Statistical Mechanics
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Lecture - 48
Canonical Formulation of Ideal Gas

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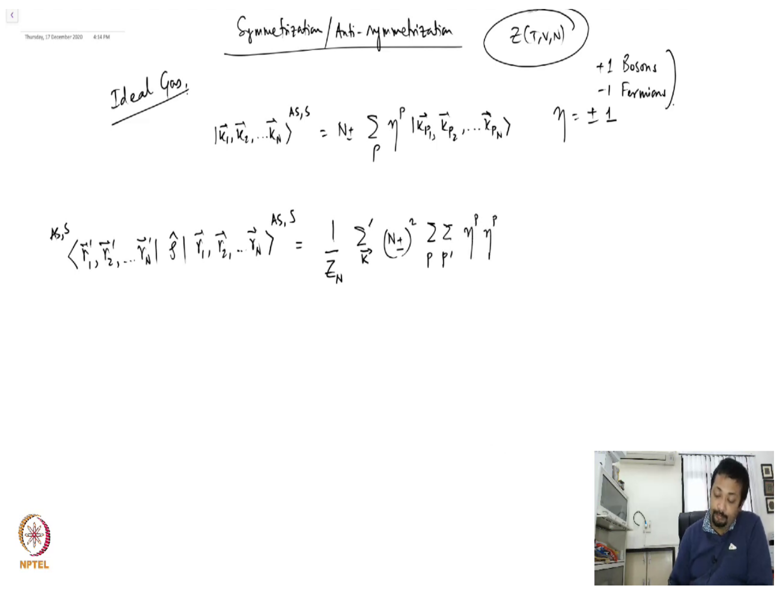

So, now we want to see what effect our Summarization and or the Anti-symmetrization of the wave function has on the canonical N particle canonical partition function T, V, N. So, we going to consider, reconsider our ideal gas again; but now, we take a definite symmetry of the wave function. So, that I have k 1, k 2, k N anti-symmetry, symmetry is given by. So, we will write them as N plus minus sum of a eta p k 1 k p 1, k p 2, k p N and the sum is over all possible permutations.

Eta is plus minus 1; plus 1 for Bosons and minus 1 for Fermions. The canonical density matrix in the coordinate representation is then r 1 prime, r 2 prime, r N prime, rho hat r 1 r 2 sorry r N anti symmetric, anti symmetric, symmetric which is going to be 1 over Z N, the N particle partition function unrestricted. So, this is a prime. We will come back to this and then, I have N plus minus whole square sum over p, sum over p prime, eta p, eta p prime.

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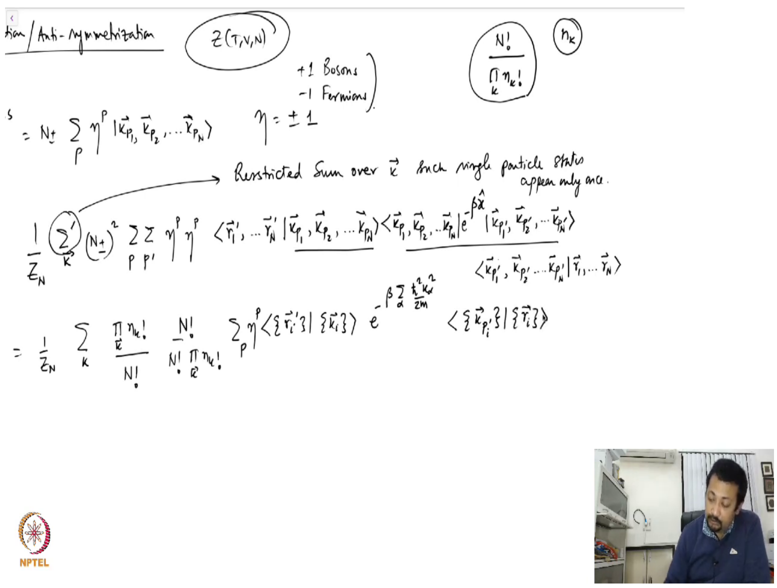

r 1 prime, r N prime k p 1, k p 2, k p N and then, I have k p 1, k p 2, k p N e to the power minus beta h hat. k p 1 prime, k p 2 prime sorry k naught k p N prime and then I have k p 1 prime, k p 2 prime, k p N prime I have r 1, r 2, r N right. Now, this is a very complicated expression; but we can simplify this further. So, I have Z of N, this is an on this sigma prime is an restricted sum over k such that single particle states appear only once.

But we can convert it into an unrestricted sum and the way to do that is to realize that the total number of permutations possible is N factorial; but I also have occupation number N k in the

K-th level right. N 1 particles in energy level 1, N 2 particles in 2, so on and so forth and the over counting that I am doing is product over k N k factorial.

It is if I now convert this restricted sum over k to an unrestricted sum over K, I am just over counting this many number of states. So, therefore, I will divide by this which makes it product over k N k factorial divided by N factorial and then, the normalization is given by 1 over N factorial product over k N k factorial.

I have a sum over p which again I can take which I can essentially manipulate getting rid of 1 sum over p and bringing in a factor of N factorial and replacing this by the original un-permutated set. So, I have sorry first I have eta of p r i prime k i. This is e to the power minus beta sum over alpha h square k alpha square over twice m and then, I have the permutated say of the k vectors k p prime i and r i. Good. Lot of things cancelled out over here, this and this and this cancel out.

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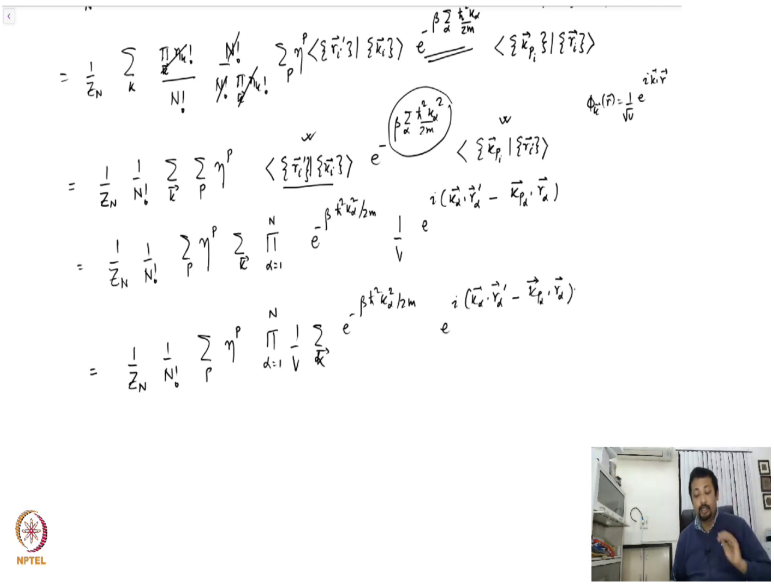

After the cancellations, you see that this becomes 1 by Z N, the N fact 1 N factorial survives I have a sum of a K, I have a sum of a p, eta of p r i prime k i e to the power minus beta sum over alpha h bar square k alpha square over twice m and then, I have the permutated set of the k vectors r i.

So, this idealize is the coordinate representation of the wave function and I can write down this as phi k of r as 1 by square root of v e to the power i k dot r, the single particle states. Let us just see whether we have everything that we have from the equation on top. I hope so.

So, then, it is 1 by N factorial sum over p, we will interchange this eta p and then, sum over k and note that, this particular sum that is argument of the exponential breaks into products. So, I am going to have a product over alpha equal to 1 to N. This is the complex conjugate of this wave function so that sorry this is a wave function so that this is going to be beta.

So, first let us write down k alpha square this term and then, this is going to be you are going to have 1 by V from these two and then, you are going to have i k alpha dot r prime alpha minus k p alpha dotted with r alpha. So, 1 over Z N, 1 over N factorial sum over p eta p product over alpha equal to 1 to N sum over alpha 1 by V sorry sum over k e to the power minus beta h bar square k square k alpha square over twice m e to the power i k alpha dotted with r prime alpha minus k p alpha total with r alpha.

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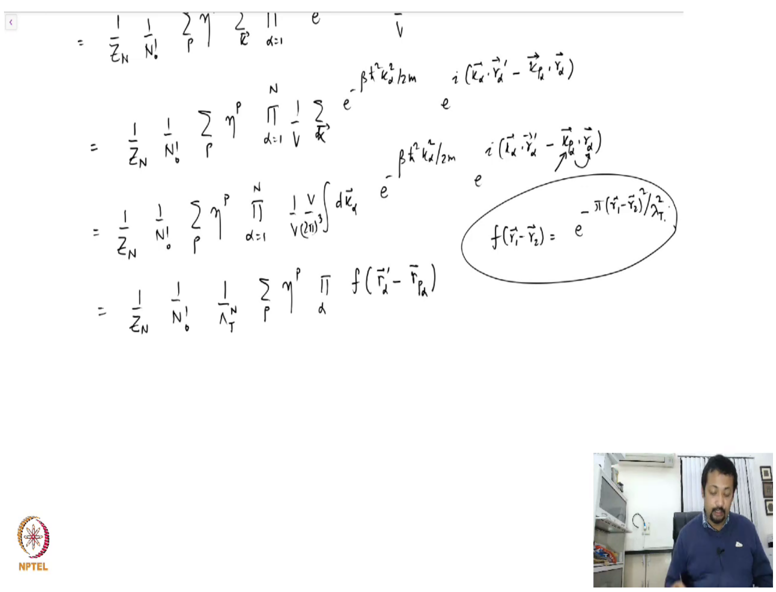

This sum over k, now I can convert it into an integral just as we did for a single particle case and we are going to come up with eta p, product over alpha equal to 1 to N 1 by V integral V over 2 pi whole cube dk alpha minus beta h square k alpha square twice m e to the power i k alpha dot r prime alpha minus k p alpha dotted with r alpha.

This integral is standard. We have done it also when we did the coordinate representation for a single particle and this is going to give me 1 over Z N 1 over N factorial 1 over lambda T to the power N sum over p eta p product over alpha f of r prime alpha minus r of p alpha. Once you do the integral over k, this indice gets transferred to this alpha; where, f of r 1 minus r 2 is e to the power minus pi r 1 minus r 2 whole square over lambda T square.

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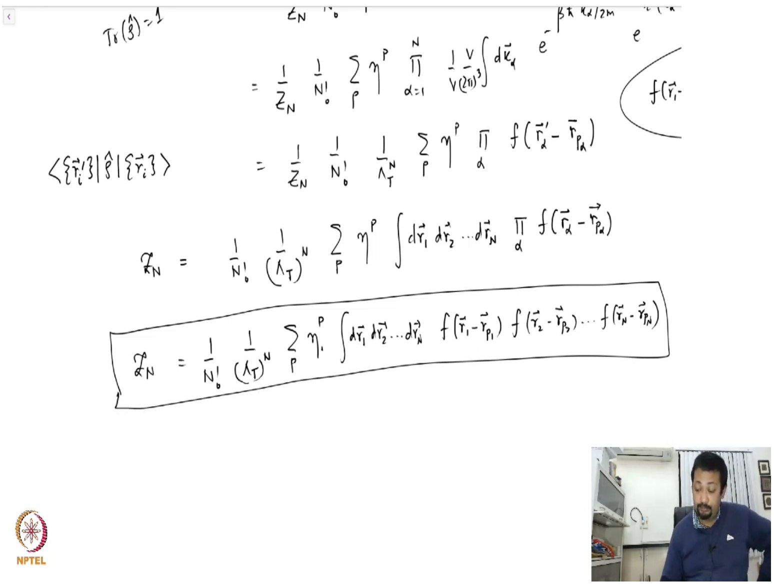

Now, this is your r prime i rho hat r i, the coordinate representation of your density matrix. The partition function follows from the fact that the trace of this quantity is trace of the density matrix is going to be 1 and therefore, Z of N is going to be 1 over N factorial 1 over lambda T raised to the power N sum over p eta p integral dr 1 dr 2 all the way up to r to r N.

I have a product over alpha f of r alpha minus r p alpha, which if you write down explicitly is going to be lambda T raised to the power N sum over p eta raised to the power p integral dr 1 dr 2 dr N f of r 1 minus r p 1 f of r 2 minus r p 2 so on and so forth and you have r N minus r p N. The quantum canonical partition function Z of N essentially involves an N sum over this N factorial possible permutations.

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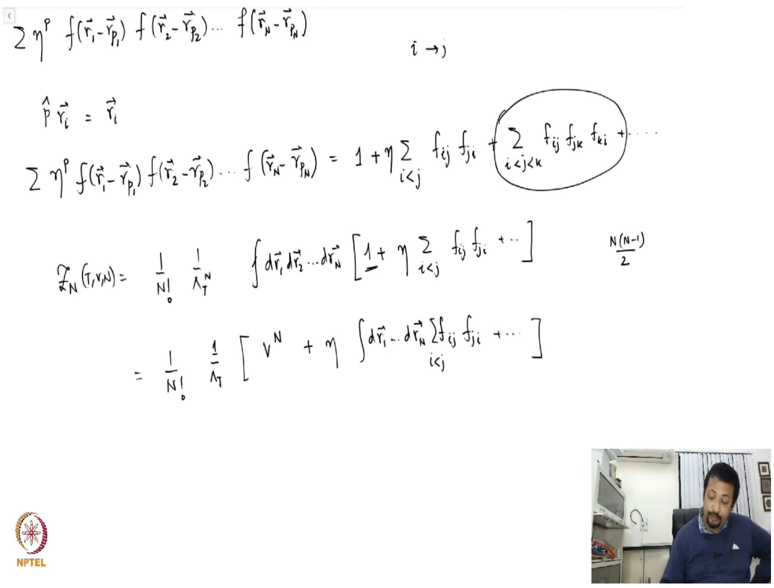

So, the idea is to consider first what this gives you. f of r 1 minus r p 1 f of r 2 minus r p 2 so on and so forth all the way up to f of r N minus r p N right. Now, what is the lowest order of permutation? The lowest order of permutation is where, p r i gives you r i. So, there is no exchange. If there is no exchange, then you see the form of this is going to give you 1.

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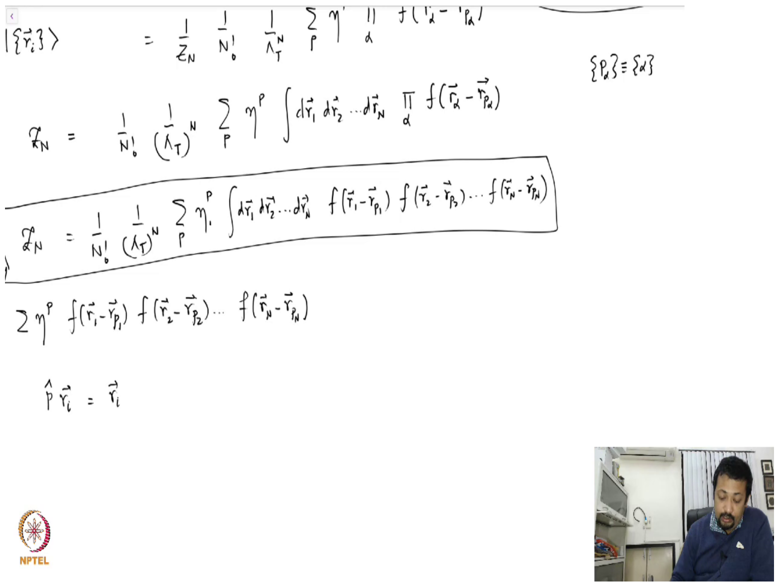

If r 1 and r 2 which means r alpha, the set p alpha is identical to alpha; that means, this function is 1 and therefore, this sum f of r 1 minus r p 1, f of r 2 minus r p 2 so on f of r N minus r p N is going to be 1 plus. The second permutation is when i goes to j that is going to be and j right; i less than j eta p is 1 is going to be f ij f ji, you have a pair. The third becomes i less than j less than k, you have f ij f j k and k goes to i and so on and so forth higher orders.

Now, keeping up to the lowest order, I have Z of N T, V, N is going to be 1 over N factorial 1 over lambda T raised to the power N and then, we explicitly write down this sum as first dr 1 dr 2 dr N and let us put the bracket 1 plus eta. So, here in this particular term, I have eta square which is going to be 1 irrespective of whether it is a fermionic or a bosonic system; sum over i less than j, f ij f ji plus higher order terms.

So, we will ignore all other higher order terms. The first term is very easy to see this integral is going to be V to the power N over lambda T to the power N. So, let us keep it within the bracket so that it is easier V to the power N plus eta times integral dr 1 dr N f ij f ji right with the sum over i less than j. Now, how many possible pairs can get? You can get N into N minus 1 by 2.

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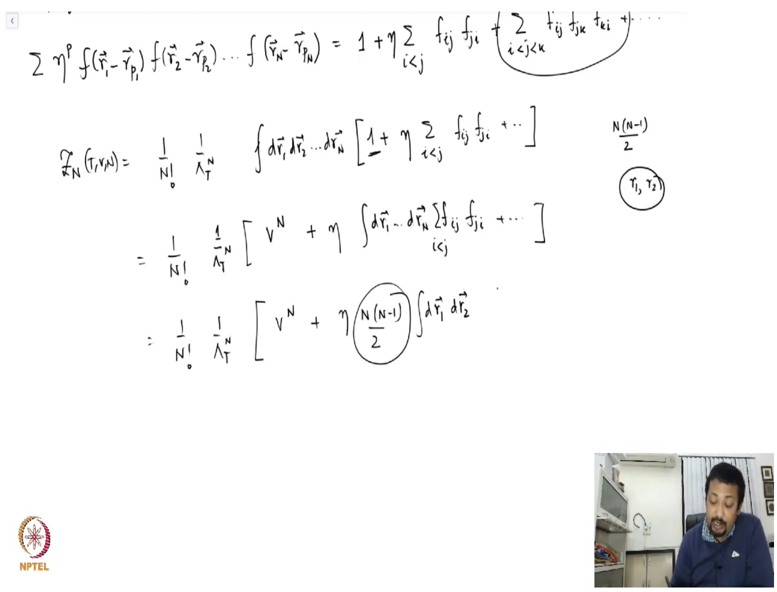

If that is the case, then, I have N factorial 1 over lambda T m sorry I missed out N factor here. This is going to be V to the power N plus eta N into N minus 1 by 2. Now, if I am choosing let us say r 1 and r 2, since they are N into N minus 1 pairs, you can form by two number of pairs you can form and if you are if you choose any two pairs, all the pairs are identical. Therefore, you can just easily choose r 1 and r 2 and simply, multiply this factor N into N minus 1 by 2 and then, you see you are going to have dr 1 and dr 2. The rest of the integral over the coordinates is going to give you V to the power N minus 1.

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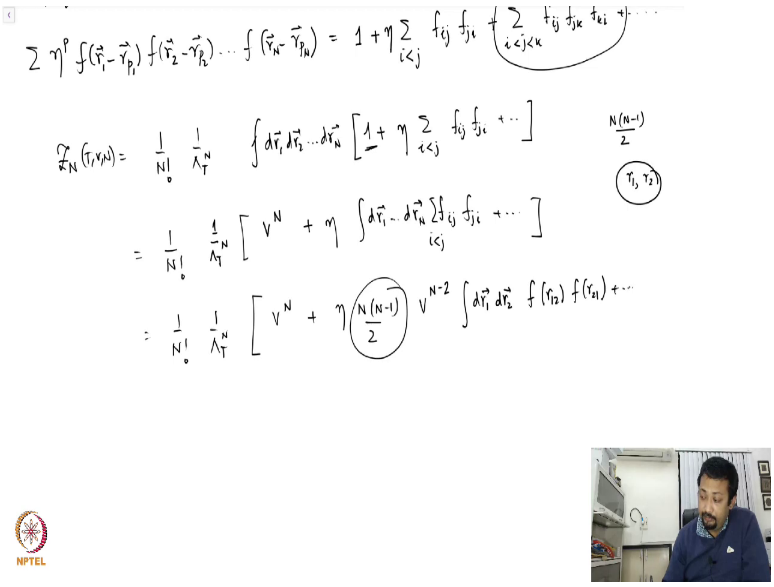

So, we will rephrase, we will rewrite this as V to the power N minus 1 integral dr 1 sorry N minus 2. There are two particles which I have chosen r 1 and r 2. I am left out with N minus 2 of them. So, V to the power N minus 2, I have dr 1, dr 2 f of r 12, r 21.

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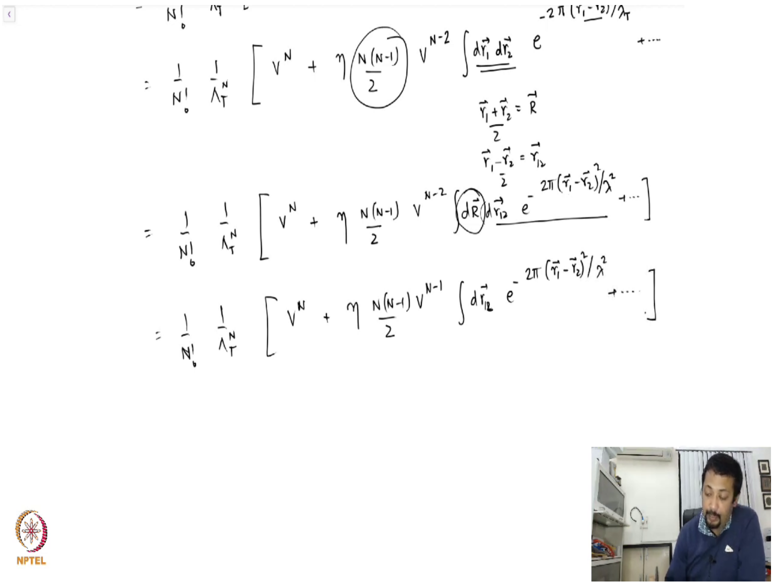

And then, I have higher order terms. This, I can simplify further and I can easily write this as 2 pi r 1 minus r 2 whole square divided by lambda T square plus higher order terms. Now, to evaluate this integral, I can go to the center of mass frame which means I choose r because this is a function of r 1 minus r 2.

So, I go to the center of mass frame which is r and r 12 which is the separation internal coordinates which is r 1 minus r 2 by 2 and then, essentially you will have 1 over N factorial 1 over lambda T raised to the power N V to the power N plus eta N into N minus 1 by 2 V to the power N minus 2 integral over dr dr 12 e to the power minus twice by r 1 minus r 2 whole square over lambda square plus higher order terms.

So, that I have 1 over N factorial 1 over lambda T raised to the power N V to the power N eta N into N minus 1 by 2. Now, the integrand over here, this part is the interesting part because it the argument of the exponential depends on r 1 minus r 2.

But this term, the center of mass is allowed to have the whole volume, if you integrate over that. So, this gives you V to the power N minus 1 and you are left out with d of r 12 e to the power minus 2 pi r 1 minus r 2 whole square over lambda square plus this.

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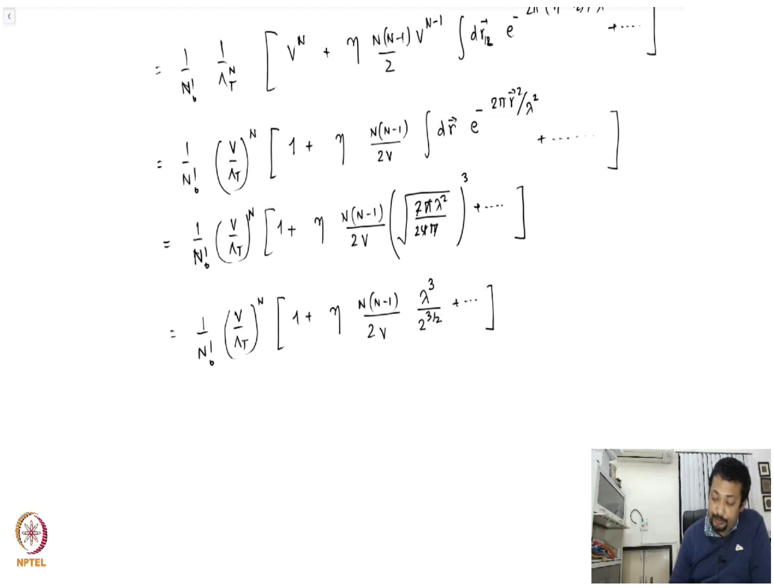

A little more simplification follows and we write them as V 2 over lambda T raised to the power N and I have 1 plus eta N into N minus 1 by twice V and I have d r e to the power minus twice pi r square over lambda square. So, this again is a Gaussian integral and once you evaluate the Gaussian integral, you have V over lambda T raised to the power N 1 plus eta N into N minus 1 divided by twice V square root of 2 pi lambda square divided by 4 pi raised to the power whole cube plus higher order terms. So, that I have 1 over N factorial V over lambda T raised to the power N 1 plus eta N into N minus 1 divided by 2 V. The pi, pi cancels out; this big gives you 2.

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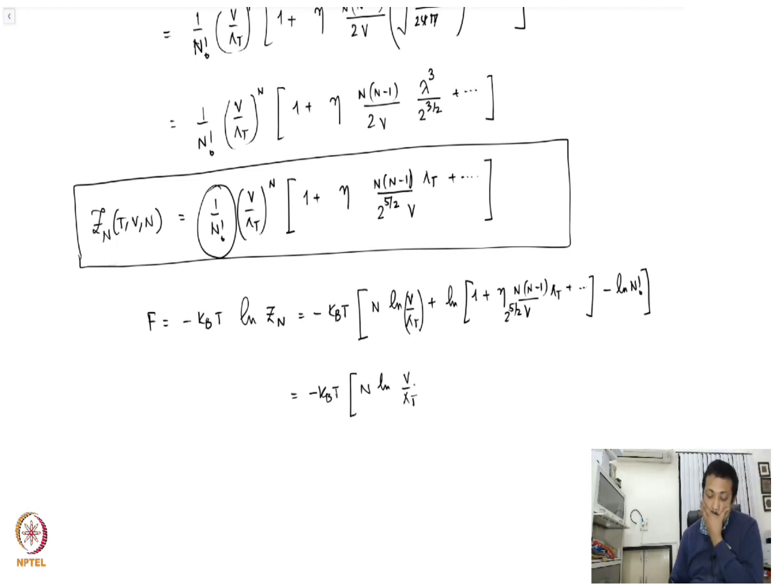

So, I have lambda cube divided by 2 to the power 3 by 2 plus higher order terms, which is going to be 1 over N factorial V over lambda T raised to the power N 1 plus eta N into N minus 1 times lambda T the thermal (Refer Time: 21:04) volume 2 to the power 5 by 2 V plus higher order terms.

The N particle, canonical partition function now take this form. What is interesting is that now you see this 1 by N factorial has appeared very naturally within the theory. So, when we started off with the name assumption or name construction of the wave function from the single particle states, we did not get this.

But now, we get this once we attach a definite symmetry to the wave function. The free energy F is minus k B T ln of Z N which is minus k B T. I will have N ln V over lambda T plus ln of 1 plus eta N into N minus 1 over V lambda T 2 to the power 5 by 2 higher order terms minus ln of N factorial.

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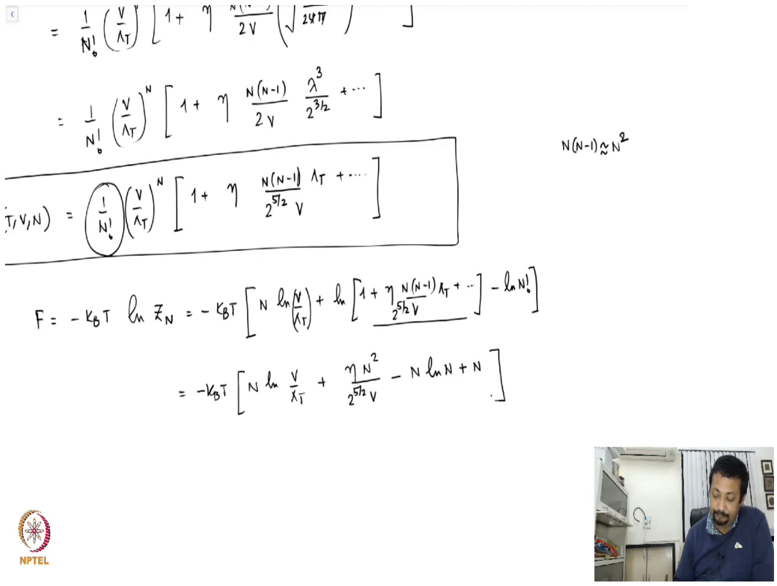

So, this is going to be minus k B T N ln V over lambda T and I can expand this log to write down this as eta N square over 2 to the power 5 by 2 V, where I have approximated for large enough N, N minus 1 is approximately, N of square minus N ln N plus N minus N k B T ln V over lambda T plus rho eta.

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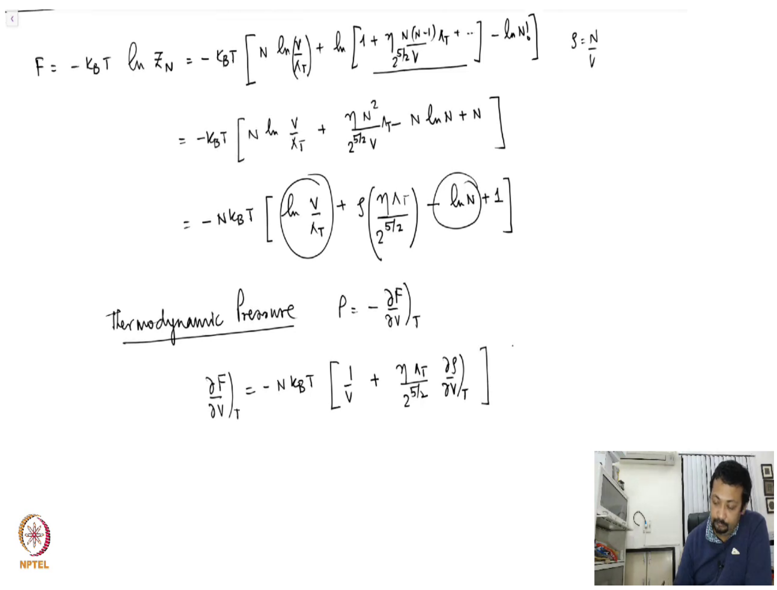

Sorry, there is a lambda T that is missing over here; rho eta lambda T over 2 to the power of 5 by 2 minus ln N plus 1. The thermodynamic pressure P is minus del F del V T constant and when T is constant, lambda T is also constant; capital lambda T is also constant and therefore, you have del F del V T constant is minus N k B T, the first term. The derivative of the first term gives you 1 by V plus eta lambda T over 2 to the power 5 by 2 times del rho del V, temperature constant right.

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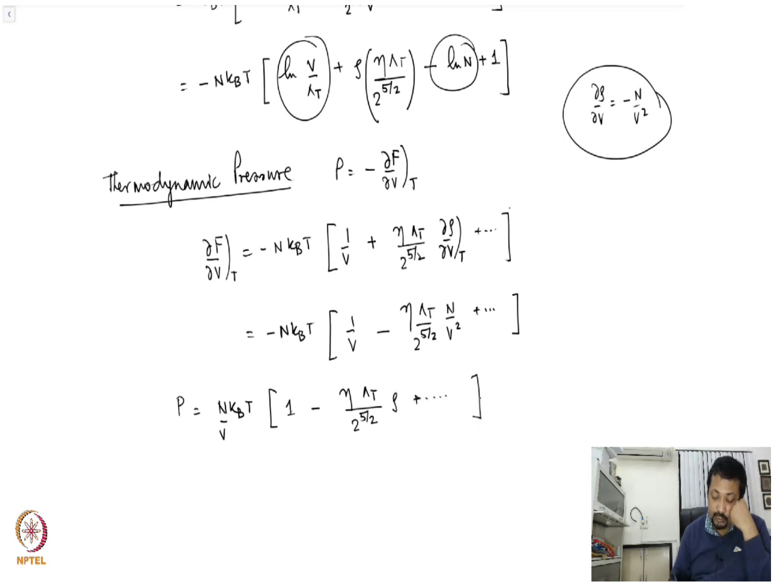

So, there is going to be higher order terms which we have ignored when we expanded the log; minus N k B T 1 over V plus eta lambda T raised to the power 2 to the power 5 by 2, rho is N by V and therefore, del u del V is minus N over V square. So, I will have N over V square plus higher order terms.

So, the pressure which is minus of del V, del F del V at temperature constant becomes N k B T 1 by V. If I take 1 by V outside, then you see I have the form which is N by V 1 plus eta lambda T over 2 to the power 5 by 2. Sorry, there is a minus sign that comes from this. Therefore, this is going to be a minus; over here minus times rho plus higher order terms.

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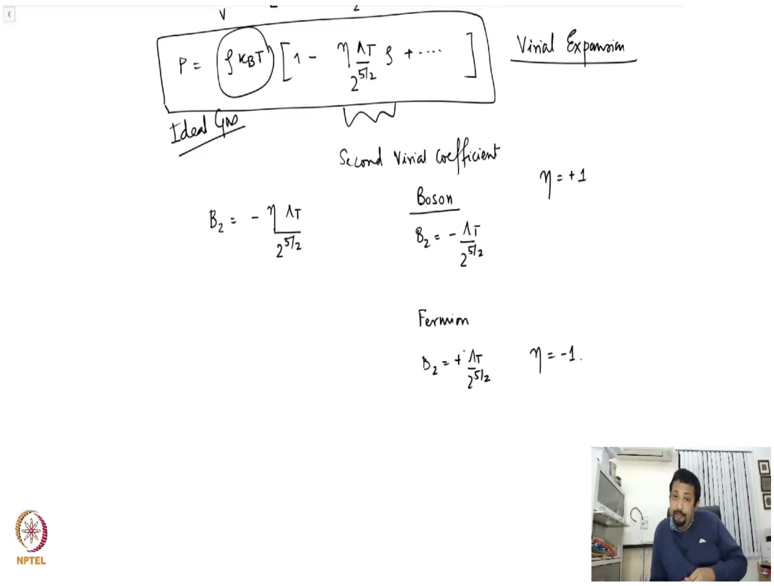

Now, what you see over here? If I recast this as rho k B T 1 minus eta lambda T over 2 to the power 5 by 2 rho plus higher order terms. This is an equation of state and the first term this corresponds to an ideal gas result that we also have several in classical statistical mechanics. But interestingly, it has corrections over this. This is what is called a Virial expansion.

And it appears that even though we have started off with an ideal gas, the moment we give a symmetry to the wave function; moment we say that the system is made up of indistinguishable particles, then we see that the equation of state tells us as if that the system is a interacting system and this quantity is the Second Virial coefficient, that is the general expansion of the equation of state in terms of your density right.

So, that you have B 2 is equal to minus eta lambda T over 2 to the power 5 by 2. For an Boson, Boson eta is equal to plus 1 so that B 2 is minus lambda T over 2 to the power 5 by 2.

For a Fermion, B 2 is going to be minus plus lambda T over 2 to the power 5 by 2, where eta since eta is going to be minus 1 for a Fermion. So, the resulting pressure correction is negative for a Boson, but is positive for a Fermion.

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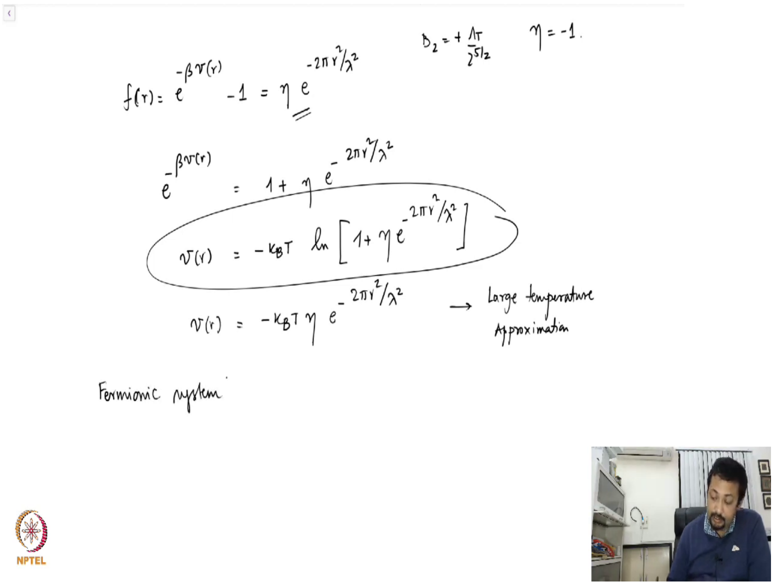

The second virial coefficient is actually obtained from the pair interaction and for an interacting system f r is e to the power beta minus beta v r minus 1 and for our case, this quantity is e to the power minus 2 pi r square over lambda square. This part comes in if you look at this and this.

So, that e to the power minus beta of v r is going to be 1 plus eta e to the power minus 2 pi r square over lambda square and therefore, the effective pair interaction between the particles is given by minus k B T ln of 1 plus eta e to the power minus 2 pi r square over lambda square.

Now, at very high temperatures when lambda is large and therefore, I can approximate v r as minus k B T eta e to the power minus 2 pi r square over lambda square. So, this is the large temperature approximation of v of r.

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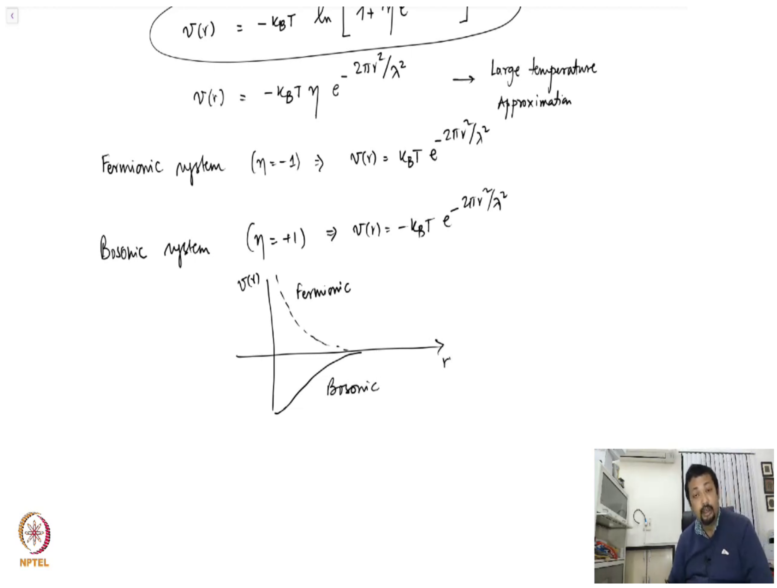

Now, clearly, you see that for a Fermionic system, where eta is minus 1, this implies that the interaction is k B T e to the power minus 2 pi r square over lambda square. For a Bosonic system, eta is equal to plus 1 and implies v of r is minus k B T e to the power minus 2 pi r square over lambda square.

So that the interaction is attractive for Bosons; but is repulsive for Fermions. One can plot this also and if you plot v of r, this is going to go like this way for a Fermionic system and it is going to go like this way for a Bosonic system. So, this is a function of r.