Introduction to Molecular Thermodynamics
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Lecture - 10
Microstates of a System (Contd.)

So let us continue our discussion on the Microscopic States of a System in Equilibrium.

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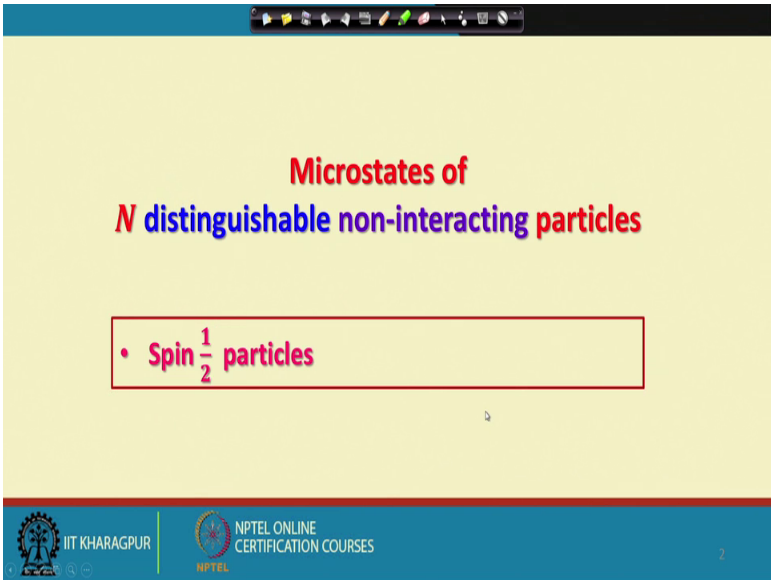

Where we are talking about the microstates of capital N in distinguishable, non-interacting particles and we are focused on the spin half particles.

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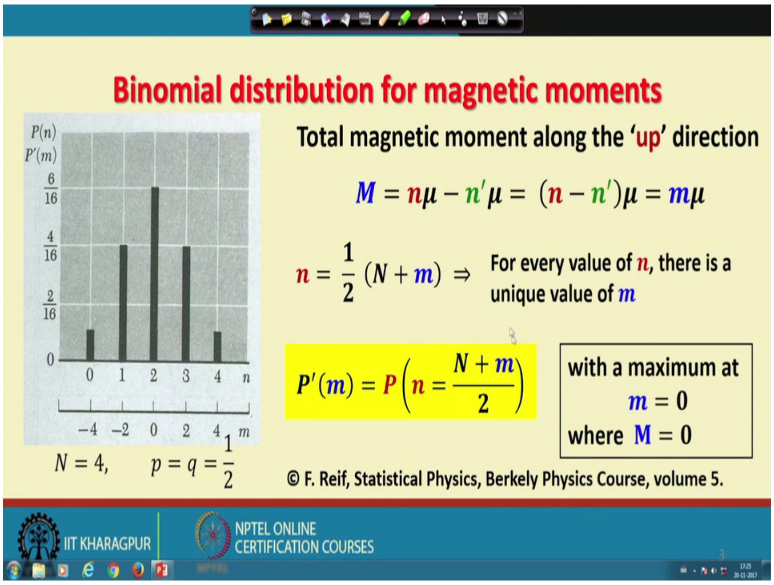

We have already talked about the binomial distribution for magnetic moments, and we find that if I have capital N equal to 4; that means, 4 spin half particles where there is no preferential orientation for either the up or the down spin, in the absence of an external field, it is possible to find out the probability associated with the total magnetic moment of each; when the total magnetic moment of the system is measured. So, the way the total magnetic moment is defined is capital M that is equal to number of up spins multiplied by the contribution to the magnetic moment that they make number of down spins and then the contribution of minus mu that they make in the up direction so that the total magnetic moment now is given by small m into mu, where mu is the associated magnetic moment for each particle.

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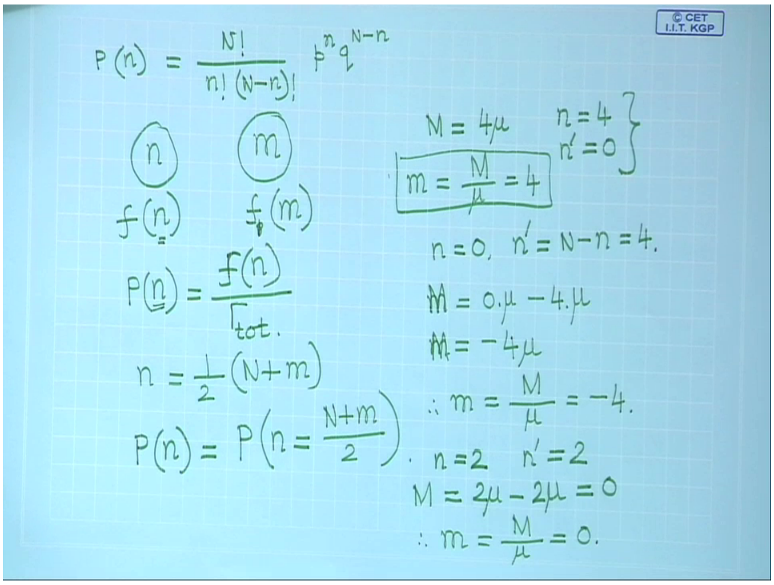

Now, I already know what P of n is and P of n is given by capital N factorial divided by small n factorial into capital N minus small n factorial into P to the power of n into q to the power of capital N minus small n.

Now, the question that we are asking here is instead of n, can I use m as the descriptor of my microscopic states. Why m? Because the different values of m will be the different outcomes of your experimental measurement of the total magnetic moment of the system. And in this case I really do not know what are, what is going to be the outcome of one particular step of my experiment.

That is because there are so many microscopic states associated with one such value of m; now what are these values of the given number of microscopic states? Let us say that f n is the number of microscopic distinct microscopic states associated with n up spins, correspondingly I would say that f 1 is the sorry f m is the corresponding number of microscopy distinct microscopic states associated with the total magnetic moment value of small m. And therefore, probability of n is given by f of n divided by gamma total. And since n is given in terms of capital N by this relationship I can always change this independent variable by m. So, what would be the mapping? The mapping would be P n would be equal to the same form of p, but I will have n equal to capital N plus small m by 2.

So, this is exactly what has been shown here. Now as you see that here n when I use n to represent the different possible microstates what I find is n can vary from 0 to 4 for the 4 particles of the system. Now when n is equal to 4 as we have already discussed then what is the magnetic moment value? I understand that capital M would be equal to 4 into mu because in this case small n is equal to 4 and n prime is equal to 0, and therefore, m that is equal to capital M by mu that must be equal to 4. So, that is this point that we have marked.

Similarly, if I look at the case where small n is equal to 0, what is the corresponding value of capital M; when small n is equal to zero obviously n prime that is equal to capital N minus small n that must be equal to 4, because capital N is equal to 4. And therefore, small m that is going to be 0 into mu, minus 4 into mu therefore, small m is going to be sorry capital M is going to be minus 4 mu. Therefore, what is small m? Small m by definition is capital M by mu that is going to be minus 4.

So, this is exactly what we have shown in this part of the plot therefore, just by changing the corresponding values that m can take corresponding to each value of n, I can map P of n the probability distribution of m to the P prime of m that is a probability distribution associated with the magnetic moment small n. And here what we note is that P prime m this distribution is the same distribution function, with a maximum that appears that small m equal to 0.

Now, please note that the small m equal to 0 is associated with small n equal to 2. Now small n equal to 2 would give me n prime equal to 2, which means the total magnetic moment is going to be equal to 2 mu minus 2 mu, that is equal to 0. Therefore, small m is going to be equal to 0 for non zero values of mu.

Now, looking at the similarity we understand that if I am measuring making a measurement of the total magnetic moment in that case, I am going to have maximum number of times in my experiment the output would be a 0 magnetic moment. This is what is meant by the interpretation of this distribution function.

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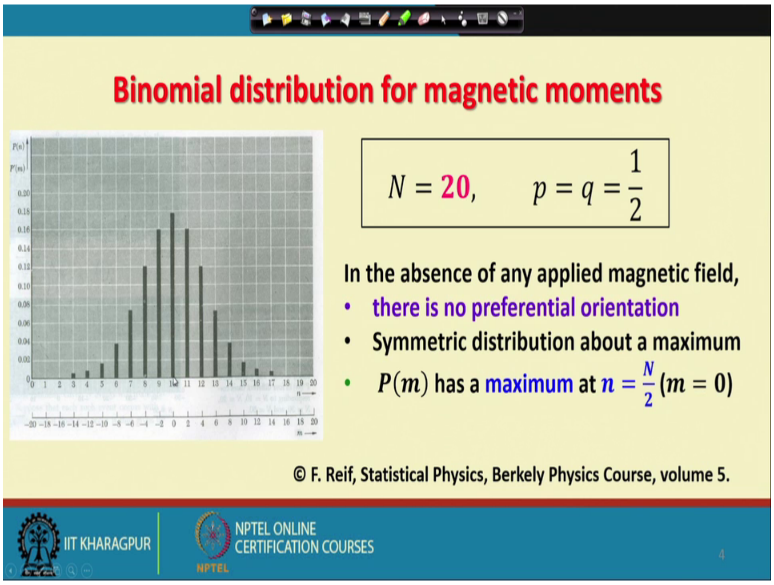

Let us next have a have a look at how we can look for a larger number of spin half particles, that is now present in the apps there is no applied external field present, but I have a much larger number of spin half particles. So, in this case let me take n is equal to 20, and for this case therefore, I will have values of n plus n prime equal to 20.

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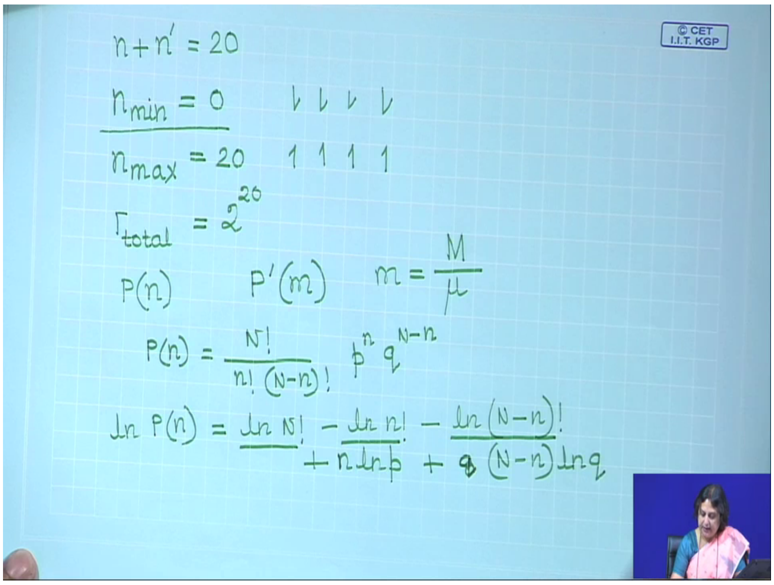

So, what is n min the minimum value of small n that is the number of up spins is equal to 0, and the maximum value of the number of up spins equal to 20. So, for this set I will have all down spin particles and here I will have all up spins particles. Now the question is what is gamma total here? The gamma total now is going to be a much larger number that is going to be 2 to the power of 20. And I can find out the probability associated with a given value of n or equivalently I can find out the probability distribution for a given value of m, where small m is equal to capital M the total magnetic moment of the system divided by mu.

Now, let us have a look at the binomial distribution once, again here the major things that you must note is that the minimum value of N is 20 the maximum value of n is a minimum value is 0 and the maximum value is 20, but still I have a symmetric distribution because there is no applied magnetic field and therefore, there is no preferential orientation for any of the sites to have an up spin or the down spin. This is the symmetric distribution about a maximum and P m this maximum appears at small n equal to capital N by 2 or in other words where small m is equal to 0.

At this point the question is what happens if the 2 orientations up and down are not equally probable, in that case you can consider the situation where you have applied an external magnetic field, and because of that you now have a situation where p is equal to 0.7 and q is equal to 0.3.

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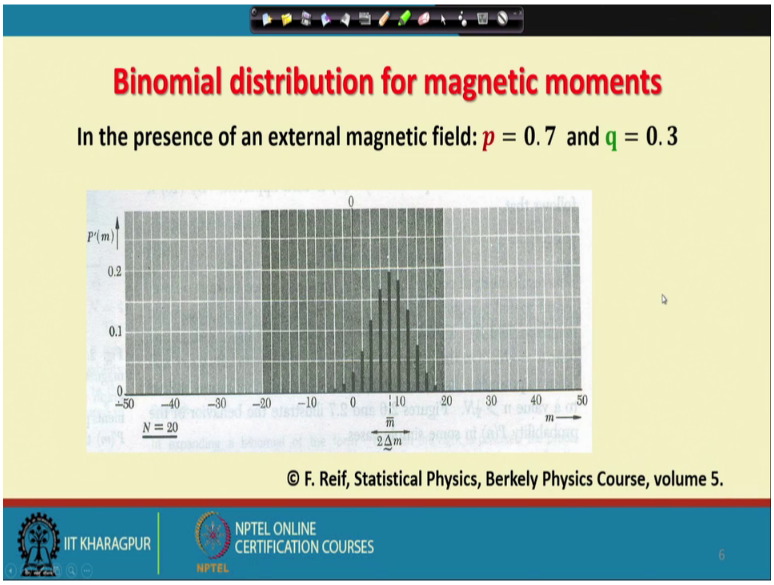

Now, if that is so, then let us have a look at what will happen to the binomial distribution if I have let us say capital N equal to 10. So, as you see that when capital N is equal to 10, the accessible values of m is minus 10 to plus 10, but here the distribution once again it has a maximum, but that maximum does not exactly appear midway between the accessible values of small m. Not only that what I find is here some of these values are this is actually pretty skewed. Now this kind of skewed asymmetric distributions we will continue to see in the presence of the external magnetic field.

So, next let us increase the number of particles and try to see how the binomial distribution changes. As you see for capital N equal to 20, what are the different values of small m possible that is given by this shaded region? And once again we find that I have an asymmetric distribution of values of m with one point that is a maximum, and once again the maximum is associated with some average magnetic moment m bar, and I find that this m bar value is flanked on both sides by nearly equal probable states corresponding to this m equal to 10 or some other values.

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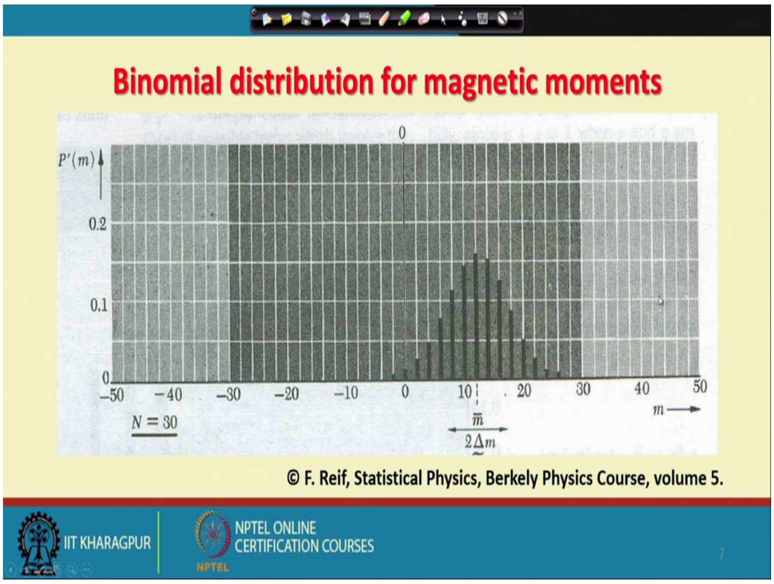

Now, if I further increase the number of particles what happens under this condition? Look at this is N equal to 30. As you see the number or the range of small m values these are increasing with the increase in the number of total number of particles.

And this is for n equal to 50, where we have covered the entire range from minus 50 to plus 50 for the m values of the system.

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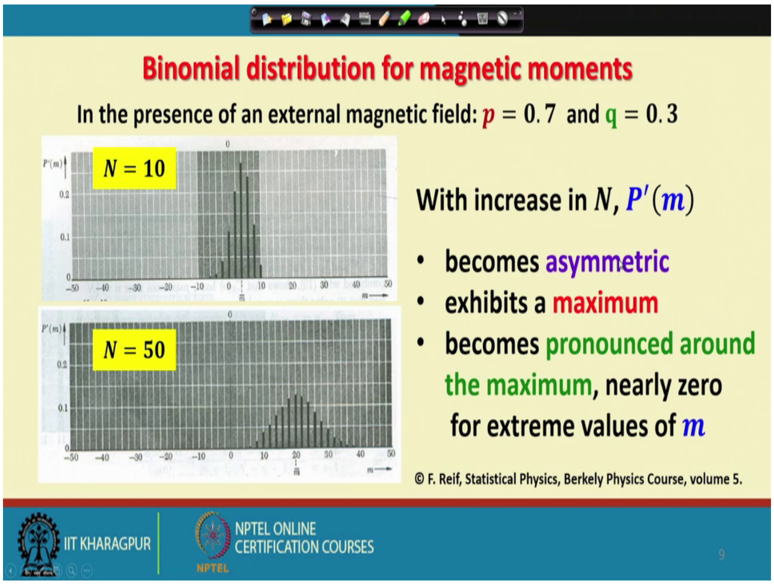

Now, with this idea in mind, let us now compare the 2 cases where I have in the presence of an external magnetic field p is not equal to q, and this is the case where n is equal to plus 10.

That is there are a total of 10 spin half particles present, and here I have another case where 50 spin half particles are present. So, what should be my major conclusion from a comparison? What I find here is that with increasing n the asymmetric nature is is observed for the case where p is not equal to q; the distribution still exhibits a maximum and as I go on increasing n what I find is that the nonzero population is pronounced only around the maximum, but if I think about the extreme values like plus 50 or minus 50 the probability of observing associated with those values of m are nearly equal to 0. So, what have we learned from here.

The major takeaway message from this slide is that, when I increase the number of particles present in the system, I have there is a very important consequence of that.

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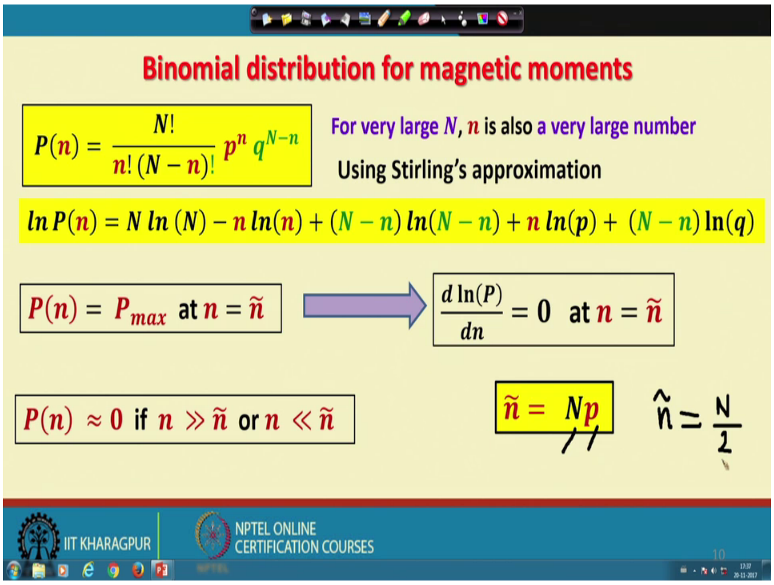

So, at this point I know that for a given total value of n, I have associated with it a binomial distribution P n where small n is the number of up spins that is observed when the magnetic moment is measured. Now if you have a system that is having a very large number of capital N, that is typically 10 to the power of 23, I would argue that the small n must also be a very large number. So, accordingly like what we have done before we can use stirlings approximation and express the natural logarithm of P n by simplifying these expressions. So, how do I do it? I know that P n is equal to N factorial.

Divided by small n factorial capital N minus small n factorial P to the power of n, q to the power of capital N minus small n if I take a log then I will be having ln N factorial minus ln small n factorial, minus ln capital N small n factorial then plus small n, ln p plus q plus capital N minus small n into ln q right. Now how do I find out these quantities, I am going to use the stirling approximation.

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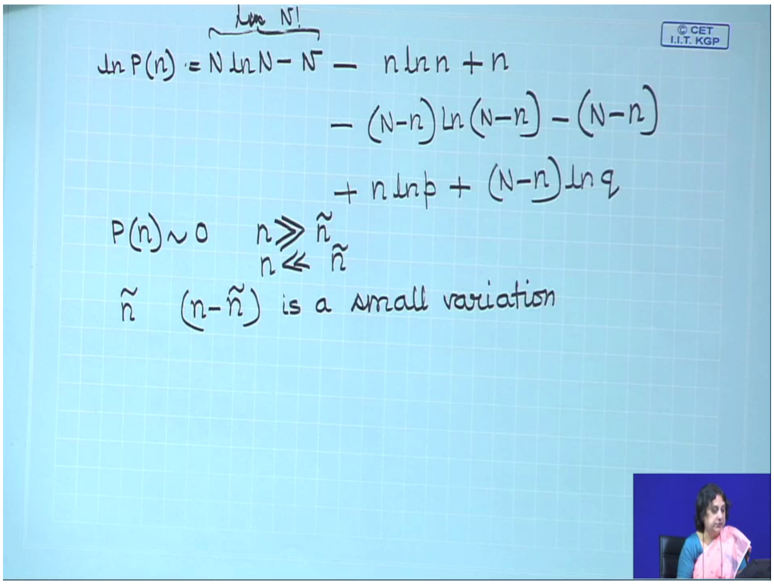

When I use the stalling approximation, I can very easily write this terms as ln P n that is equal to capital N ln N minus capital N this is for ln capital N factorial.

I can also write for minus of ln small n factorial a term like this, also I can have the term corresponding to capital N minus small n factorial and finally, I retain the terms plus n ln P plus capital N minus small n into ln q. I can do a little bit of algebra get rid of all the terms like that I do not really require and this is what I am going to get. Now this also tells me that if I go on increasing capital N, I am going to see one prominent maximum in P of n. And most of the nonzero values of P of n will be located around this location of the maximum.

This is what has been the observation from the binomial distributions that have been showing to you before. Now let us see what is the consequence of this observation? First of all if I have P n equal to P max at n equal to n tilde say, in that case I can very easily say that if I take a derivative of ln P with respect to n, I can put it equal to 0 at n equal to n tilde. So, this is a little bit of mathematics if you know ln P, you can always find out the first derivative of ln P with respect to n, and if you then put n equal to n tilde you will find that n tilde is equal to capital N that is the total number of particles present in the system, multiplied by the probability of observing one particle in the system with an up spin.

And therefore, for the system where I talked about the symmetric distribution P was equal to half, as a result we saw that n tilde the location of the maximum was at capital N divided by 2.

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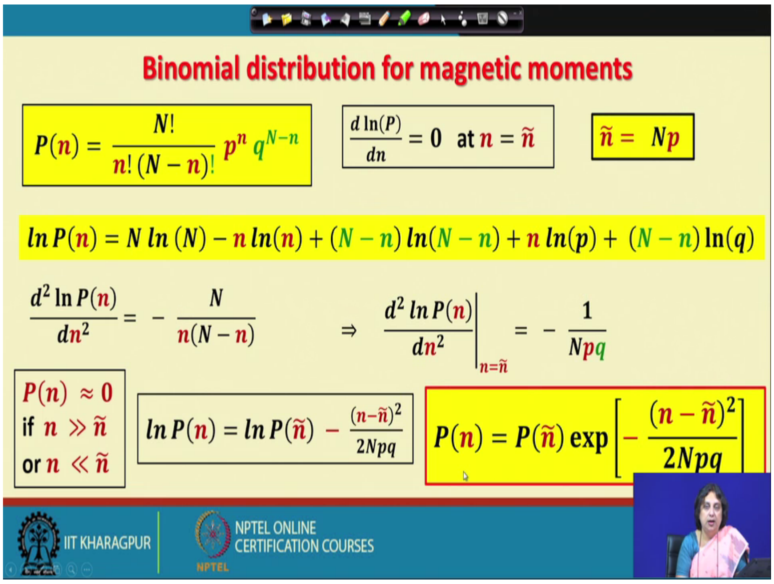

Now once we understand this, let us go one step further and trying to see the consequence for the consequence of this equation. I can take the second derivative of ln P n with respect to n and you can very easily show that, this second derivative will be given by this expression. I am not going to do this algebra here, but I am going to tell you that well if you are going to evaluate this second derivative, at the location of the maximum.

Where n is equal to n tilde and in tilde is equal to capital N into P you can very easily show that the value of the second derivative at the location of the maximum in the probability distribution is given by minus of inverse of n capital N p q, but why is it that I am interested in the second derivative? I am doing this because as I said that P n is not equal to 0 is roughly about 0 if small n goes much greater than n tilde or small n falls much much less than n tilde, which means that in the vicinity of n tilde n minus n tilde is a small variation. So, accordingly what I can do is, I can use a Taylor expansion and express ln P n as follows.

Let us now see; what is the further consequence of having a binomial distribution, for a very large number of magnetic moments. Now let us have a look at the second derivative of ln P n. Now what I find here is that the second derivative can be evaluated very easily from this algebraic expression. If I do that and evaluate this second derivative at the location of the maximum, what I find is that that depends on capital N, it depends on small p and small q. But what do I need this second derivative for. I can use the value of the second derivative around the position of the maximum to approximate what ln P n is going to be in the vicinity of n equal to n tilde and you will be very easily able to show that ln P n tilde minus only this term will be will survive.

Now this basically says that I have here log of P n natural log of P n is equal to natural log of the maximum probability minus some square term in n minus n tilde. And this means that I can now write the overall distribution function like this. Now this distribution function is not exactly the binomial distribution function that we have been looking at, rather this has a form which is known as the Gaussian distribution. So, I have now shown to you how to arrive at the Gaussian distribution from the binomial distribution that is typically applicable to the spin half particles.

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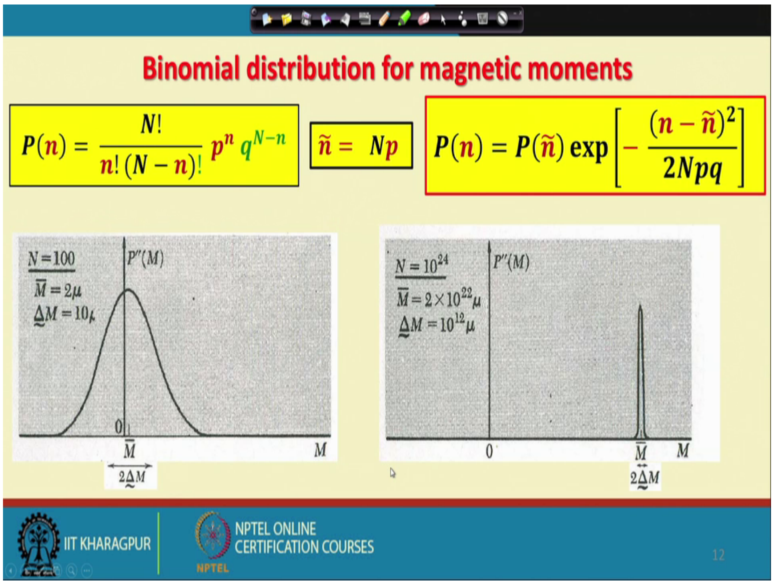

Now, what I have now here is that for n equal to 100 I saw that the values of capital M are equivalently small n, they were nearly a continuously changing.

Therefore the distribution function could be represented like this with a maximum around m bar, but if we change the number to 10 to the power of 24, that is typically what we have in a realistic system, then itself the average magnetic moment is going to be very large and this is located somewhere here. Then the main 2 differences that you see over here is that here you have a wide distribution, but here compared to the allowed values or all possible values of capital M you have only a very narrow distribution and the next question that I ask is, is it possible to find out what this m bar is and what the width of this distribution is.

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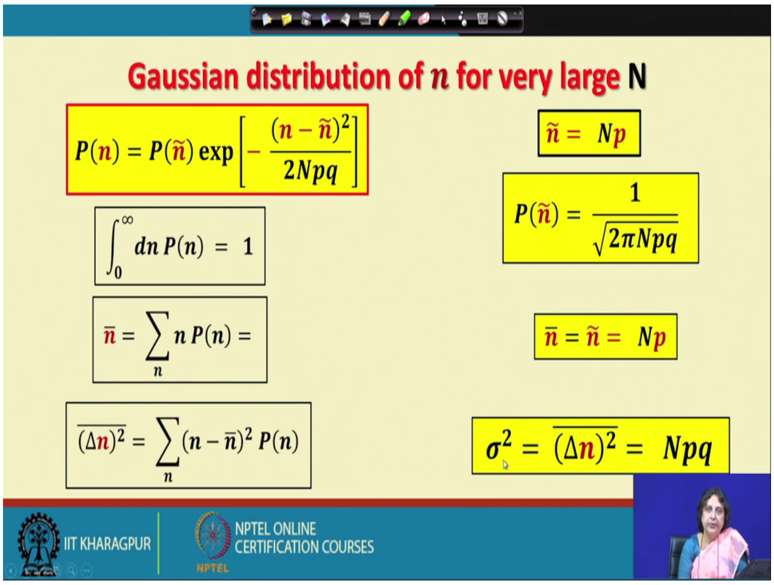

In order to do that, basically now I have this Gaussian distribution, which is given by this expression.

And I know that the maximum of this appears at n tilde equal to capital N into P. The next step is to demand that certain properties of the distribution we met, and that is the normalization property. Now if I want to know what is the condition of normalization. If you have a continuous variable then this is the condition of normalization, that if you sum over or integrate over all possible values of n you should get 1.

So, if I do it, if I repeat this exercise for this Gaussian distribution what I get is P of n tilde that is equal to 1 by root over of 2 pi capital N p and q. And also it is possible to find out quantities like the average value of n, and this average value of n can be shown to be equal to the value of n where the maximum of P n appeared and this is given by capital N into P. Similarly one can do a little bit of mathematics and find out the standard deviation in this particular system. If sigma is the root min square deviation then this is sigma square is the mean square deviation and it can be very easily shown that this is related to capital N p and q.

So, what is it that we have learned from here? We have learned from here the following fact.

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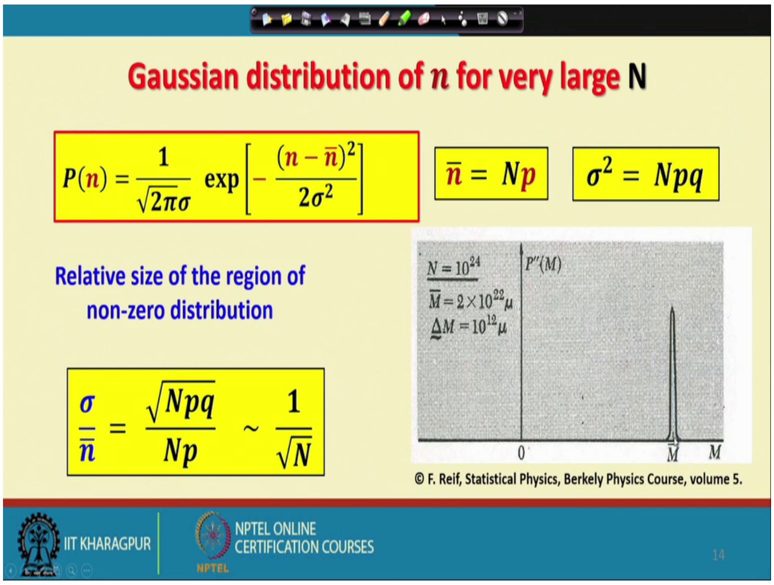

If I have a very large number of spin half particles, then the different microscopic states associated with small n up spins can be represented in terms of a distribution function which is Gaussian in nature, and this is the general form of the Gaussian distribution function. Now here I see that there are 2 parameters appearing, one is n bar and another is sigma. So, for the given system what do I think are n bar and sigma are? N bar and sigma are given by capital N into P and sigma square is given by capital N p and q. Now please try to understand if capital N is a very large number and small p is a fraction, n bar itself is still a very very large number now look at the possible values of sigma.

Now, sigma square is capital N into p into q. Now p q typically they are in the absence of the field equal to half, but sigma square is then dictated how big sigma square is it is been dictated by the value of n. So, once again this is a large number, but when we are talking about large numbers, you must realize that for capital N a big number the possible values of small n are also varying from a very big from 0 to a very big number capital N. So, the more relevant quantity that we should probably be talking about is the relative size of the region where the nonzero probability appears, and this is defined in terms of sigma divided by n bar.

So, if you look at the value of n bar and sigma is a dispersion of this distribution about n bar. So, if I compare these two the number that I am going to get, is going to be independent of how big either sigma is or n bar is for the given case, but we will let us know about the relative size where the distribution is nonzero, and in this case I find that this goes as 1 by root N. Now N is typically 10 to the power of 23 to 24, which means that the relative size is very very small and that explains why we have got this very sharp distribution where m bar that is the average magnetic moment, it falls off around has a distribution that picks at m bar and sharply falls off as we move away from m bar.

So, the basic idea that we would take away from this lecture is as follows; when I have a complex system comprised of many different particles, the simplest way we can approximate is it is I labelled them as distinguishable particles and I do not allow them to interact with each other. But even that this kind of a simplified system tells you that if you fix the total number of energy of the system; total amount of energy of the system you keep it in a constant volume and you have a very large number of particles, then the outcome of your measurement is a function of all possible values of energies that the system can take. And these different possible values of energies are associated with different number of particles. And if I look at the distribution for a very large number of particles, I find that for a given system you will see that there is some average value where the system is most probable.

In our next lecture, we will see how such considerations can be generalized for a system of simple harmonic oscillators, and from there we will take up the discussion of micro canonical ensemble.

Thank you.