Statistical Mechanics

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Lecture - 49
Grand Canonical Formulation of Ideal Gas

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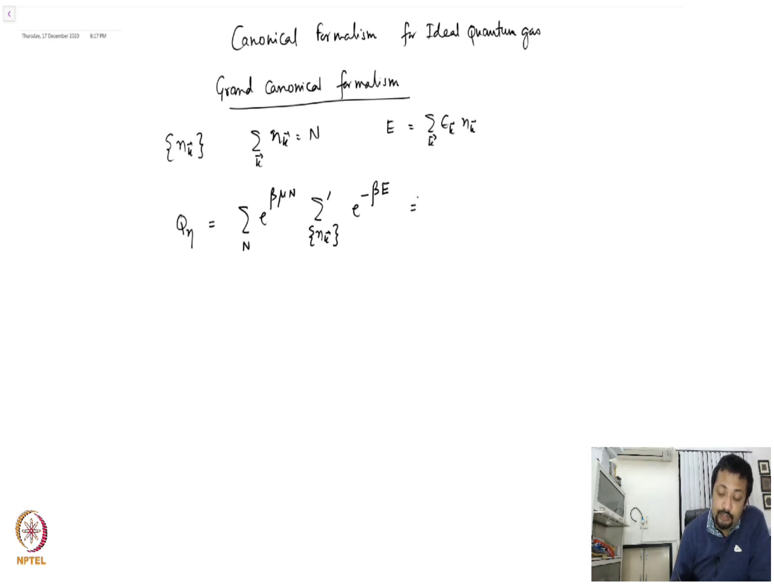

So, we now want to look at the Grand Canonical Formalism and this turns out slightly easier to handle. Of course, in the grand canonical formalism we know that the particle number is varying and if n k denotes the occupation number of the kth level then I know that sum over k n k must be equal to the total particle number and the energy is given by epsa k n k sum over k.

So, that the grand canonical partition function Q. Now eta denotes both for fermionic as well as bosonic systems is given by N e to the power beta mu N sig. So, the prime that you see over the sum essentially denotes a restricted sum you will see now while why is that is minus beta E which is going to be if I replace the e from here is going to be sum over k epsa k n k.

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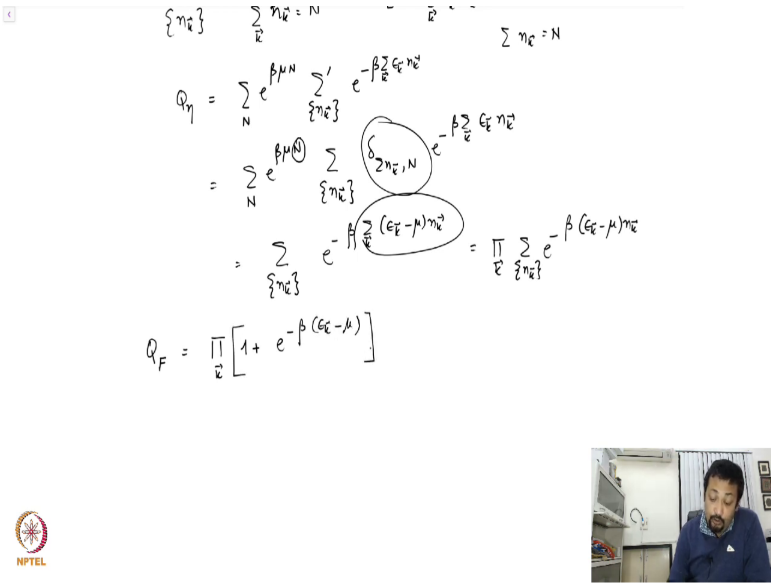

Now, the restricted sum essentially means that one has to ensure that this occupation number if you once you are summing over all possibilities, but one also has to ensure that these possibilities must also sum over to N the total particle number. So, therefore, it is an restricted sum over this occupation numbers. One can convert this restricted sum into an unrestricted sum by introducing a delta function and writing down this as k epsa k n k.

Now, we carry out the sum over N first and take care of this delta function and replace the N by sum over n k. So, that I have sum over n k the unrestricted sum e to the power beta sum over k epsa k minus mu n k. This sum over k becomes a product because it is in the exponential and we take it out and rewrite our partition function in this way, beta epsa k minus mu n k for a fermionic system lets say we write Q F.

Now n k can be either 0 or 1. So, essentially then you have product over k 1 plus e to the power minus beta epsa k minus mu.

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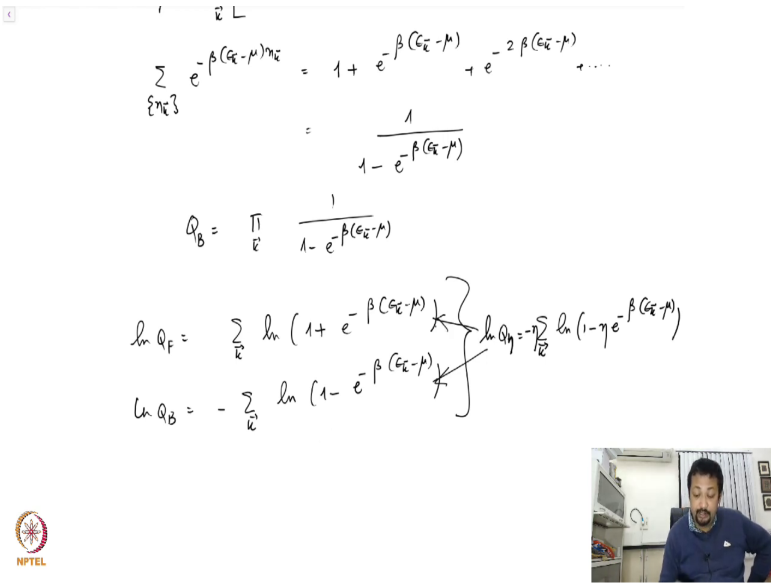

For a bosonic system n k can be anything for a bosonic system this sum e to the power minus beta epsa k minus mu n k is equal to 1 plus e to the power minus beta epsa k minus mu plus e to the power minus 2 beta epsa k minus mu so on and so forth and this is nothing but a geometric series which you can sum as 1 minus beta epsa k minus mu, right?

So, that the product the partition function the for the bosonic case becomes 1 minus e to the power minus beta epsa k minus mu. Fortunately we do not have to deal with Q, but we have to deal with ln Q and then the advantage is if I took if I take ln of Q F, you will see that this quantity is nothing, but sum over k ln 1 plus e to the power minus beta epsa k minus mu and the bosonic partition function is sum over k minus ln 1 minus e to the power minus beta epsa k minus mu.

Both of these I can combine and write down Q eta not Q eta, but rather ln of Q eta is minus sum over k ln 1 minus eta e to the power minus beta epsa k minus mu, but I also note that there has to be a eta outside. So, that for a bosonic case when eta is plus 1 I get this answer and for a fermionic case when eta is minus 1 I get this answer.

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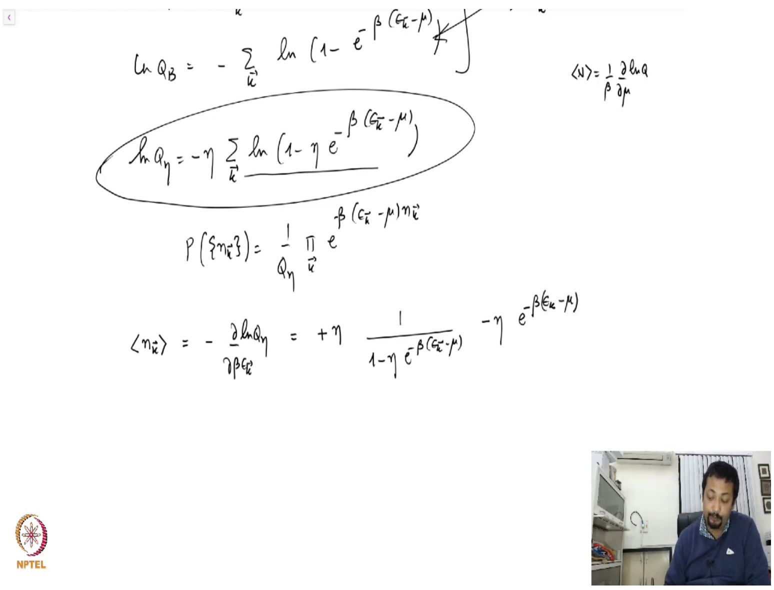

So, I have ln Q eta as minus eta sum over k ln 1 minus eta e to the power minus beta epsa k minus mu. In the grand canonical ensemble the different single particle states are occupied independently with the joint probability P of n k, which is given by 1 over Q eta product over k e to the power beta minus beta epsa k minus mu n k. So, once you know this ln of Q eta I can calculate the thermodynamic quantities and we start off with the average of the occupation number n k.

Now, when we did grand potential we calculated average of n was del del mu of ln Q, I think there was a 1 by beta outside, but here one has to be careful because mu is tied to the total particle number. On the other hand I want the average occupation number in the kth level. So, what I do here is essentially I do minus del del beta epsa k which does the same job of ln Q eta and this is given by then ln Q eta is this.

So, this becomes plus eta I am choosing only one value specific value of k. So, therefore, I will pick up only one term in the sum and the kth term which then becomes 1 minus eta e to the power minus beta epsa k minus mu and then you have eta minus eta e to the power minus beta epsa k minus mu.

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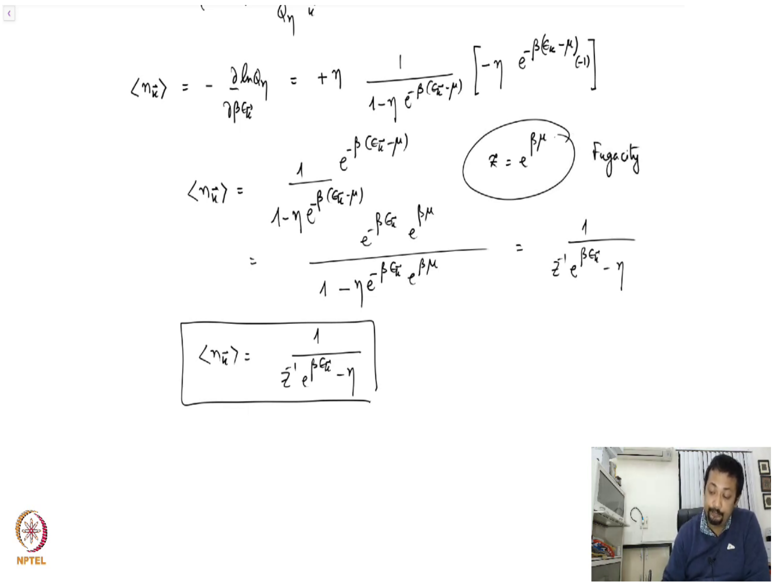

So, that your average occupation number is going to be you are going to have a minus one from this derivative it is going to be 1 over 1 minus eta e to the power minus beta epsa k minus mu times e to the power minus beta epsa k minus mu. So, let us call Z as e to the power beta mu, then I can rewrite this expression as minus beta epsa k e to the power beta mu.

And here I have 1 minus beta epsa k beta epsa sorry beta mu times eta. So, that if I bring everything down then this becomes Z inverse e to the power beta epsa k minus eta. So, this is your average occupation number which is Z inverse e to the power beta epsa k minus eta.

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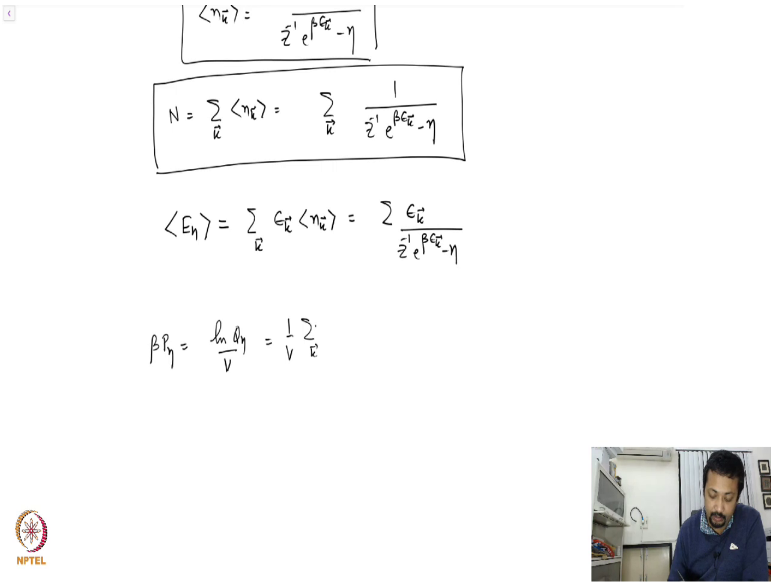

This quantity Z is known as the fugacity total particle number is given by sum over k average of n k. And therefore, this becomes sum over k 1 over Z inverse which does not contain the k index it is just e to the power beta mu is e times beta epsa k minus eta. What is the average energy?

Is sum over epsa k n k, which is going to be sum over epsa k average of n k which is Z inverse e to the power beta epsa k minus eta. The thermodynamic pressure if you recall beta P eta is ln of Q eta divided by V which is 1 by V sum over k.

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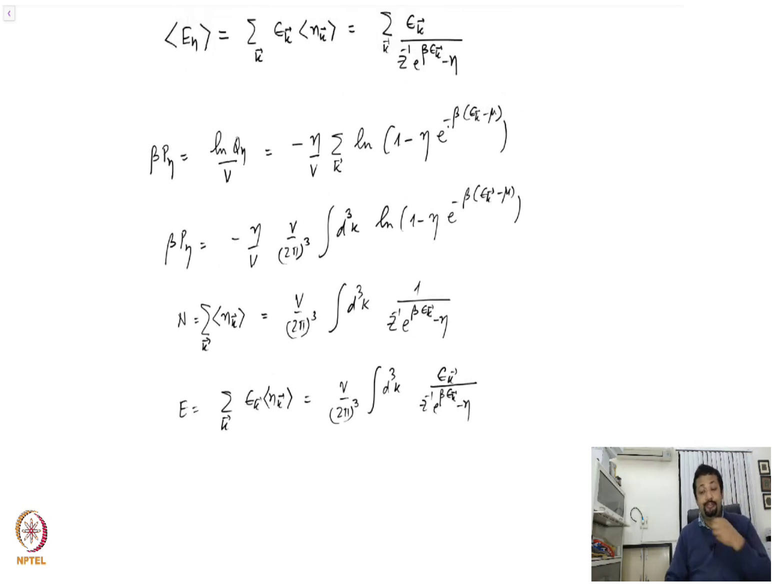

So, this is going to be minus eta over V sum over k ln of 1 minus eta e to the power minus beta epsa k minus mu. Now, in evaluating these sums the idea is to convert them into an integral and we have seen how to do this. So, for example, then beta P eta is minus eta over V, V over 2 pi whole cube integral d cube of k ln 1 minus eta e to the power minus beta epsa k minus mu.

The particle number N is sum over n k sum over k is equal to V over twice by whole cube integral d cube k 1 over Z inverse e to the power beta epsa k minus eta and energy is sum over k epsa k n k, which means this is going to be V over 2 pi whole cube integral d cube k epsa k Z inverse e to the power beta epsa k minus eta.

So, to proceed further let us just briefly summarize that we what we have been doing we have been looking at the ideal quantum gas from a grand canonical perspective in which the particles in the energy state and the kth energy levels are allowed to vary. So, you do not have a fixed number of particles.

So, your n k are different for different k levels they can vary, but the condition is that sum over n k must be equal to the total particle number and from this you calculate using this you calculate the canonical, grand canonical partition function and you relate it to the thermodynamic quantities that we have done over here. Since, its a free particle I mean since its not note that I have missed out the degeneracy factor which is g over here.

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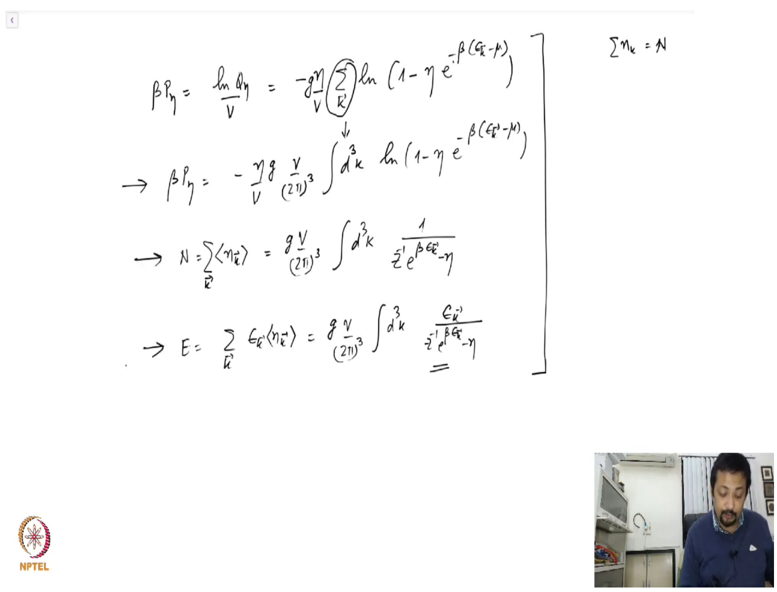

So, for example, if you are looking at a fermionic system with each particle having a spin s then this degeneracy factor is 2 s plus 1 that needs to be accounted for good. So, we will take this expressions and we will proceed further.

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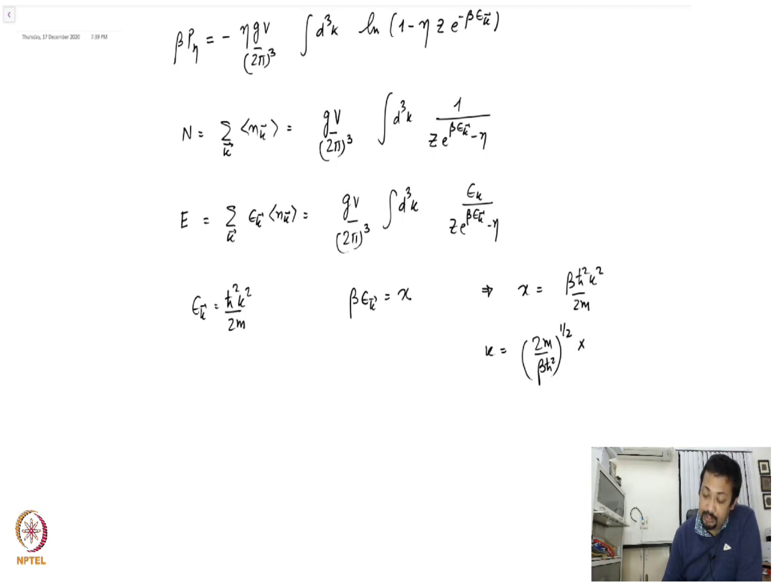

So, let us write down them as beta P eta is minus eta gV over 2 pi whole cube integral d cube k ln 1 minus eta Z e to the power minus beta epsa k. The total particle number which is sum over k this gets converted into gV twice pi whole cube integral d cube of k 1 minus Z e to the power beta epsa k minus eta.

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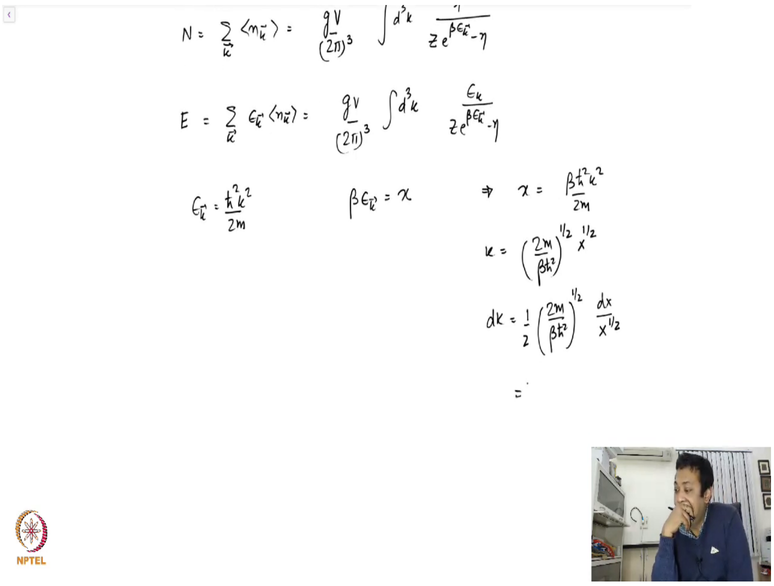

And the total energy is sum over k epsa k average n k is gV twice pi whole cube integral d cube k epsa k Z e to the power beta epsa k minus eta. Now, we are looking at a free particle system on interacting and therefore epsa k is h square k square over twice m. So, that we I did not redefined our variable as x and this implies x is beta h square k square over twice m.

So, that k is twice m beta h square half times x to the power half and d k becomes twice m beta h bar square raised to the power half d x over X to the power half with the factor of half. Now, so now if I look at this particular expression it looks very very familiar to me.

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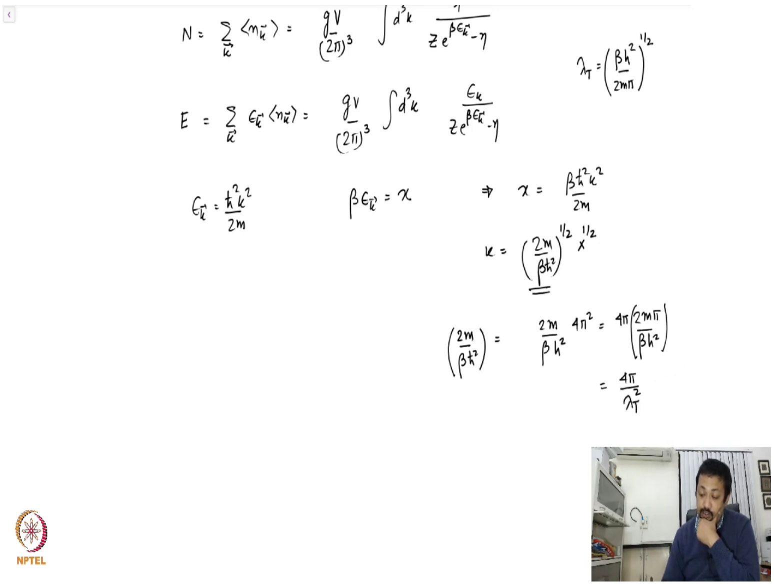

Now I know that lambda T was beta h square over 2 m pi raised to the power half. So, then twice m over beta h bar square is nothing, but twice m over beta h square times 4 pi square. So, which means I can write this as 4 times 2 m pi over 4 pi times 2 m pi over beta h square and therefore, you see that this is 4 pi over lambda T square.

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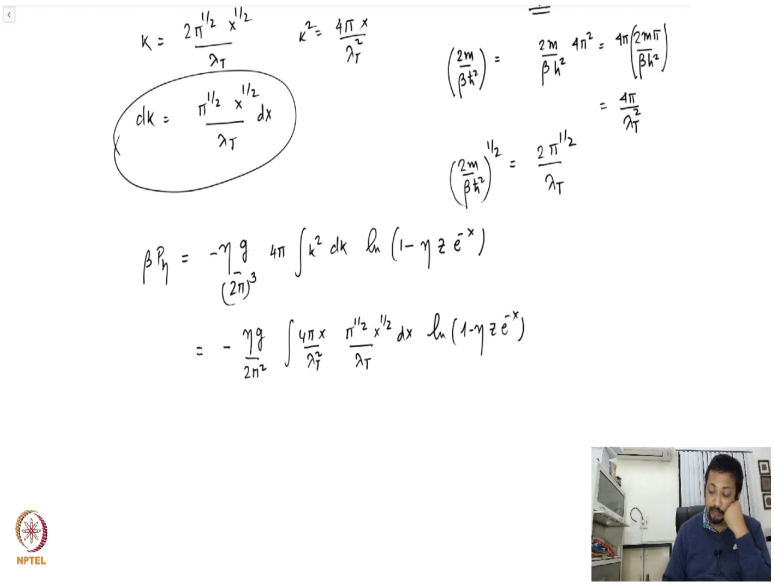

So, that twice m over beta h bar square raised to the power half is going to be 2 pi to the power half lambda T, very nice. So, then I have the relation that k is going to be 2 pi to the power half x to the power half divided by lambda T and d k is going to be pi to the power half x to the power half over lambda T. So, we are repeatedly going to use this as a measure. So, starting from the expression for the pressure, which is minus recall.

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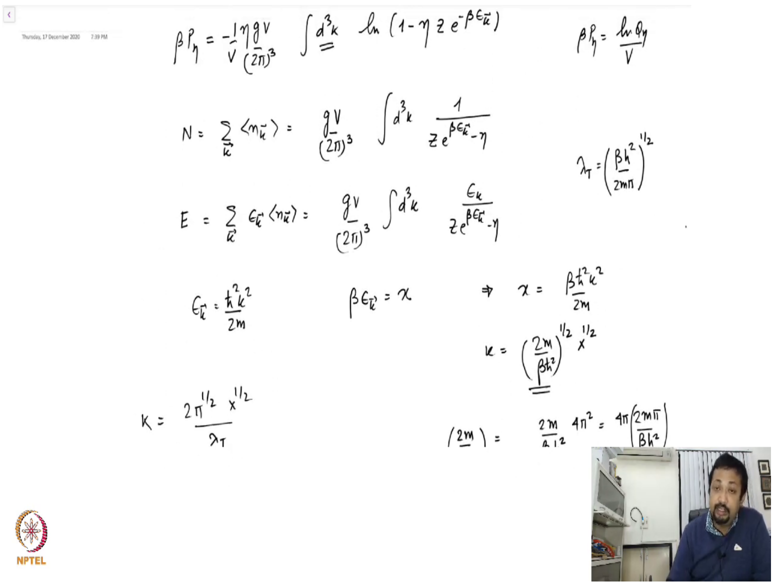

When I have this beta p eta there was a 1 by V sitting over here because beta P eta is essentially ln Q eta over V. So, the V V gets cancelled out and therefore, I will have minus eta g over twice pi whole cube and then this measure becomes 4 pi k square dk. So, I am going to have 4 pi integral k square dk ln of 1 minus eta Z e to the power minus x good. So, let us simplify this further eta g this becomes 8 pi cube. So, you are going to have 2 pi square k square is going to be 4 pi x over lambda T square.

So, you are going to have integral 4 pi x over lambda T square and d k is going to be pi to the power half x to the power half, there is a d x missing over here, I am terribly sorry for this silly mistakes dx ln 1 minus eta Z e to the power minus x.

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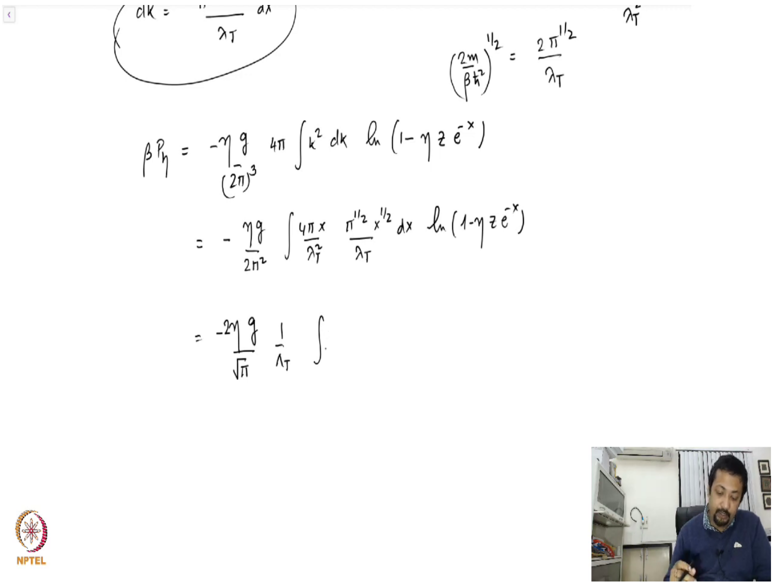

This is minus eta g you see this factor gives you 2 and you have pi to the power three half and pi square in the denominator. So, you get a square root pi straight forward and then you get 1 over lambda T the thermal De' Broglie volume and you have.

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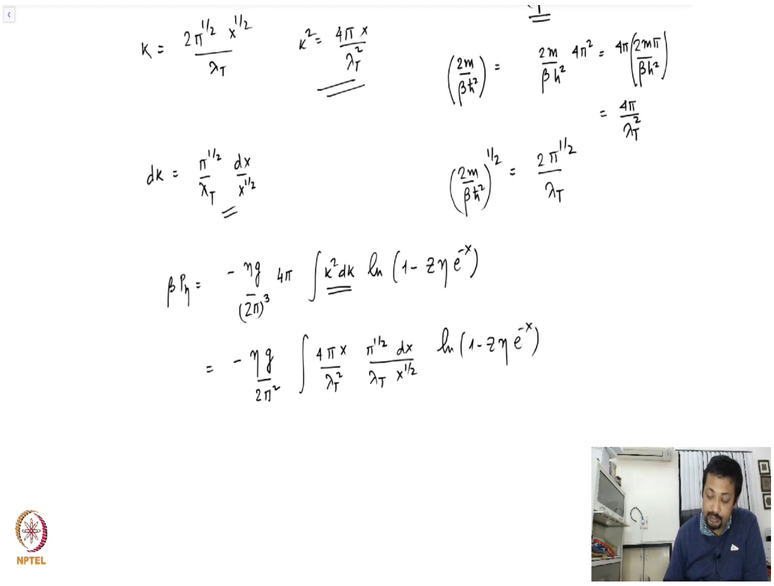

So, this means dk is going to be pi to the power half over lambda sorry lambda T dx over x to the power half. Now, in the expression for beta P eta there is a 1 by volume factor. So, that the expression for beta P eta becomes minus eta g over 2 pi whole cube the measure d cube k becomes k 4 pi k square d k. So, the angular integral gives you 4 pi I have 4 pi k square d k ln 1 minus Z eta e to the power minus x.

So, that this is minus eta times g this gives me 8 pi cube in the denominator and 4 pi in the numerator that gives me 2 pi square and the integral case. This I will change to now my transformed variable in terms of x this gives me 4 pi x over lambda t square this is k square as and then dk is this which is going to be pi to the power half dx lambda t x to the power half ln 1 minus Z eta e to the power minus x minus eta g 2 pi square.

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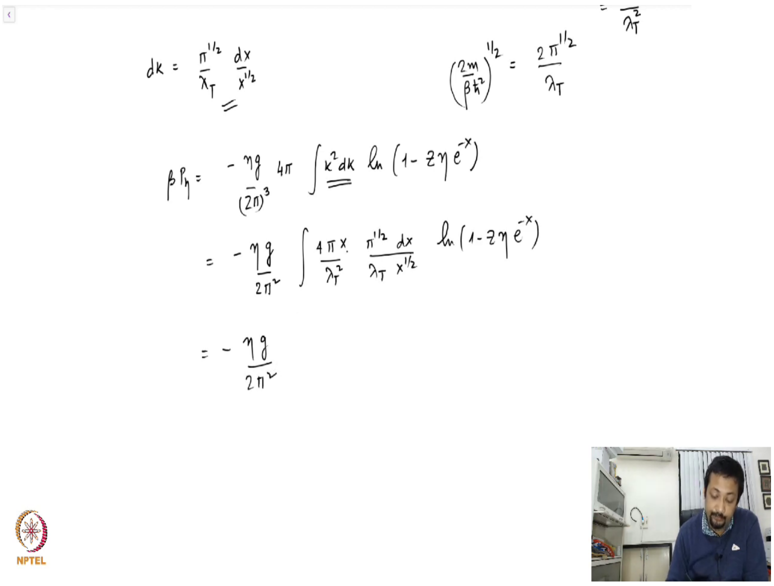

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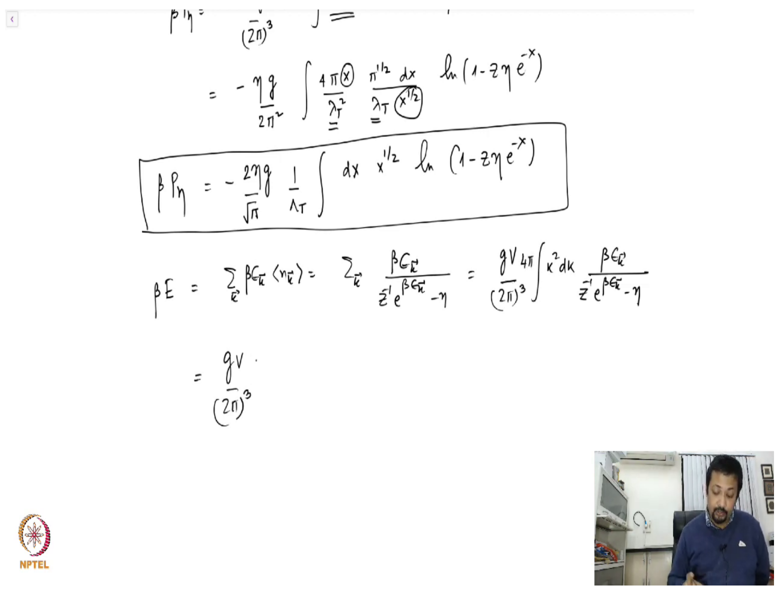

Now, let us not do it over and over it let us just do a little bit of a mental math. So, this is 4 in the numerator 2 in the denominator I straight forward have a 2 in the numerator, numerator also has pi to the power 3 half and denominator has pi square. So, I have a square root pi and then this and this gives me the thermal De' Broglie volume. So, that I have dx this and this gets me x to the power half ln 1 minus Z eta e to the power minus x.

So, it is important that we do we rewrite this in terms of x because we are going to repeatedly use it later on. Let us look at the energy the energy is sum over k epsa k average n k, which means this is going to be sum over k epsa k Z inverse e to the power beta epsa k minus eta. And this if I convert it to an integral this is going to be gV over 2 pi whole cube integration k square dk we will multiply this with beta.

So, that I have beta epsa k throughout and the reason is because I have defined beta epsa k as x. So, my life is going to be simpler e to the power beta epsa k minus eta k square gV twice by whole cube sorry there is a 4 pi also that comes from the measure.

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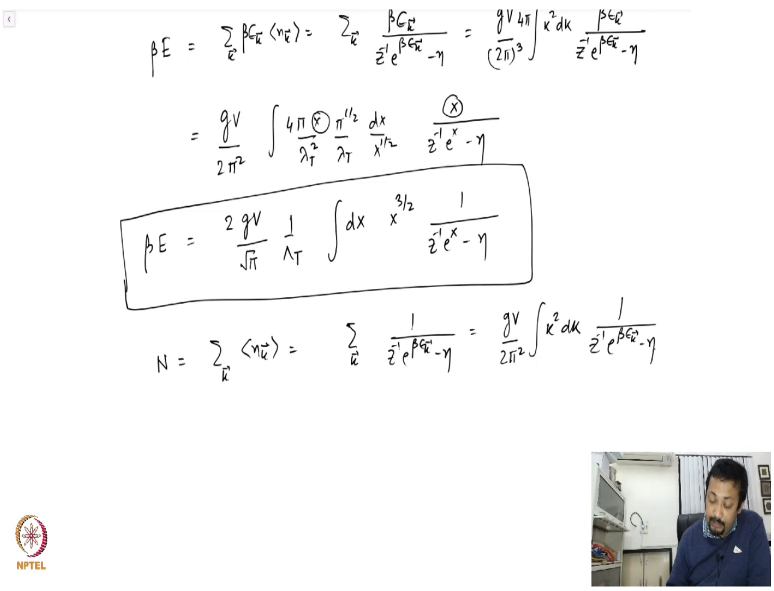

So, this is straightforward we do not want to do it over and over again, 2 pi square k square is going to be 4 pi x over lambda T square and dk is going to be pi to the power half dx over x to the power half and 1 over lambda t. And then I have x Z inverse e to the power x minus eta. So, this integral gives me twice gv over square root of pi 1 over lambda T integral dx.

Now do a power counting in x this is 1, this is 1. So, x square divided by x to the power half. So, you get x to the power 3 half 1 over Z inverse e to the power x minus eta. So, this is beta e and N is going to be sum over k n k which is sum over k 1 over Z inverse beta epsa k minus eta. And therefore, this is going to be gv over 2 pi square integral k square dk 1 over Z inverse e to the power beta epsa k minus eta.

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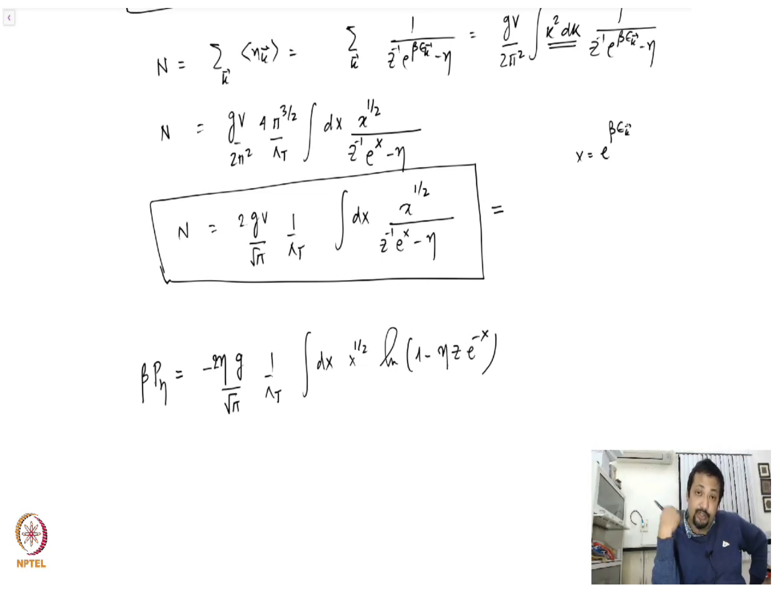

So, that means, this term is going to be gv over 2 pi square. I am going to have 4 times pi to the power 3 half from k square and d k both and this is going to be dx x to the power half Z inverse e to the power beta sorry not beta x epsa k, but just e to the power x minus eta. So, that this again becomes twice gv sorry there is also going to be a thermal volume lambda T do not forget that 1 over lambda T dx x to the power half Z inverse e to the power x minus eta.

So, these three expressions this one this one and finally, this one we are going to use later on, but right now let us focus on the pressure equation the pressure equation tells you beta P eta is minus eta g twice eta g over square root pi 1 over lambda T dx x to the power half ln 1 minus eta Z e to the power minus x good.

Now, x recall is e to the power beta epsa k. So, momentum can have 0 values to infinity. So, k is being can be integrated from 0 to infinity and therefore, x also runs from 0 to infinity.

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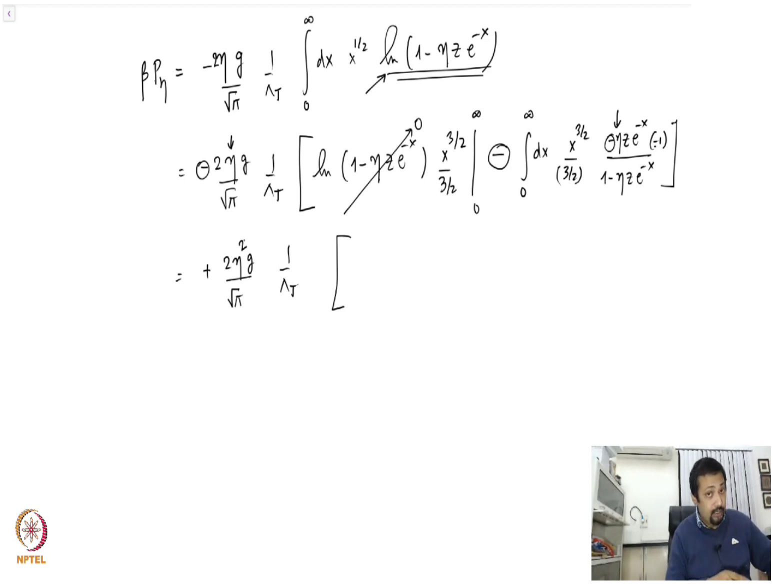

And now I can integrate over parts. So, that the first term I will take this as a first function I have ln 1 minus eta Z e to the power minus x and the integral of x to the power half is x to the power 3 by 2 divided by 3 by 2 0 to infinity minus 0 to infinity d of x x to the power 3 by 2 3 by 2 derivative of this function with respect to x which gives you eta Z e to the power minus x, then you have minus eta Z e to the power minus x and the minus 1 because it is d d x of minus x close the bracket.

Now, if x is equal to 0 ln 1 is 0 if x is equal to infinity ln 1 is 0. So, both the cases this is 0 ok, before we proceed further let us just complete write down the limits. So, that we do not get confused later on 0 to infinity come back to this. This is minus twice eta g over square root pi

1 over lambda T and now I have a minus over here I have a minus over here that makes here plus, I have a minus over here and a minus over here that makes it a plus so I have a plus.

This term is 0 further note that I have a eta over here and the eta over here, that makes it eta square and eta square is always 1 irrespective of whether you have fermionic system or a bosonic system.

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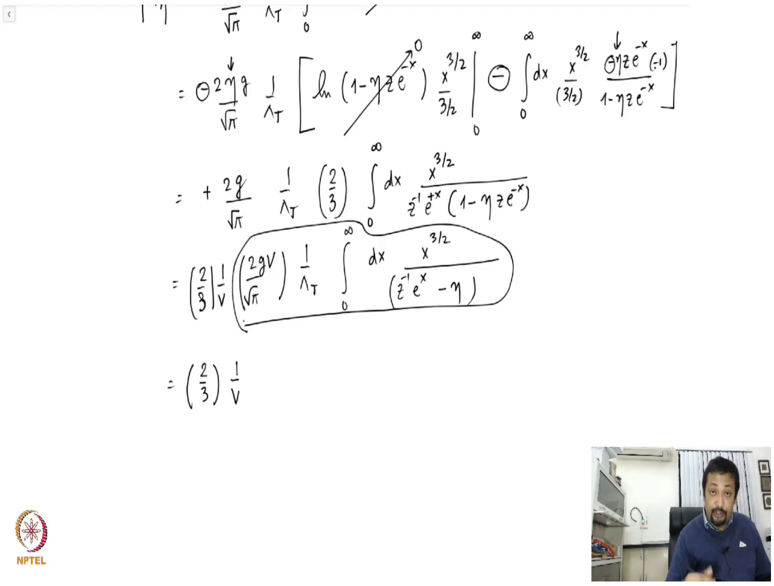

So, I can straight forward remove this and I am going to have g then I am left out with 2 by 3 0 to infinity dx x to the power 3 half eta eta I have taken care of, Z inverse e to the power minus x times 1 minus eta Z e to the sorry Z inverse e to the power plus x and this. So, this is going to be 2 by 3 2g over square root pi I will multiply this by V and I will bring down a factor 1 by V over here, you will see a little later y and then this integral becomes dx x to the power 3 by 2 Z inverse e to the power x minus eta.

Now, 2 by 3 this is 2 by 3 1 by V and if you look at this expression that we have come to after using integration by parts. You will see that this is exactly this expression there is a 1 by lambda T 2 gV square root by 1 by lambda T 0 to infinity x to the power 3 half Z inverse and say this is the same thing that we are looking at. And therefore, you come up with the answer this beta times E.

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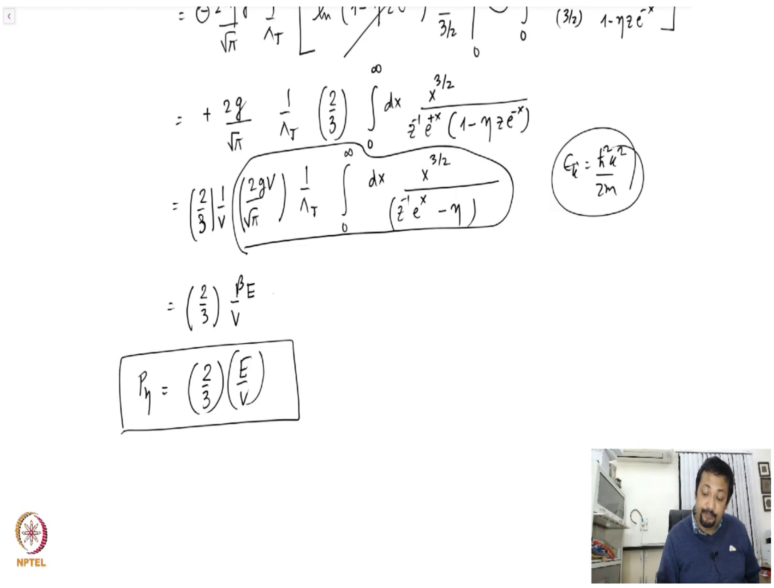

So, that P eta is 2 by 3 E over V. Therefore, the pressure irrespective of a fermionic gas or a bosonic gas if its a non relativistic gas where epsa k is a square k square over twice m the pressure is two third the energy density something we derived in classical statistical mechanics, but we have done it now for quantum gases quantum ideal gases.