Statistical Mechanics
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Lecture - 37
MicroCanonical to Canonical – Part II

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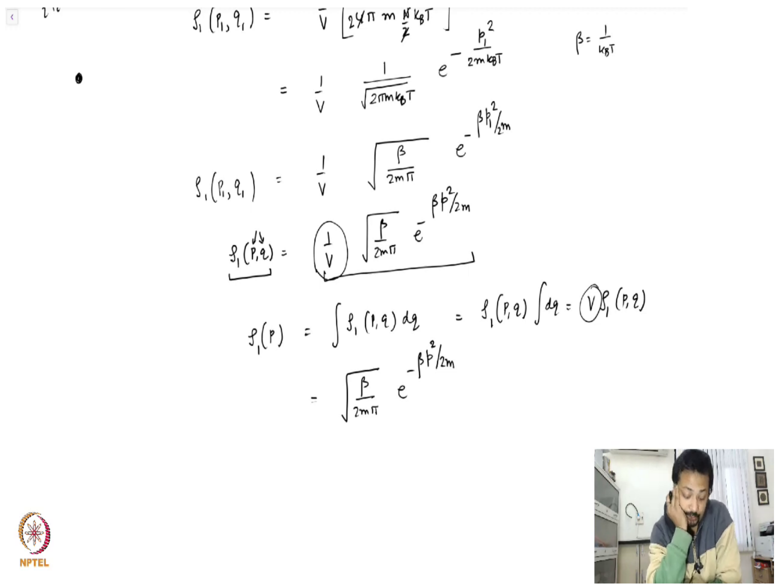

Welcome back. So, we saw how the ideal gas result I mean one can go from the Micro Canonical to the Canonical.

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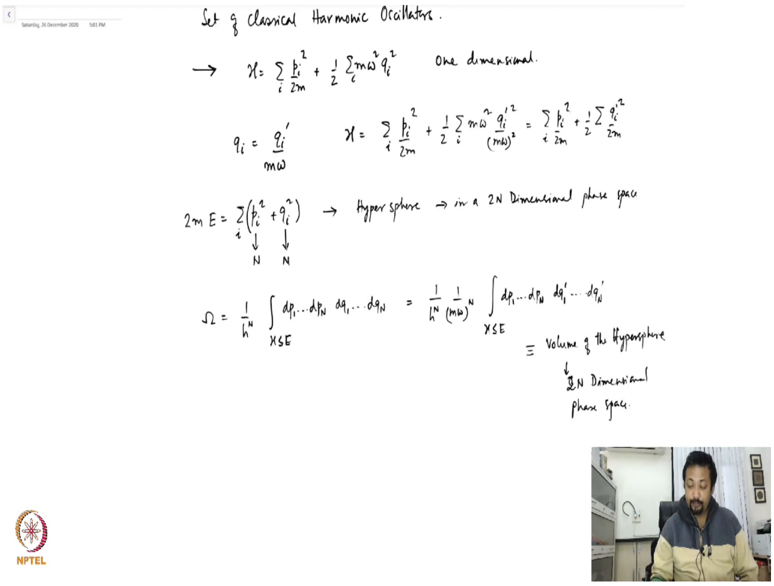

Now, we want to take another example and that is of a set of classical Harmonic Oscillators. The Hamiltonian of the system was pi square over twice m plus half sum over m omega square qi square. This is a one dimensional case; the generalization to higher dimensions is very trivial to do.

So, that when we did this in the micro canonical ensemble, we essentially made a change of variable where we had written that q y is q y prime divided by m omega so, that the Hamiltonian is i. So, in this transform variable the Hamiltonian is pi square over twice m plus half of sum over i m omega square qi prime square over m omega whole square, and that gives me sum over i pi square over twice m plus half sum over qi prime square over twice m.

So, the hyper surface so essentially, the hyper surface is given by twice m E is sum over i pi square plus qi square and you are looking at a hyper sphere just as we had for an ideal gas except that this is in a 6th sorry this is N dimensional so, you are looking at a 2N dimensional phase space. So, please be careful in keeping count of the dimension of the phase space because, I have started with one dimensional I come up with 2 N dimensional.

N coordinate and N sorry N momenta and N coordinate. The total number of microstates we calculated was h to the power N integral h of E less than equal to E dp 1 to dp N dq 1 to dq, N which in using the transform variable becomes 1 over m omega raised to the power N h less than equal to E dp 1 to dp N and then I have dq 1 prime to dq N prime, and this is equivalent to the volume of the hyper sphere in 2 N dimensional phase space.

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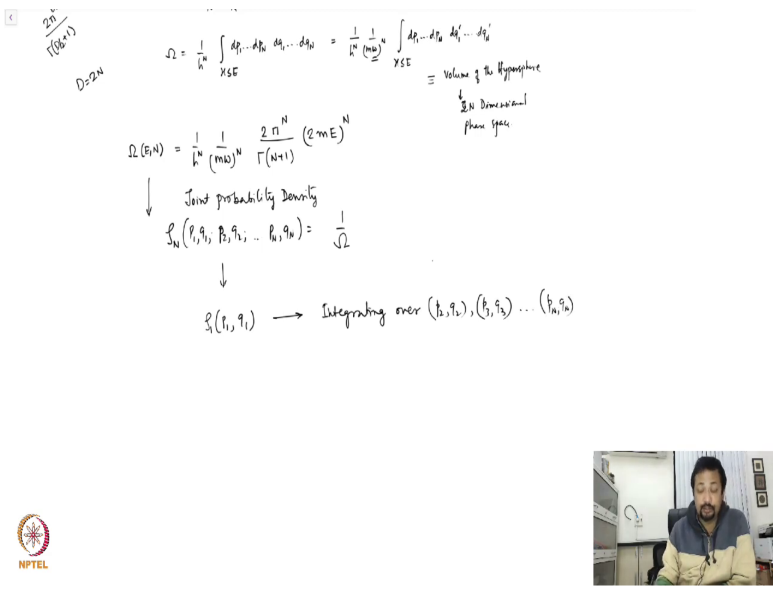

Now, I know what this volume is please note that there is no N factorial here, because these particles are distinguishable by their position. The mean position 1 over m omega raised to the power N 2 pi to the power N divided by gamma N plus 1, remember that the general result for a volume of a hyper sphere in D dimension was 2 pi D by 2 divided by gamma D by 2 plus 1 raised to the power R to the power D by 2; and in this case D is equal to 2N I have twice m E raised to the power N.

So, starting from this expression, I can define the N probe N particle joint probability density rho N of p 1, q 1, p 2, q 2, p N q N as 1 over omega. So, this is the joint probability density and our interest lies in the single particle probability density rho 1, p 1, q 1 for one particle to be in a microstate defined by p 1 q 1 and this we do by integrating over p 2, q 2, p 3, q 3, p N q N, the other decrease of freedom.

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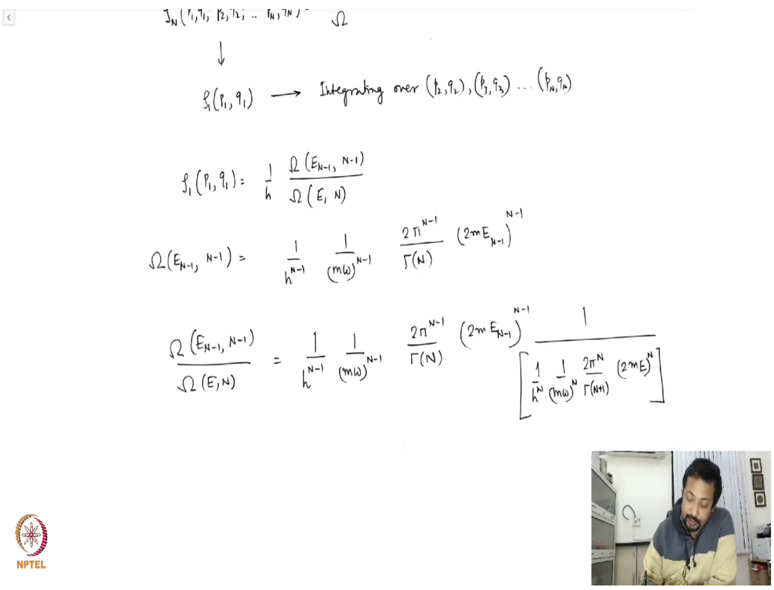

The answer we already know, we have done it in the last lecture and I have rho 1 of in terms of the number of microstates, the single particle partition probability density is given by 1 over h omega of E N minus 1 N minus 1 divided by omega of E comma N.

So, using this expression for the total number of microstates for N particles with energy E I can write down omega of E N minus 1 N minus 1 is going to be 1 over h to the power N minus 1, 1 over m omega raised to the power N minus 1 twice by raised to the power N minus 1 divided by gamma of N and I have twice m E not.

So, it has to be E of N minus 1 times raised to the power N minus 1. So, the two ratios then becomes N minus 1 N minus 1 divided by omega of E comma N is 1 over h to the power N minus 1 1 over m omega raised to the power N minus 1 2 pi to the power N minus 1 divided by gamma of N.

And I have twice m E N minus 1 raised to the power N minus 1 1 over now, we write down the expression for omega E N and that is going to be 1 over h to the power N 1 over m omega raise to the power 2 pi to the power N gamma of N plus 1 and I have twice m E raised to the power N.

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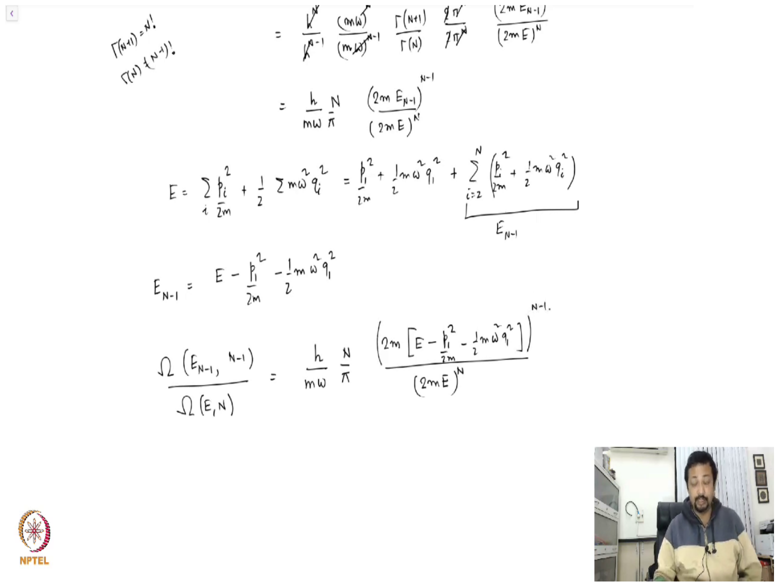

Let us collect the terms p factors and then we will write down EN minus 1 is so, this is going to be h to the power N h to the power N minus 1 m omega raised to the power N m omega raised to the power N minus 1 gamma of N plus 1 gamma of N. Then, I have 2 pi raised to the power N minus 1 divided by 2 pi raised to the power N I have twice m E N minus 1 raised to the power N minus 1 divided by twice m E raised to the power N.

A lot of cancellations follow and I have h then this gives me over m omega this cancels this N cancels, I have 2, 2 canceling out pi to the power N cancels with pi to the power N, I will be left out with 1 over pi gamma of N plus 1 gamma of N plus 1 is N factorial gamma of N is N minus 1 factorial. So, that I have N coming in the denominator and then I have twice m E N minus 1 raised to the power N minus 1 twice m E raised to the power N.

Now, if you look at the conservation of energy, then the total energy E is going to be sum over i pi square over twice m plus half m omega square iq sorry omega square qi square. And this I can split as the energy of the first particle which is p 1 square over twice m plus half m omega square q 1 square plus sum over i is equal to 2 to N pi square over twice m plus half m omega square qi square and this is the part which I identify as the energy of my N minus 1 oscillators.

So, that this becomes E of N minus 1. As we had done in the free particle case, so, E of N minus 1 is then E minus p 1 square over twice m minus half m omega square q 1 square. Therefore, the ratio omega of E N minus 1 N minus 1 omega of E comma N is going to be h over m omega N by pi, I am going to have twice m E minus p 1 square over twice m minus half m omega square q 1 square divided by twice m E raised to the power N and this one raised to the power N minus 1.

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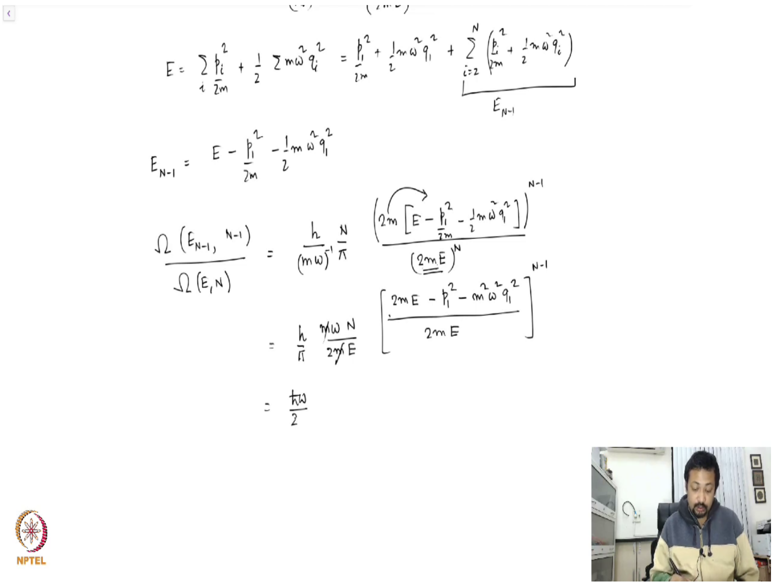

Once again let us rewrite this by taking one factor of 2 m E outside this bracket in the denominator so, this gives me h over m omega is this correct?

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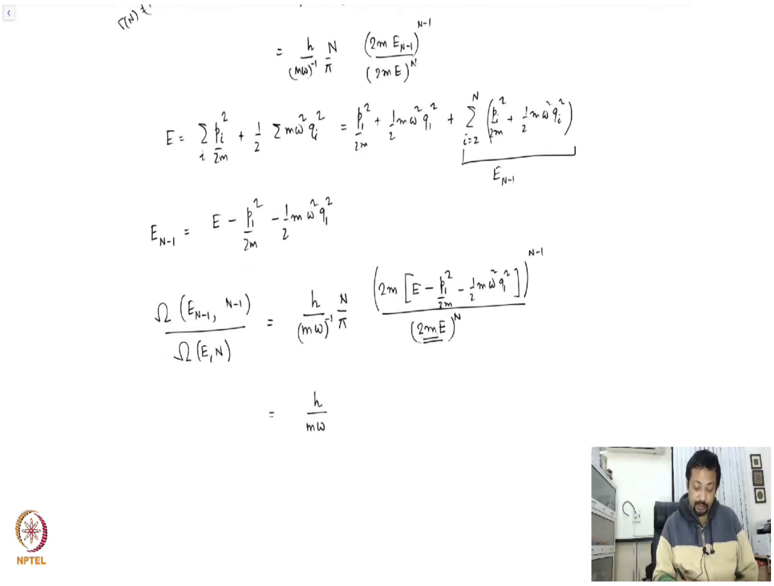

Let us just see yeah. So, this is not right because, this is going to be m omega inverse so, this is m omega inverse this is a mistake that I made and I have m omega inverse, which essentially means that I have h by pi m omega times N divided by twice m E. And I have if I take the twice m inside the bracket, then essentially I have twice m E minus p 1 square minus m square omega square q 1 square divided by twice m E raised to the power N minus 1. A little simplification then gives me mm cancels out h bar omega over.

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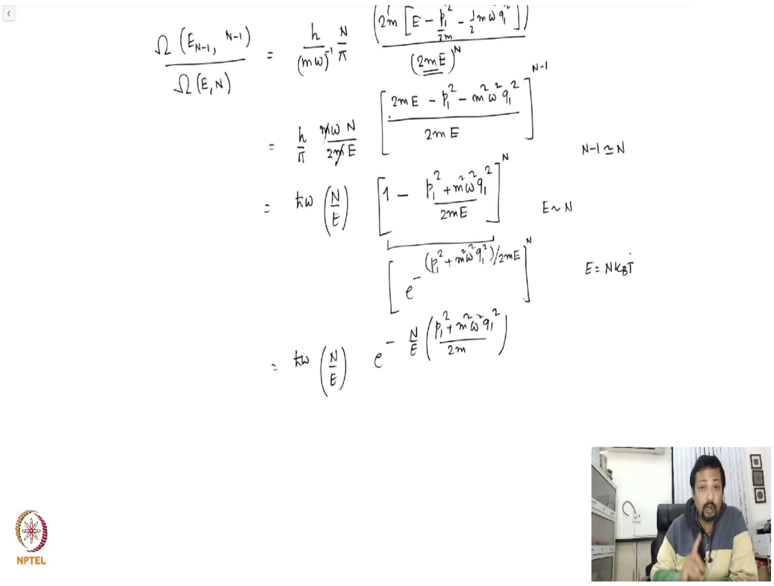

So, I have the 2 pi takes care of h bar omega I have h bar omega N over E and this one I can simplify 1 minus p 1 square plus m omega square q 1 square divided by twice m E raised to the power N here, I have again use the approximation N minus 1 is going to be N..

Now, once again you see the argument is that E is an extensive quantity, therefore the E energy scales with N and I can approximate this bracketed expression as e to the power minus p 1 square plus m omega square m square omega square I miss the m square in the above expression q 1 square divided by twice m E.

And this is being raised to the power N. So, that this is h bar omega N by E I have e to the power minus N by E times p 1 square m square omega square q 1 square divided by twice m. Now, for a set of N oscillators I know that E is equal to N K B T in one dimension.

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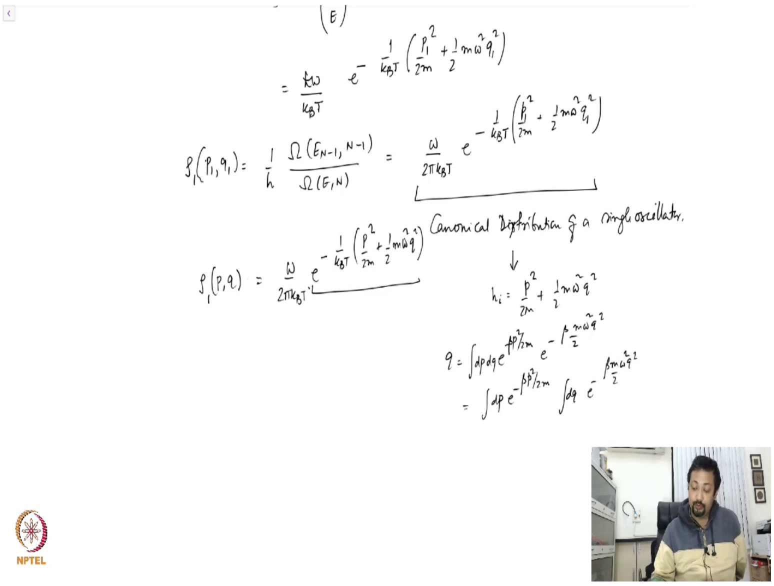

So, if I now substitute this result, I have h bar omega N by E is 1 by K B T, K B T and then I have e to the power minus 1 over K B T p 1 square over twice m plus half m omega square q 1 square. So, that if you recall rho of p 1 q 1 was 1 over h omega of E N minus 1 m minus divided by omega of E comma N the ratio of these two quantities. And this becomes, omega over 2 pi K B T e to the power minus 1 over K B T p 1 square over twice m plus half m omega square q 1 square.

So, this is exactly the canonical distribution of a single oscillator, we have done this in the class and we are also invited to check this. So, essentially since I can choose any arbitrary oscillator I mean I can choose the second oscillator third oscillator. So, p 1 q 1 does not make any sense I can replace this by writing rho 1 of p q.

The single particle density as omega over twice by K B T e to the power minus 1 over K B T p 1 square over twice m plus half a sorry not no longer identified by the index plus half m omega square q square. You can check the normalization of this so, a very briefly if for a single particle the Hamiltonian is given by p 1 p square over twice m plus half m omega square q square.

And the canonical partition function is Z single particle partition function is q is going to be dp dq e to the power minus p square over 2m e to the power minus beta, beta m omega square q square by 2. Both these integrals separate out and you have dp beta p square over twice m dq minus beta m omega square q square over 2.

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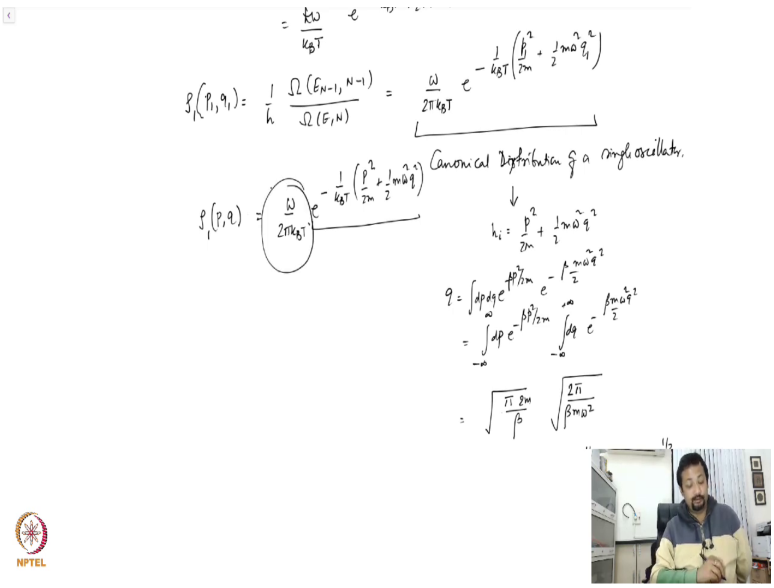

Their Gaussian integrals ranges running from minus infinity to plus infinity minus infinity to plus infinity. The first answer is square root of i 2 m over beta and the second answer is pi beta m omega square times 2. So, that if you take everything common simplify this 2 m pi by beta into 2 pi over beta m omega square, mass, mass cancels out and this is raised to the power half.

We are going to have 2 pi over beta square omega square 2 pi whole square and this is being raised to the power half; and the single particle partition function becomes twice pi over beta omega. So, this is exactly the factor that you have, beta omega over twice pi which is also the inverse of the normalization.

So now, in both the cases that we have looked at so far essentially our microstates were continuous lessons they are now discrete in microstates; and we would now want to take a look at the system where my microstates are decreased where my microstates are discrete.

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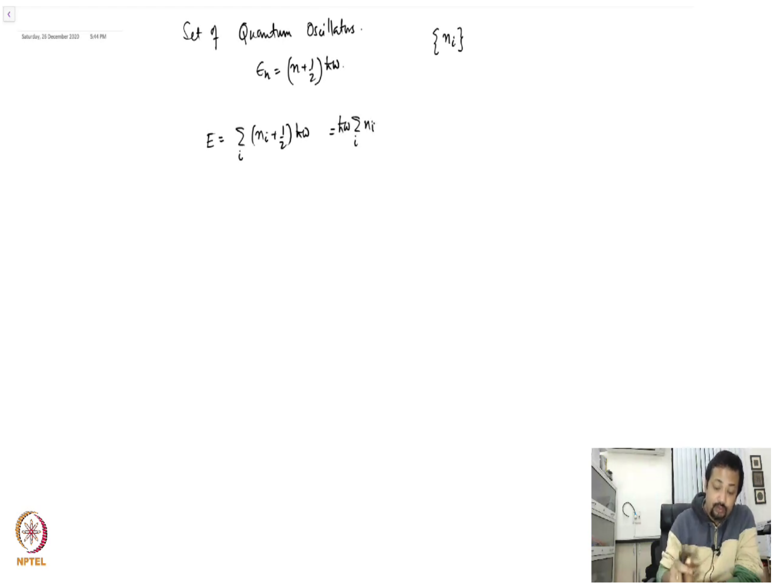

And that essentially corresponds to a set of quantum oscillators. And here you have the energy Eigen values, which are n plus half discrete n plus half h bar omega and when we did look at this system using the macro canonical approach we said that the microstates are defined by the occupation numbers n i right. So, the total energy was given by sum over i n i plus half h bar omega, which is sum over i h bar omega times n i.

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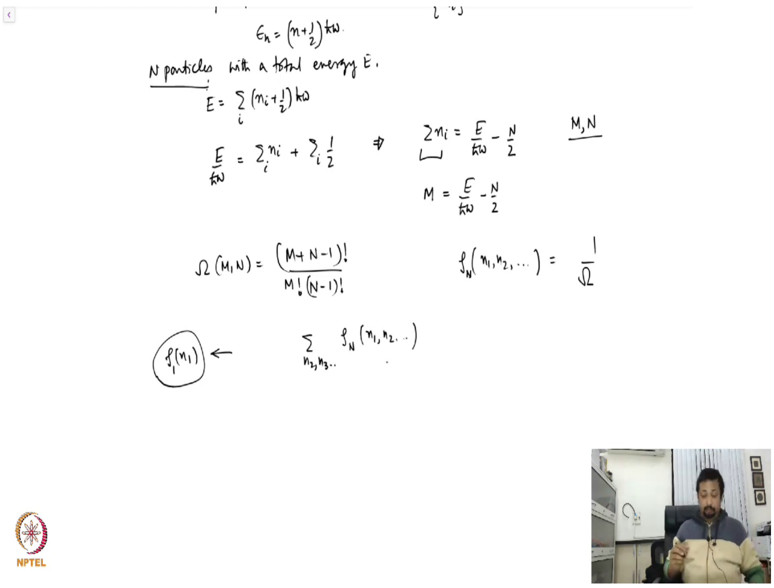

So, we can recast this by writing E over h bar omega was sum over n i i plus sum over i half and this implied that sum over n i was E over h bar omega minus N by 2. And this sum we call it as M and this is what we had the expression. So, N particles there were N quantum oscillators with a energy with the total energy E.

And this means, that you have the set of numbers integers M and N that we are looking at and we said look this essentially translates to n minus to m balls or m particles and n boxes. How many possible ways of putting that so, n boxes means n minus 1 partitions. Therefore, the total number of objects possible was m plus n minus 1 because the two of them are fixed at the ends. So, the total microstates that we obtained was M plus N minus 1 these are all possible permutations that have been considered combinations.

And therefore, the double counting comes if you replay if you change interchange the particles nothing changes and if you interchange the partitions nothing changes we had M factorial N minus 1 factorial. Now, the idea is I want to determine the single particle density. So, we had rho of n 1 n 2 was 1 over omega, now from this I want to find out rho of n 1.

And it is the same procedure where we have to sum in order to get this single particle so; we will call it rho 1 as before and rho 1 as this. In order to get this quantity I have to sum over n 2 n 3 rho N of n 1 n 2 right. You will come up with the same expression that we have that we had before except these are discrete microstates so, we do not need the h factor.

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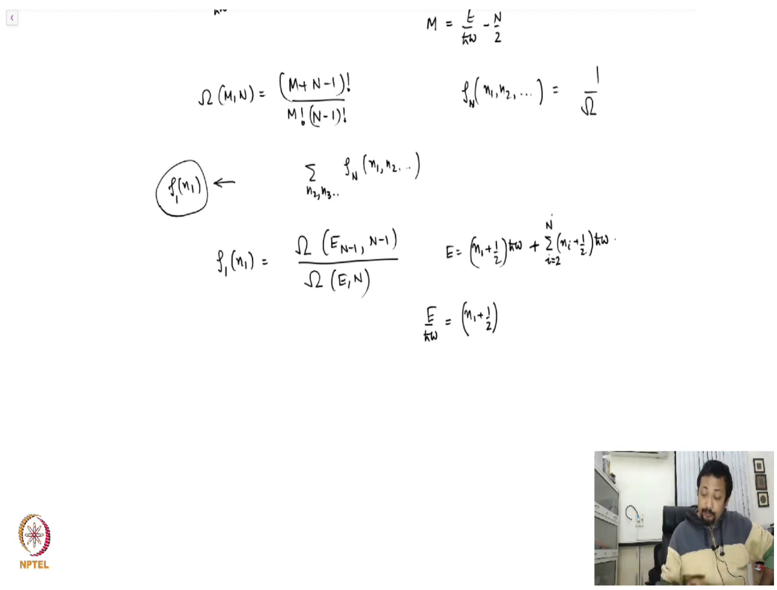

So, essentially rho 1 of n 1 was going to be omega of E minus so, we will write down E N minus 1 with N minus 1 particle divided by E comma N. The h factor is not there right because, here that microstates are discrete so, there any case dimensionless number. Now, if I have n minus 1 particles that means, E is going to be N 1 plus half h bar omega minus sum over i n i plus half sorry plus n i plus half h bar omega. So, that E over h bar omega is going to be n 1 plus half and this sum runs from i equal to 2 to N.

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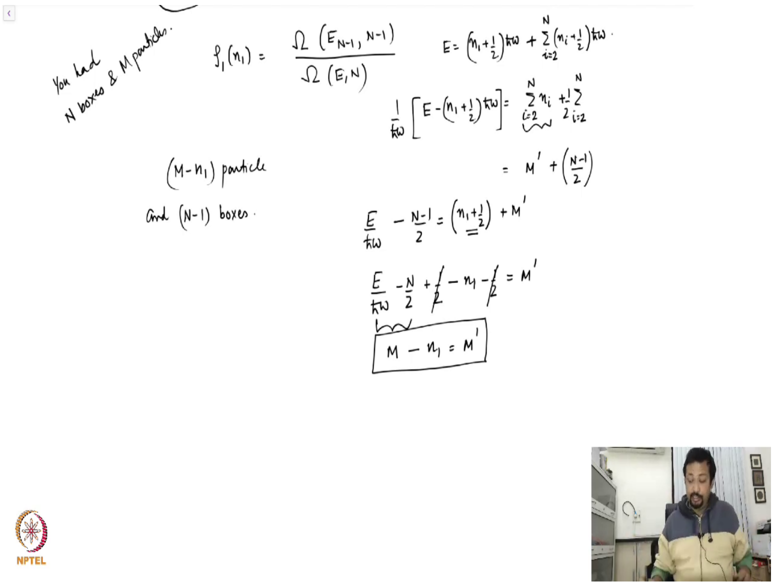

So, let us see instead of writing E divided by h bar omega I have E minus n 1 plus half h bar omega is sum over and then I have 1 over h bar omega is sum over n i plus sum over i equal to 2 to N half of that. And this sum is now 2 to N. So, let us call this sum as M prime plus N minus 1 divided by 2 then, I have E over h bar omega minus N minus 1 by 2 is going to be n 1 plus half plus M prime.

So, we somehow have to relate this with M. If I take look at the left hand side and I have N minus 2 plus half and this one is minus N 1 minus half is going to be your M prime right. Then, you see the half half cancels out and this is already you have defined it as M. So, that you have M minus n 1 as M prime.

So, now what does this mean that if you have I picked up one particular oscillator, then essentially you are left out with M minus n 1 particles and N minus 1 boxes, originally when you were considering n particles you had N boxes and M particles. Now, if you pick up the n 1 oscillator this occupation number and you want to know the probability density p rho 1 of n 1 then essentially looking at m minus n 1 particle and N 1 boxes.

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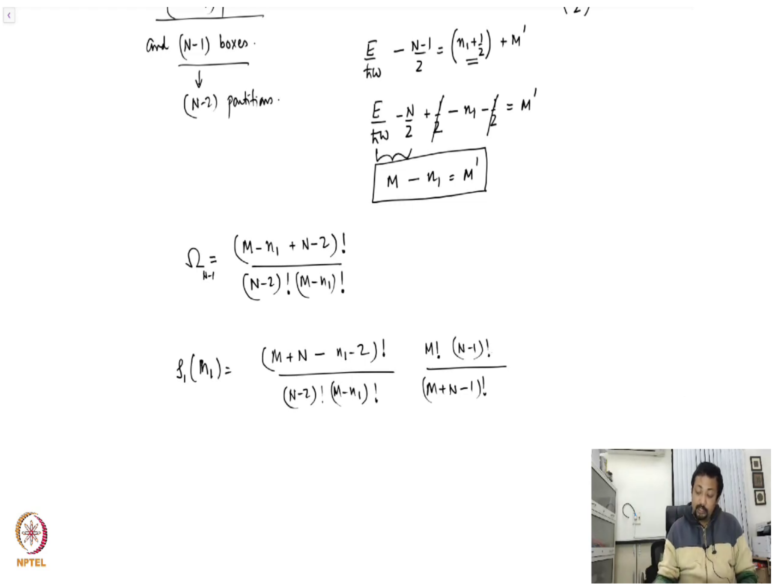

So, that you have essentially N minus 2 partitions. So, therefore, you have M minus N 1 the total number of objects is N minus 2 factorial divided by N minus 2 factorial and then you have M minus N 1 factorial. So, that this is omega N minus 1 in shorthand notation and therefore, rho 1 of n 1 is going to be M minus so, let us just write it down here M plus N minus n 1 minus 2 factorial divided by N minus 2 factorial M minus n 1 factorial.

And then we had the original which was M plus N minus 1 factorial and we had M factorial N minus 1 factorial.

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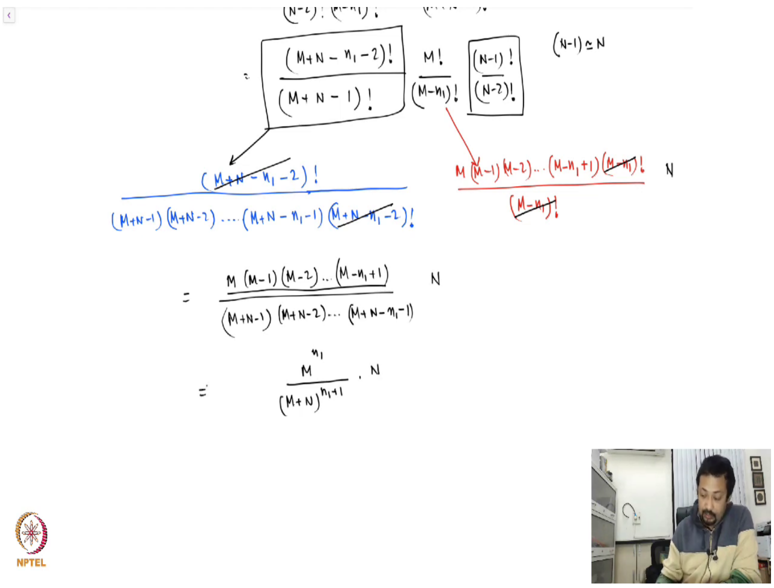

Now, let us group the terms together so, that it is easier to see what we are going to get M plus N minus n 1 minus 2 factorial divided by M plus N minus 1 factorial and then, I have M factorial M minus N 1 factorial and then I have N 1 factorial N minus 2 factorial. The most trivial of this is the last term, which is going to be N minus 1 and is going to be approximate it by N.

Let us look at this, let us look at the denominator first I have M plus N minus 1 M plus N minus 2 all the way up to M plus N minus n 1 minus 1; and then I have M plus N minus n 1 minus 2 factorial. The numerator is M plus N minus n 1 minus 2 factorial, this term is M M minus 1 M minus 2 all the way up to M minus n 1 plus 1 and then I have M minus n 1 factorial divided by M minus n 1 factorial and of course, I have the last term which is N.

A simplification would mean that this and this cancels out and this and this cancels out. So, that I have M M minus 1 M minus 2 M minus n 1 plus 1 divided by M plus N minus 1 M plus N minus 2 and all the way we are going to M plus N minus n 1 plus sorry n 1 minus 1. So, you are almost there, you have to just hold on a little bit more and then I have N.

Now, clearly in the thermodynamic limit what I can do over here is I can there n 1 such terms so, that this is going to be M to the power n 1 and this is going to be M plus N, there are n plus 1 such terms is going to be n plus 1 times N.

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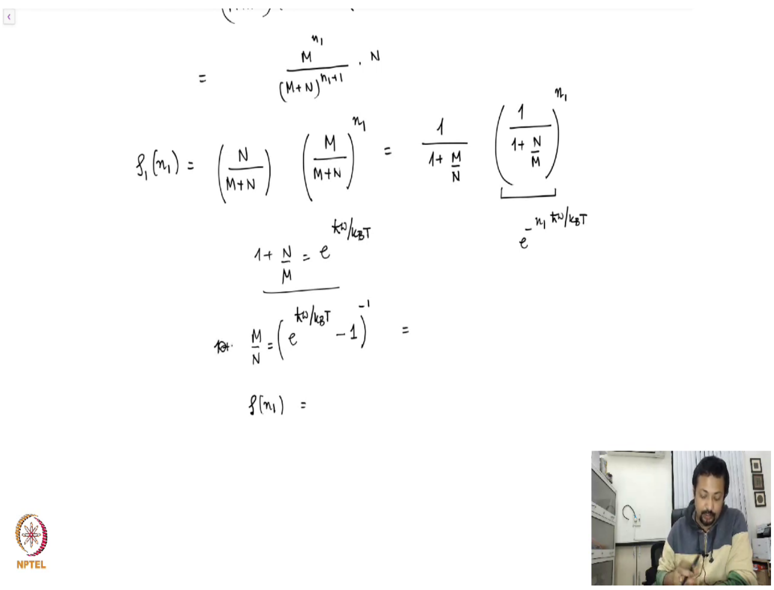

So, that rho 1 of n 1 is going to be N divided by M plus N times M over M plus N raised to the power n 1. Now, I can recast this as well here this becomes 1 over 1 plus M over N and this is 1 over 1 plus N over M raised to the power n 1. Now, if you go back to the lecture on this quantum oscillator treated micro canonically you will see that 1 plus N over M was e to the power h bar omega for K B T.

So, that the this factor is e to the power minus n 1 h bar omega K B T and from this I can write down M by N as e to the power h bar omega over K B T minus 1 inverse. So, that I have rho of n 1 is 1 plus ok.

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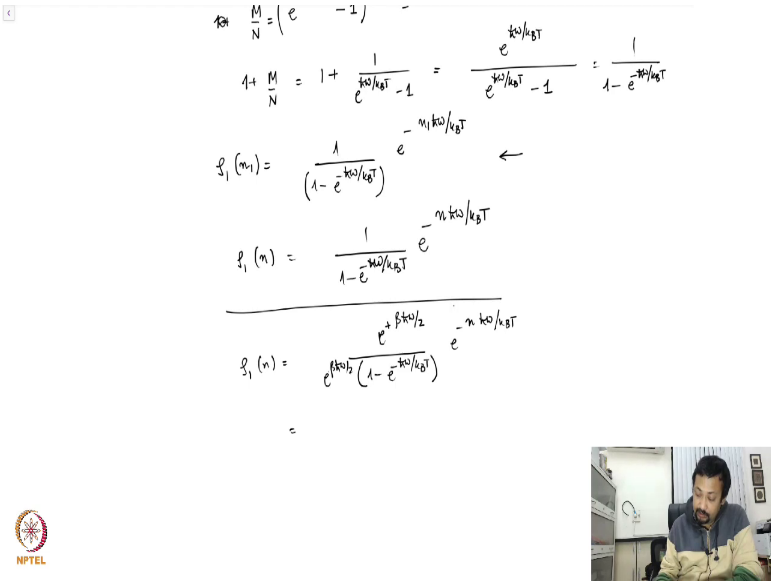

We have to take do one more step, I am interested in now 1 plus M over N which is going to be 1 plus e to the power not e to the power 1 divided by e to the power h bar omega over K B T minus 1 and if I do this, it is going to be e to the power h bar omega over K B T minus 1. You see the minus 1 in the numerator is going to cancel with this one you will be left out with h bar omega over K B T, which is nothing but 1 minus minus h bar omega over K B T.

And therefore, rho 1 of n 1 is going to be 1 over 1 minus h bar omega over K B T e to the power minus n 1 h bar omega over K B T; and this is essentially the probability that a particle or an oscillator is in the nth quantum level, here of course n 1 is nothing special so, one can write down rho 1 of n as 1 over 1 minus h bar omega over K B T e to the power minus n h bar omega over K B T.

So, now with this expression we can take it a little bit further, let us say I have rho 1 of n is going to be 1 over I want to multiply by e to the power minus beta h bar omega by 2 and divided by or let us say plus and e to the power beta h bar omega by 2 1 minus h bar omega over K B T; and this becomes minus n h bar omega over K B T.

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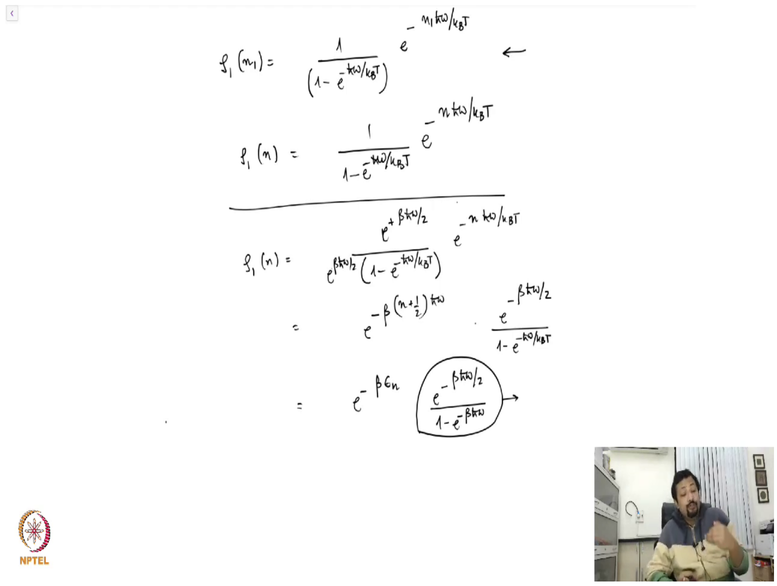

You immediately see that this results in the following simplification the numerator. Now, I can write down minus beta, beta is K B T inverse n plus half h bar omega times e to the power minus beta h bar omega over 2 divided by 1 minus h bar omega over K B T. So, that I have e to the power minus beta epsilon n and then, I have e to the power minus beta h bar omega by 2 divided by 1 minus beta h bar omega.

If you see if you recall this is a single particle canonical partition function for single for a harmonic oscillator we have done it explicitly. So, essentially here also it we explicitly showed that you can go from the micro canonical to the canonical probability density.