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

Lecture - 30
Canonical Ensemble Paramagnet

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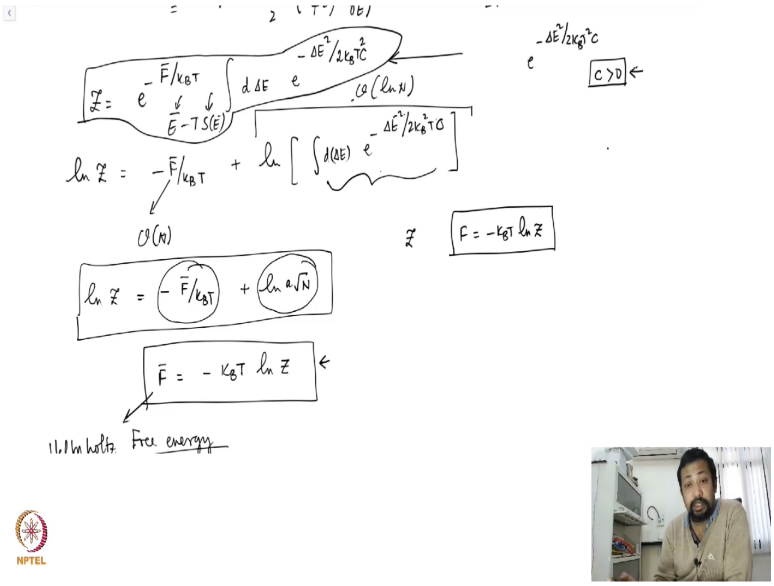

Right, so we were looking at the Canonical Ensemble and we derived the connection between thermodynamics and saying that, once you calculate the partition function Z; then the free energy, the Helmholtz free energy is given by minus K B T l n of Z. And once you know this relation, one can calculate all the other thermodynamic quantities.

There is one more thing that I want to highlight over here that one in the way of calculating the partition function; we had come to this expression that you see over here . What you notice is that, K B T square, this exponential factor has minus delta E square 2 K B T square over C.

Now, this necessarily means that, C must be a positive quantity. So, the specific heat is positive, because otherwise the fluctuations would diverge; because of it specific heat is negative, this becomes a plus and the fluctuations will diverge. So, the larger fluctuations are more probable.

So, thermodynamics also gives you this same conclusion that the response functions are positive; but it derives it from the stability of the thermodynamic potential. On the other hand, in statistical mechanics, we come to the same conclusion; but from the viewpoint of the fluctuations, right.

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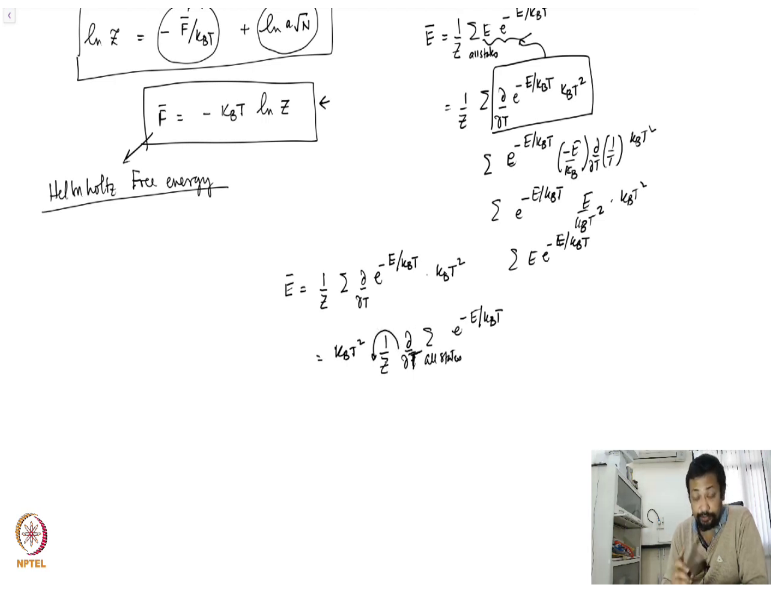

Now, F is minus K B T l n Z. So, let us write this as F bar, the average energy is sum over E 1 by Z E e to the power minus E over K B T, where the sum is again over all states. So, I note that within the sum, I can manipulate this part by writing del del T of e to the power minus E over K B T. And this is going to give me a 1 by K B T square, which we have seen in the earlier derivation.

So, I if I multiply this with K B T square; then the, this expression is identical to the one over here. If you are not convinced, you can easily expand this; we can write down this as, if I operate the derivative, it is e sorry e to the power minus E over K B T minus E over K B times del del T of 1 over T times K B T square, right.

So, this gives me sum over e to the power minus E over K B T E over K B T square, times K B T square and we recover the expression E e to the power minus E over K B T. So, therefore, the average energy is 1 over Z sum over del del T of e to the power minus E over K B T right, times K B T square.

So, I can bring the K B T square outside and I can write this as 1 over Z del del T of sum over all states e to the power minus E over K B T. Please do not sorry, del del capital T; do not take the derivative over here, because Z is also a function of T, then that is the wrong calculation you are doing.

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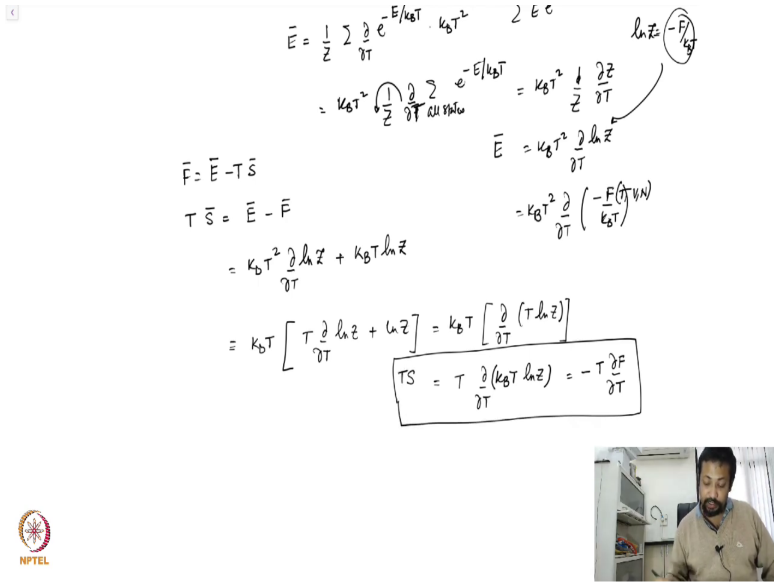

So, K B T square 1 over Z this is del Z del T, which is K B T square del del T of l n Z, right good. But l n Z is minus F over K B T. So, one can replace this over here and take this further; which means I can write down this as K B T square del del T of minus F over K B T. But I have to be careful that, this there will be two terms; because F is also a function of T, it is a function of T, V and N and in the denominator there is a 1 by T sitting, good.

The entropy is E bar minus T S bar. So, the entropy is F, sorry E bar minus F bar T S bar. Let us see K B T square del del T of l n of Z, that is my expression for E bar minus this becomes a plus K B T l n of z. So, this I can write down del del T sorry, of T l n Z; I can put a K B over here and then.

So, now, I can take K B T common; if I take K B T common, the first term is del del T of l n z plus l n z, which is K B T del del T of t l n Z K. So, as furthermore simplification happens;

if I just put T del del T of K B T l n Z, which is minus T del F del T, that is your entropy right, T times S. Therefore, S is minus del F del T, right.

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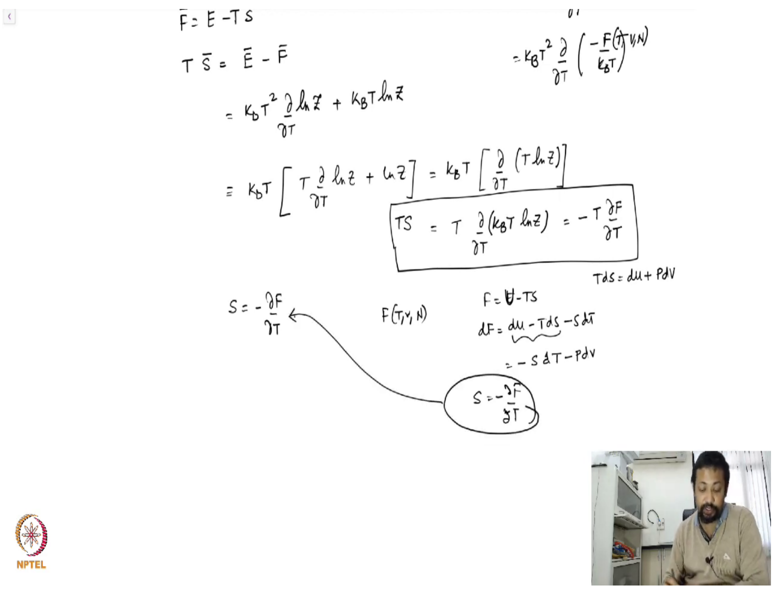

Recall, when we did thermodynamics, we had written F as a function of T, V and N, which is E minus T S. Well in thermodynamics it was U minus T S, so that d F was d u minus T d S minus S d T, right. And T d S, d u minus T d S; so our T d S was for a hydrostatic system, let us worry about the hydrostatic system for the time being was plus P d V.

So, the d u minus T d S is minus P d V. So, I can replace this as minus S d T minus P d V and therefore, you immediately see that, S is minus del F del T. So, we are all going in the right direction, good.

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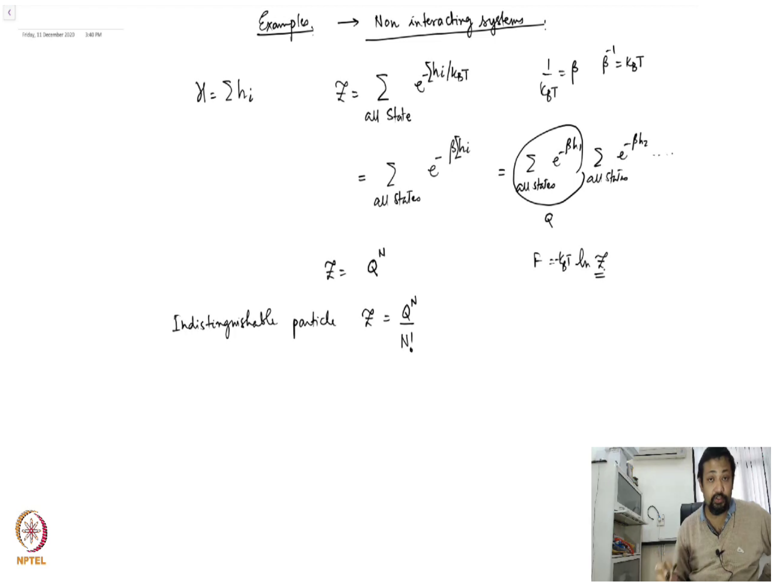

Now, let us look at examples of how to handle canonical ensemble. So, first thing that we will be worried about is throughout this, we are only going to be worried about non interacting systems, right. Now, when you have a non-interacting system; then the Hamiltonian can be written down in terms of single particle Hamiltonians, right. So, that the partition function, the single particle partition function. So, well let us see, the partition function, the total for the whole system is all states e to the power minus h i over K B T, right.

Now, introduce K 1 by K B T as beta. So, that beta inverse is therefore, K B T; which means this one all states e to the power minus beta h i, sum over h i sorry, this has to be sum over h i. But the sum now breaks into products; so all states for particle 1, all states for particle 2 so on and so forth. But each of this is what is called a single particle partition function Q. So, your total partition function is Q to the power N, right.

If the particles are indistinguishable, so for indistinguishable particle; Z is Q to the power N over N factorial. Once again one has to realize that for discrete systems, the free energy is l n of Z, sorry not for not only for the discrete system for all the system my free energy is K minus K B T l n Z. So, the Z has to be a dimensionless quantity and we know how to do it for a ideal, for systems where my state can take continuous values, good.

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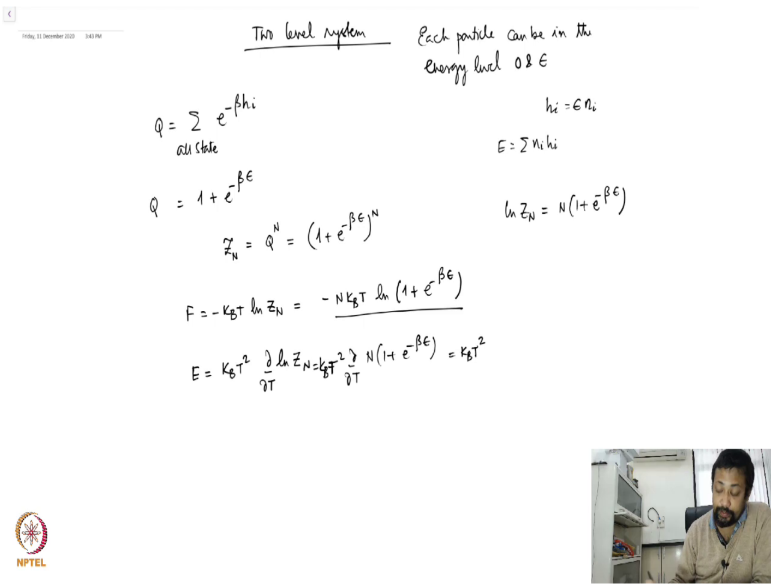

So, we take the example of a two level system that we had done in the micro canonical ensemble. Here each particle can be in the energy level 0 and epsilon. So, what is the first? They are noninteracting, whether if particle one is in count in energy level 0; particle 2, particle 3 can also be there, because there is no interaction between 0 and 1 and 2, they are independent of each other in whatever level they are.

So, my single particle partition function is sum over all states e to the power minus beta h i, and h i is individual particles is epsilon times n i. If you recall the total energy E was sum over n i times h i, right. So, this means that, the single particle partition function can be either 1 for corresponding to when the particle is in the ground state with energy 0 or minus beta epsilon.

Therefore, the N particle partition function will now introduce a subscript N to indicate that this is an N particle partition function. This is Q to the power N over N factorial if they are indistinguishable; if they are distinguishable, then this N factorial does not come in. So, that we have 1 plus e to the power minus beta epsa raised to the power N.

The Helmholtz free energy is minus K B T l n of Z N, which is minus N K B T l n 1 plus e to the power minus beta epsa. F is an extensive quantity, which is evident from the right hand side, correct. The energy is going to be K B T square del del T of l n Z and l n Z is N times 1 plus e to the power minus beta epsa.

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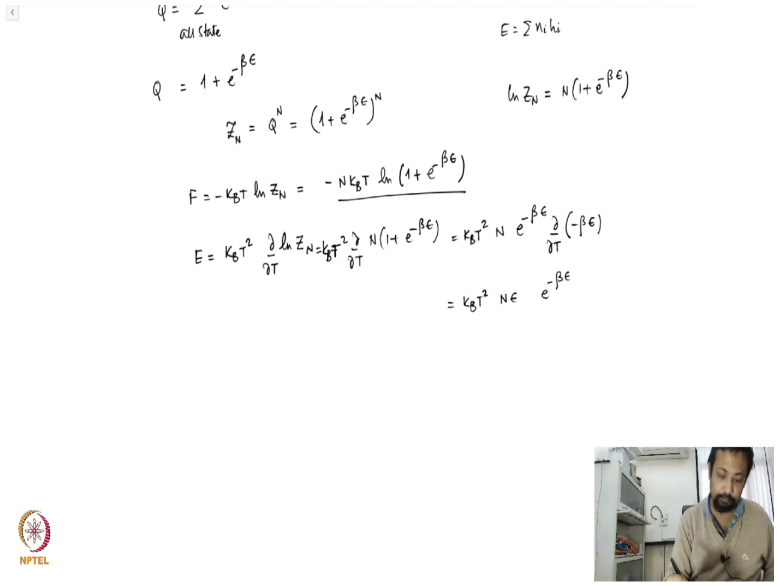

So, this is del del T of N 1 plus e to the power minus beta epsa times K B T square, K B T square; is N del del t is going to give me e to the power minus beta epsa times delta T of minus beta epsa. So, this is K B T square N epsilon e to the power minus beta epsa; this is not right.

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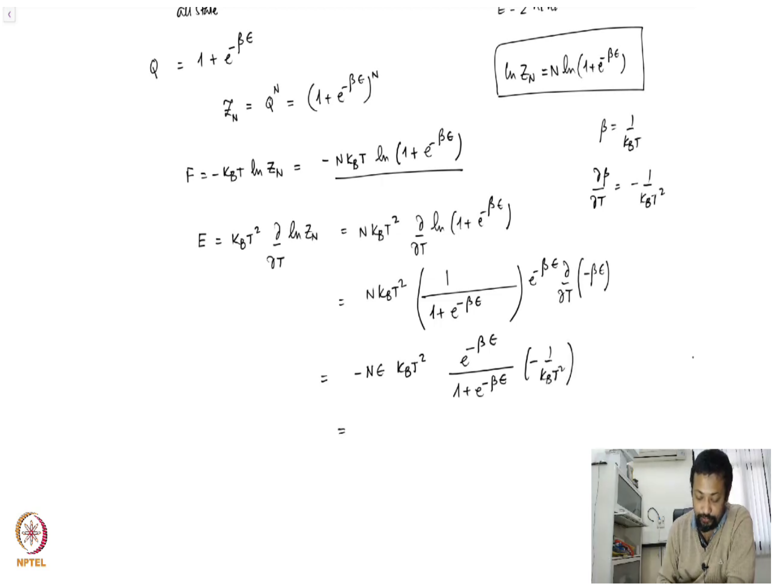

So, we now want to calculate the energy. Now, the energy we did derive the expression it is K B T square del del T of l n of Z. And l n of Z N is n sorry; this is not the right expression l n of Z N is N l n 1 plus e to the power minus beta epsa. So, this becomes N K B T square del del T of l n 1 plus e to the power minus beta epsa, which is N K B T square, 1 plus e to the power minus beta epsa times e to the power minus beta epsa times del del T of minus beta epsa.

So, that this becomes minus N epsilon K B T square e to the power minus beta epsa 1 plus e to the power minus beta epsa, correct good. Then it is a derivative of del del beta, beta is 1 over K B T; del beta del T is minus 1 over K B T square. So, I can replace this quantity, this derivative by minus 1 over K B T square.

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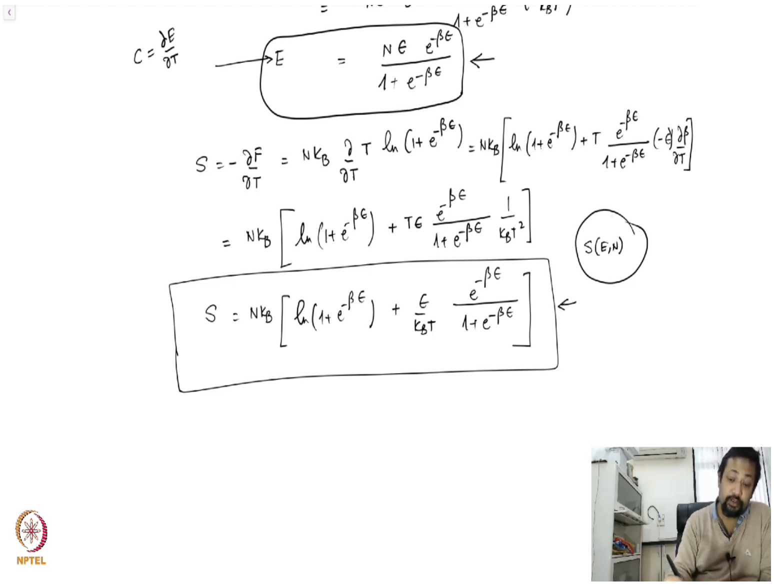

So, that my average energy E has a very nice and elegant form, which is N epsilon e to the power minus beta epsilon 1 plus e to the power minus beta epsilon. If you recall, this is exactly the form that we got, when we did when we treated this problem using the micro canonical approach, right.

S, I want to now calculate the entropy S is minus del F del T. And I just now did the Helmholtz free energy which is n K B del del T of T l n 1 plus e to the power minus beta epsa. Note that, if I have the energy; I can also calculate the specific heat by using del E del T right, this I leave it to you as an exercise.

But this is also just simple calculus, it is going to be l n 1 plus e to the power minus beta epsa plus T 1 plus e to the power minus beta epsa e to the power minus beta epsa minus epsilon. And then I will have del beta del T, which is going to be N K B l n of 1 plus e to the power minus beta epsilon plus T e to the power epsilon beta epsilon 1 plus e to the power minus beta epsilon 1 by K B T square.

The minus epsilon from here and del beta del T will also carry a one this will cancel out. So, that this becomes N K B l n 1 plus e to the power minus beta epsilon plus epsilon over K B T e to the power minus beta epsilon 1 plus e to the power minus beta epsilon, and this is the expression for the entropy.

One can of course ask that, look I want S as a function of E and N; that itself is going to be a complicated procedure, because here then you have to fig, from this expression that you see over here and from this expression you have to eliminate the temperature to write down S as a function of E and N. It is still a dribble and then finally, you arrive at the fundamental relation that, we that is very sought after N.