwhile studying them, so even though I am not inventing new questions but I am telling you how to solve them on my own, so alright. So, the interesting part of this question they have asked is you know show that the specific heats when you hold magnetic field fixed or when you hold you know the magnetization fixed they are different. So, you can you know change temperature holding magnetic field fixed which is easier.

But you can also do the other thing which is change temperature holding the magnetization fixed so and you can ask yourself what is the specific heat in each situation and they are going to be different and so we are asked to show that the difference between these two is precisely this constant $c\frac{B^2}{T^2}$ okay. So, the question is how do you do this okay. So, let us try and see if we can do this.

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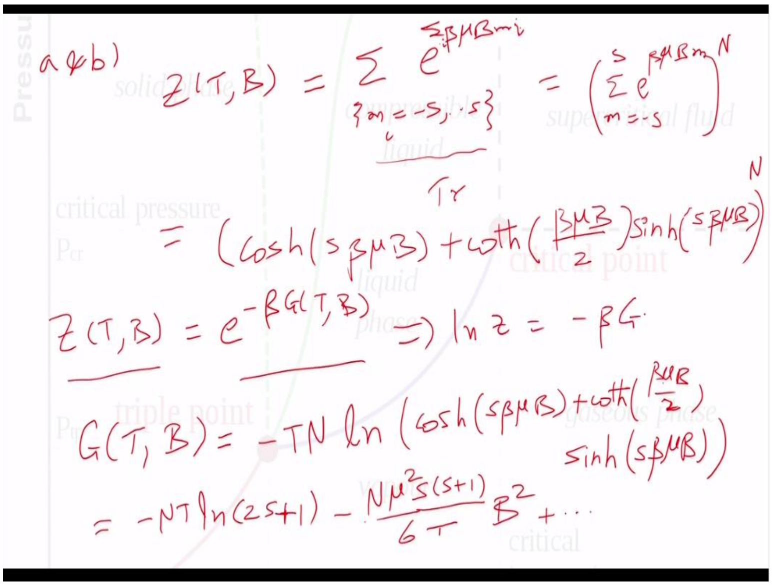

So, in order to do this, the first thing you have to do is calculate the Gibbs partition function which is so it is as simple as you know $\mathrm{Z}\,(\mathrm{T},\mathrm{B}) = \sum_{m=-s,..s} e^{\sum_i \beta\mu B m_i}$ okay. So, this is going to so using the idea that you can flip the order of taking the trace, so this is speaking trace and this is so there is a summation in the exponent.

So, if you can interchange those two, so this is going to be something raise to N and that something is basically $\sum_{m=-s,..s} e^{\sum_i \beta\mu B m}$. So, it is going to look like this and the answer is going to look like this okay raise to N. So, of course, this is a simple you know geometric series which you can do and get this answer. So, I prefer to do this on the computer.

So, that like I told you I use you know symbolic algebra packages to do this alright. So, now notice that Z is given, so the Gibbs free energy, so in terms of the Gibbs free energy you can write the partition function as follows. So, from this you can deduce the Gibbs free energy itself as

$$G(T,B) = -TN\ \ln(\cosh\,(s\beta\mu B) + \coth\left(\frac{\beta\mu B}{2}\right)\sinh(s\beta\mu B)$$

okay.

So, now the question asks you to expand in powers of the magnetic field, it asks you to expand in powers of the magnetic field and explain how the leading terms look like. So, if you expand this out in powers of the magnetic field, it is going to look like this okay. So, that is what it looks like when you expand it out and the magnetization itself it is kind of easy to find.

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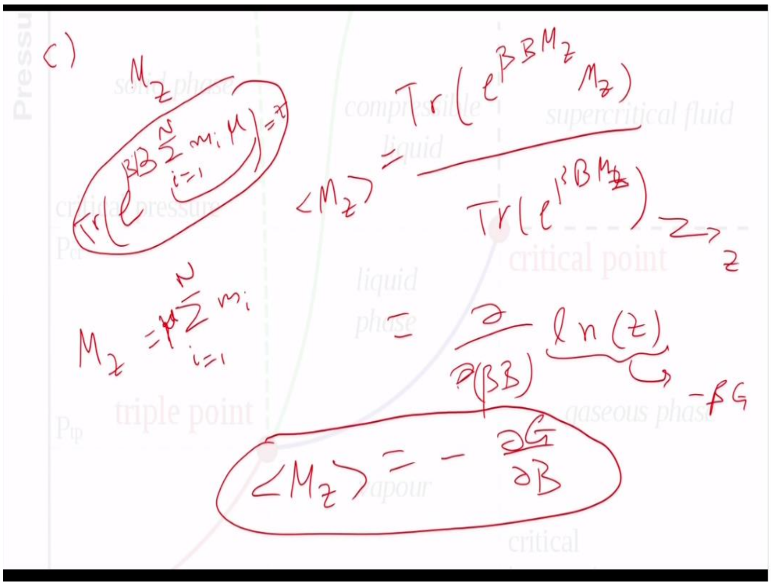

So, the magnetization you see notice that there is an $e^{\beta B \sum_{i=1}^{N} m_i \mu}$. So, actually the, so there is this term in the partition function. So, this is basically the partition function. So, now you see this is your magnetization. So, if I want to find the average of this what I have to do is I have to bring this. So, it is basically trace of, the average of magnetization is basically

$$< M_Z > = \frac{Tr(e^{\beta B M_z} M_z)}{Tr(e^{\beta B M_z})}$$

So, the question is how do you do this? So, this is clearly basically if you call this Z right, so that is basically take the log(β B) and log Z and you differentiae that is what you get alright. So, I am going to do this, so remember that we just derived Z so or you can write this Z as you know log Z, so this means basically log Z = - β G.

So, this is nothing but - β G. So, if you think of differentiating with respect to magnetic field, so this is because - dG by dB basically, so that is what that is. So, the average magnetization is nothing but the derivative of the Gibbs free energy with respect to the magnetic field okay. So, let me go ahead and do that. If I do that, I get this result.

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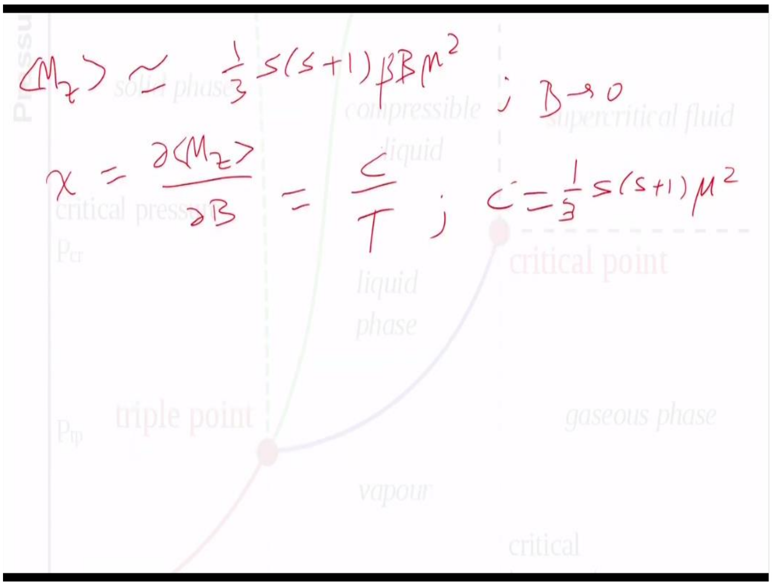

So, because I have already calculated, so recall that I have already calculated the Gibbs free energy and this is my Gibbs free energy. All I have to do is take and derivative with respect to magnetic field. Of course, it is more and I mean I could get the general formula which is uninteresting but I am going to use this. So, if I use this I get this result which is basically $\frac{1}{3}s(s+1)\beta B\mu^2$

So, that is going to be my magnetization, so for small magnetic field, B is small. So, the linear susceptibility is basically defined as the magnetization for small magnetic fields and the rate of change of that with respect to magnetic field. So, the slope, so MZ is going to be proportional to the magnetic field for small magnetic field and the coefficient of proportionality is called the susceptibility of the linear susceptibility. So, this comes out as c by T where c is the Curie constant which is $C = \frac{1}{3}s(s+1)\beta B\mu^2$

So, that is one of the questions that was asked. So, this is all fairly straightforward but what is more interesting is the last part okay. So, the part d was show that that if you have a constant magnetic field, this specific heat is going to be different from what it is when you have a constant magnetization and the difference between the two is basically given by this result. So, let us see if we will be able to derive this. So, the question is how do you derive this.

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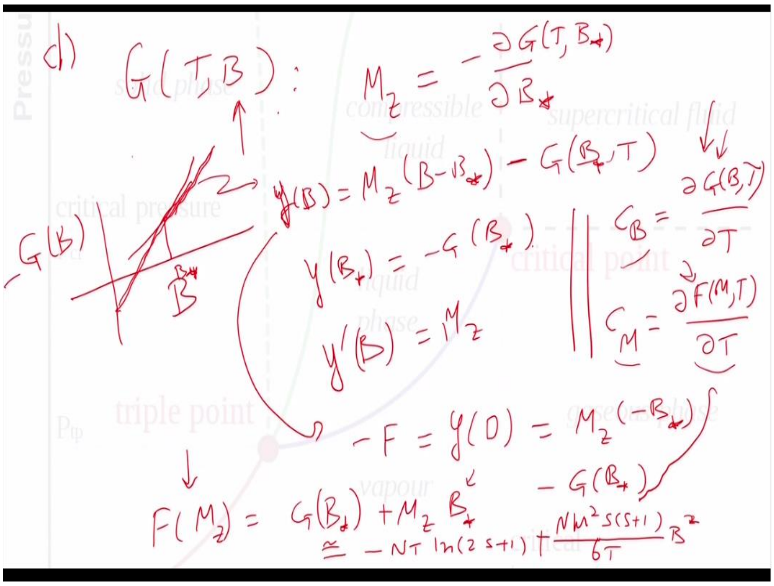

So, you see in order to derive this, so we perform a Legendre transformation. So, remember that you have the Gibbs free energy which depends upon temperature and magnetic field okay. So, you can choose to trade the magnetic field with magnetization. So, remember that I have explained to you in great detail the geometrical meaning of this transformation which is basically your suppose you have a function of a quantity like the magnetic field you can either define it or you can either describe it by providing the values of B and values of G.

So, that is like the usual way. The other way is to provide the value of the slope and the intercept of the tangents to that curve. So, G versus B is a certain curve and you can either describe the curve itself through its x and y values that means your ordinate and abscissa values or you could, you choose to define it in terms of the, you can describe that curve using a family of tangents.

So, by specifying again 2 numbers, one is the intercept and the other is the slope. If you provide the slope and intercept, then the straight line is unique and then if in addition you postulate that that has to be tangent to the curve so that it makes the straight line completely unique. So, providing a family of such straight lines gives you alternative description of the system different from what it is by providing Gibbs free energy.

So, as a result, so let us do the Legendre transformation and it is done in the following way by so imagine that I focus my attention to some particular value of magnetic field and this is the definition of magnetization and then I can create a, so if you have you know, so imagine you have something like this. So, this is your B_* okay. So, you have a whole bunch of slopes here.

So, the idea is that you create a straight line which is tangent to this curve okay. So, this tangent to the curve is going to look like this. So, I am going to define the tangent to the curve, it is kind of defined with a negative, so I am going to think of it as MZ times B - B star + the value of B at B star is G. So, this is how I choose to define that straight line. So, the tangent to this straight line, so MZ is the slope of - G versus B because there is a minus sign there okay.

So, I am going to put minus sign there okay. So, now this makes sense because at

$$y(B_*) = -G(B_*)$$

$$y'(B) = M_z$$

which is a slope of - G versus okay. So, if this is the case, then the free energy is going to be defined as the negative of the intercept. So, it is going to be defined as the negative of the intercept. So, I define the free energy as y at 0.

So, this is going to look like $y(0) = M_z(-B_*) - G(B_*)$. So, the new free energy at constant magnetization is now going to be $G(B_*) + M_z(B_*)$ okay. So, that is what that is. So, now let us go ahead and see if we can calculate. So, as a result, you see that the specific heat at constant magnetic field by definition is this. So, it is the derivative of the Gibbs free energy with respect to temperature.

And the derivative of the constant of the free energy with constant magnetization is going to be with respect to the temperature is going to be the specific heat with respect to when you hold the magnetization fixed. So, these are 2 different types of specific heat. This specific heat is when you hold the magnetic field fixed and vary the temperature. So, that means B is fixed and you are changing temperature you get a specific heat.

So, you are supposed to differentiate the corresponding free energy. So, when you hold the magnetic field fixed, the corresponding free energy, the Gibbs free energy and when you hold a magnetization fixed, it is a different free energy which is the Legendre transform of the

Gibbs free energy and it does not have a particular name. So, it is some kind of free energy and it says the free energy corresponding to the situation where the magnetization is fixed.

So, when the magnetization is fixed, you get a different free energy and if you find the rate of change of that free energy with respect to temperature, you get a certain specific heat and that is called CM. So, now we will have to calculate these kinds of free energies and so how do we do that. So, to calculate this you see I am going to do it this way. So, this is my free energy when the magnetization is fixed.

So, remember that I am only interested in the situation where the magnetic field is small. So, I am as a result allowed to expand in powers of the magnetic field. So, when I do that so remember we did that for Gibbs free energy and we got this result, so it is G of 0 is something uninteresting. Well it is I mean; let me write it down because it also depends on temperature G of 0.

So, it is going to be

$$F(M_z) = G(B_*) + M_z(B_*) = -NT\ln(2s+1) - \frac{N\mu^2 s(s+1)}{6T}B^2 + \frac{1}{3}s(s+1)\beta B\mu^2/T$$

So, you see that it is the same thing. This is - 1/6 and this is + 1/3. So, that means this is basically this whole thing put together becomes + 1/6 right because this is going to be 2/6 - 1/6, so this is + 1/6. So, I might as well simplify it this way right here and get rid of this altogether. So, that is going to be my new free energy. Now, if I differentiate with respect to temperature okay, so I get.

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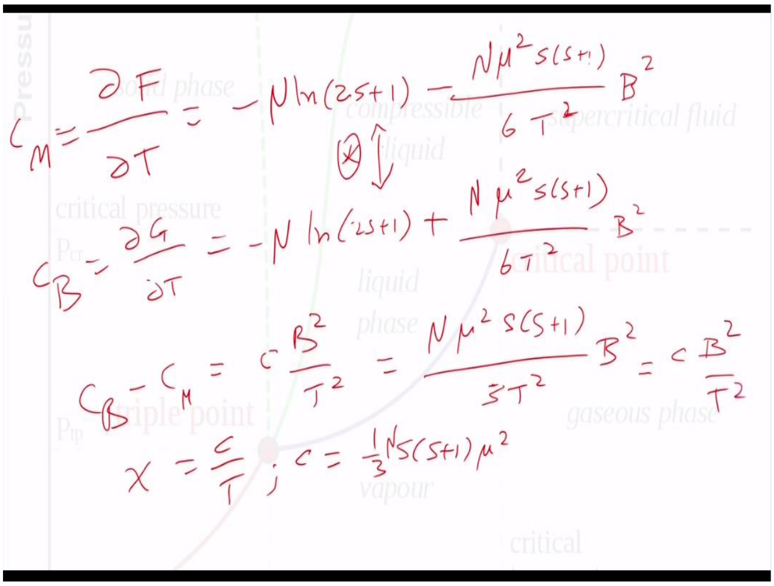

So, if I differentiate dF/ dT, so that is my C_M. So, that is going to look like

$C_M = -N\ln(2s+1)$ - $\frac{N\mu^2 s(s+1)}{6T^2}B^2$okay. So, that is what that is and if I take the Gibbs free energy and so remember that Gibbs free energy was this one. So, this was Gibbs free energy. So, if I take dG / dT, I get CB, so that is what that is. So, if I take dG / dT, I get the same thing with a plus sign for the second term.

So, that means CB is same thing here but the next term is the same thing with a different sign, with opposite sign okay. So, the question says show that CB – CM is basically C times B squared by T squared and where a C is given by chi equals C by T. So, this is Curie constant. So, we know that the Curie constant, we just calculated the Curie constant if you remember as $\frac{1}{3}s(s+1)\mu^2$

So, now let us subtract this with this C rather this with this okay. So, if I subtract this with this, I get you see I get exactly this. So, this will cancel out, so CB – CM. So, these two will cancel out whereas this will add up. So, it becomes $\frac{N\mu^2 s(s+1)}{3T^2}B^2$. So, that is basically what it is okay. There was a per particle never mind, so there was a per particle.

You can define magnetization per particle so but point is that that is what this is. So, it is C times B squared by T squared. So, this is an interesting problem because it kind of explicitly forces you to think of the Legendre transformation and that too in this peculiar context where normally in Legendre transformation you are trading energy for temperature like you are going from suppose you are going from microcanonical to canonical ensemble.

Typically, what you do is you have a system with fixed energy and a Legendre transformation will tell you how to transform the entropy which is the fundamental quantity in the microcanonical ensemble to the fundamental quantity for the canonical ensemble which is basically the Helmholtz free energy. So, Legendre transformation enables you to connect these 2 potentials, the microcanonical potential which is just the entropy and canonical potential which is Helmholtz free energy.

So, the connection between these two is established using Legendre transformation but then so in a less familiar context the Legendre transformation is introduced in this particular problem where you start with the Gibbs free energy where you fix the magnetic field and then you ask yourself what would things look like if you choose to fix the magnetization instead. So, given that you know magnetization is the slope of the Gibbs free energy with respect to the magnetic field, so this is an interesting and valid question to ask okay.

So, that is as far as this problem is concerned and we will discuss some of the other questions subsequently okay. Thank you.