Statistical Mechanics
Prof. Dipanjan Chakraborty
Department of Physical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture - 31
Canonical Ensemble Ideal Gas

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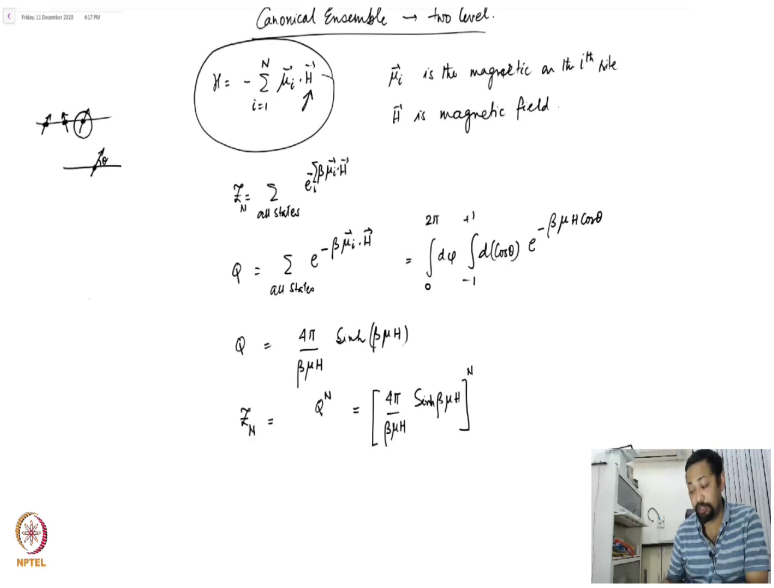

Welcome back, good; so we looked at the Canonical Ensemble and we looked at a two level system right. So, we want to look at some other models; application of canonical formalism to the model of paramagnetism right. And our model Hamiltonian is sum over minus; mu i; dot H; i is equal to 1 to N; where mu i is the magnetic moment on the ith site and H is the magnetic field which has been applied externally.

So, the thing is that I have this spin sitting on the lattice; except that they are no longer plus 1 minus 1, but they can rotate freely on this circle of radius given by the modulus of this. So, therefore, you see the configuration of this rotor or this spin with the angle theta is a one which essentially describes the microstate of the system. And the partition function is given by sum over all states; e to the power minus beta mu i; H dot H; sum over i.

The single particle partition function; this is where the N particle partition function is; the single particle partition function is sum over all states; e to the power minus beta mu i, dot H right and since it can rotate in a circle; so that we can write down as 0 to 2 pi minus 1 to plus 1; d of cosine theta; e to the power minus beta mu H, cos theta.

The integral is very easy to do. So, one recovers 4 pi by beta; mu H sin hyperbolic, beta mu H; if you do the integral right. The N particle partition function; Z of N is e to the power; sorry is Q to the power N which is equal to 4 pi; beta mu H, sin hyperbolic beta mu H and this is being raised to the power N. Note that here I have not used an N factorial in the denominator. Because I assume that the particles are distinguishable by their lattice points.

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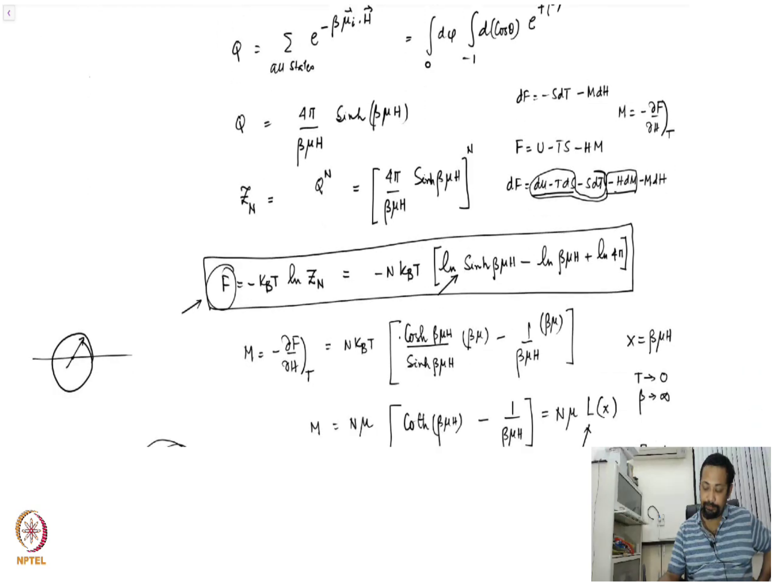

The free energy is minus k B T l n of Z N which in this case becomes minus N; k B T; l n sin; hyperbolic beta mu H minus l n beta mu H plus l n of 4 pi. It is not very significant for us it is because it is just a constant number. Good, but with the free energy F from the partition and particle partition function; we would like to proceed further, but there is a word of caution over here.

Now, if you identify this with the Helmholtz free energy; even though I have written notation F. If you identify this with the Helmholtz free energy, you will probably you will be in trouble. Because you see the thermodynamic when we did in thermodynamics; when we did the Helmholtz free energy that thermodynamic potential was defined in the presence of no mechanical work.

On the other hand, the Gibbs free energy was defined in the presence of a constant mechanical; for your, constant force constant conjugate force. And if you look at the Hamiltonian over here, you see that the magnetic field has already been applied over here. So there is a presence of a constant magnetic field.

So in fact, therefore, the legendary transformation that you are looking for is just not this, but H times M. So, d F is d u minus T d S; minus S d T minus H d M minus M d H; d u minus T d S; minus M d H is the first law; sorry not minus M d H, I beg your pardon it is minus H d M which forms the first law right. And therefore, this is 0; so what you are left out with this minus S d T minus M d H and it follows therefore, the magnetization is del F; del H temperature constant.

So, M is minus del F; del H temperature constant and this is the equation of state. So, let us see this is going to be N; k B T del del H of the first term which is this one is going to give you sin hyperbolic beta mu H; times cos hyperbolic beta mu H; times beta mu minus 1 over beta mu H; times beta mu. Once the beta mu come outside, you can immediately see that this is going to be N mu; this is cot hyperbolic; beta mu H minus 1 by beta mu H; so which we write down as N mu, L of x where x is equal to beta mu H.

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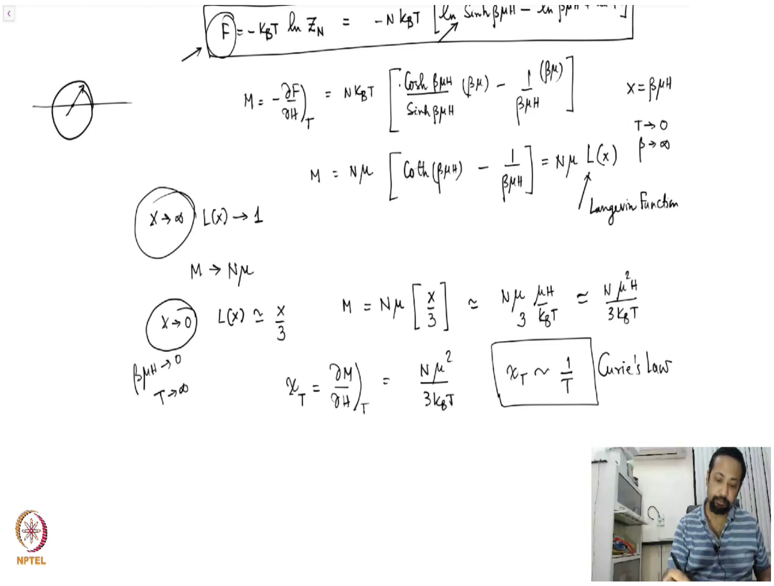

And this function is called the Langevin function. As x tends to infinity; L of x approaches unity and this tends to infinity means that the temperature tends to 0; so that beta tends to infinity. So, at very low temperatures; you find that the magnetization is equal to the magnetization tends to the limit N times mu. All of them are pointed along the same direction, there are not enough thermal fluctuation or thermal energy in the system to make them fluctuate right; the fluctuations are suppressed.

As x tends to 0; L x is approximately x over 3. So, therefore, M x; sorry magnetization is N times mu, one can just do it; x is mu H over 3 k B T right. So, that this is approximately N times mu square H times 3 k B T. And the susceptibility is del M, del H at constant temperature which is chi of T and which you get as N mu square over 3 k B T.

So, your susceptibility; x tends to 0 means beta mu H tends to 0 which means T tends to infinity which means you have a large temperature so that your fluctuations of are more. So, you can imagine that this rotation of this is more; as opposed to a low temperature and this goes as 1 by T; this is what is called Curie's law of paramagnetism. Now, what about the quantum mechanical analog of the same problem where I have the same Hamiltonian?

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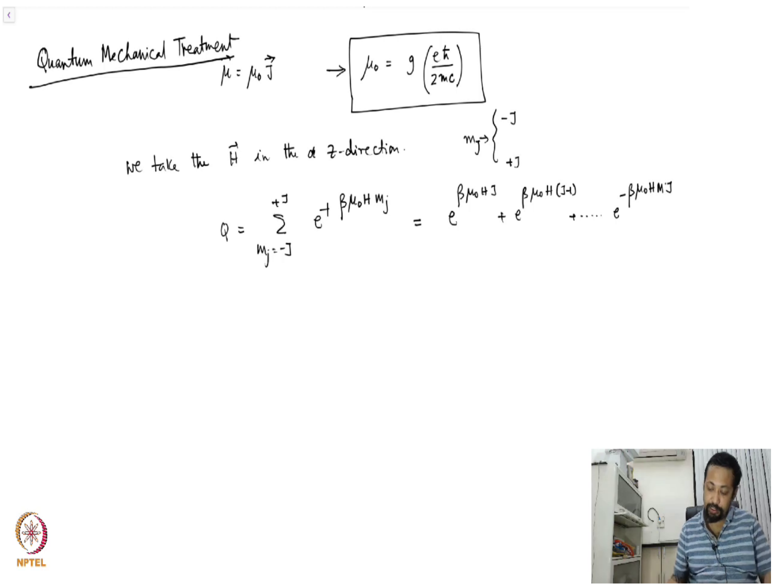

But there are several changes one has to realize that the magnetic moment. If J is a spin, then the magnetic moment is oops is mu naught times J where mu naught is given by is a product of two terms; one is the Lande g factor which is g and then it is e h bar by 2 m c right. So, this is where we are looking for the quantum mechanical treatment of the; at same problem.

So, J is the spin of the particle; therefore, this means that the magnetic moment of the particle is given by mu naught times J, where mu naught is this quantity. Without loss of generality, we take the magnetic field; we take H in the direction or let us say in the Z direction right. In this case, the Z component of the moment cannot be arbitrary and it has eigenvalues m j where m j now runs from minus J to plus J; this all of you could have done in quantum mechanics.

So, the single particle partition function is now sum over m j; minus J to plus J; e to the power minus beta mu naught H m j right; sorry e to plus and yeah this also has to be plus in the classical limit which is now one has to just write down the whole terms. So, it runs from beta mu naught H J plus beta mu naught H J minus 1 so on and so forth to e to the power minus beta mu naught H; M times J.

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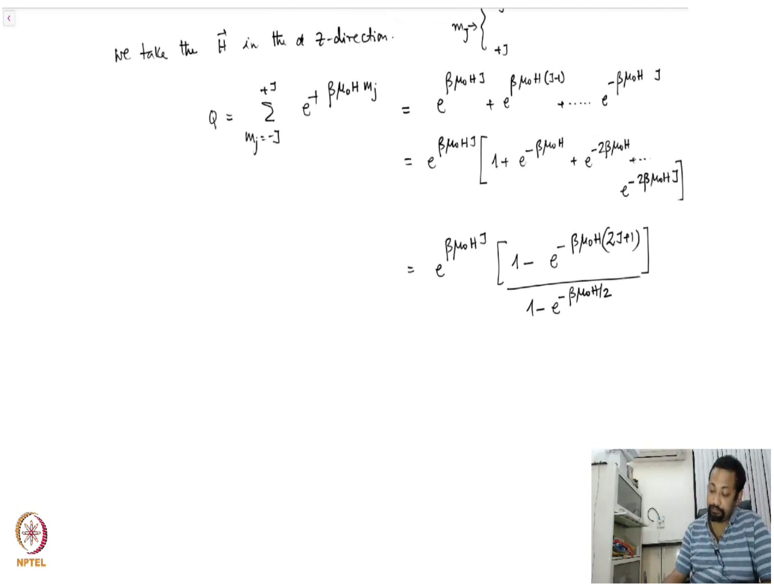

So, now we can take e to the power beta mu naught H; J common and the series is going to be minus beta mu naught H plus e to the power minus 2 beta mu naught H so on and so forth ending up to e to the power minus 2 beta mu naught H J. So, sorry there is not going to be an M here. This series can be very easily summed and you will have beta mu naught H J; 1 minus e to the power minus beta mu naught H; 2 J plus 1 divided by 1 minus beta mu naught H by 2 right.

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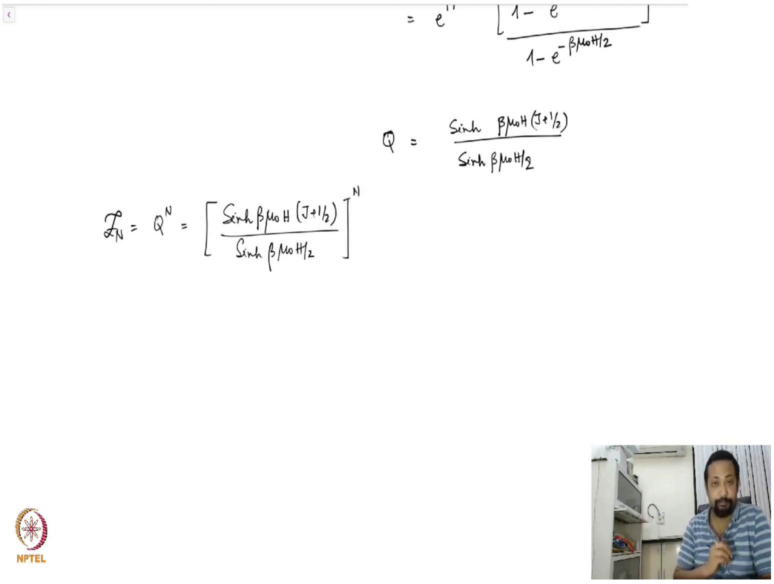

So, which becomes with a little bit more simplification; if you manipulate this, this becomes sin hyperbolic beta mu naught H times J plus half divided by sin hyperbolic beta mu naught H by 2, this is your single particle partition function. Once you have the single particle partition function, the N particle partition function is given by Q to the power N which becomes sin hyperbolic; beta mu naught H, J plus half divided by sin hyperbolic beta mu naught; H by 2, raised to the power N.

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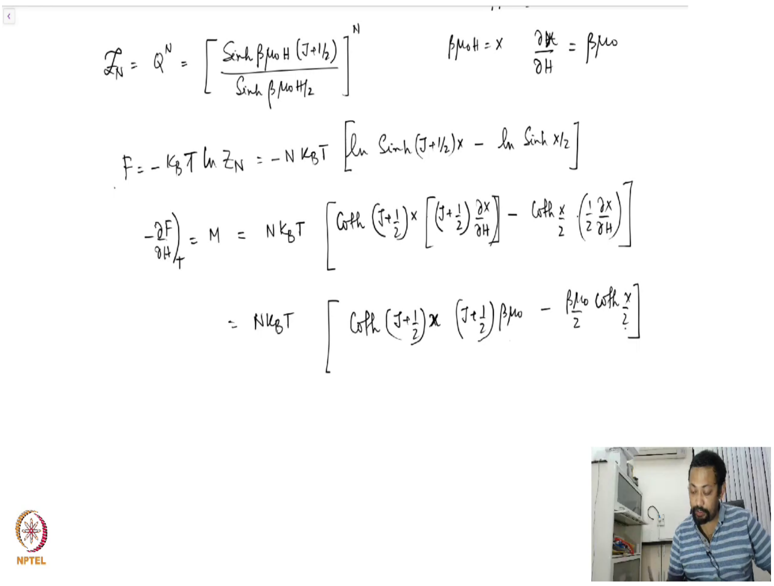

Free energy is minus k B T; l n of Z N which you have as N k B T minus; you will have l n of sin hyperbolic; we will call beta mu naught H as equal to X. So, that J plus half times X minus l n; sin hyperbolic X by 2. The equation of state which is del F; del H with a minus sign, temperature held constant is a magnetization M gives me N times k B T.

The first term is going to give me cot hyperbolic J plus half times X multiplied by J plus half times del X del H. The second term is going to give me cot X by 2 times half; del X; del H which is N; k B T cot hyperbolic; J plus half times x times; J plus half del X; sorry del X; del H is beta mu naught times beta mu naught minus beta mu naught by 2; cot hyperbolic X by 2.

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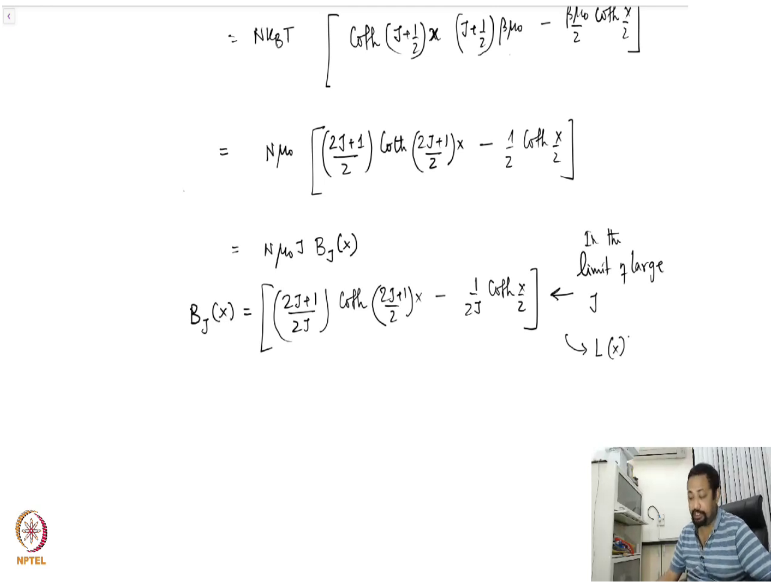

Good; let us simplify let us take the beta mu naught outside so that I have N times mu naught; J; 2 J plus 1 by 2 cot hyperbolic; 2 J plus 1 by 2 times X; minus 1 by 2; cot hyperbolic X by 2. So, this we define as N times mu naught times J times B J of X where your B J of X is 2 J plus 1 by 2 J; cot hyperbolic; 2 J plus 1 by 2 times X minus 1 over 2 J cot hyperbolic; X by 2 and this function is what is called the below function. If you take a large value of J in the limit of large J; in the limit of large J, this function will go to the Langevin function L of x which we have seen earlier.