Statistical Mechanics
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Lecture - 43
Free Particle Quantum Canonical Partition Function Free

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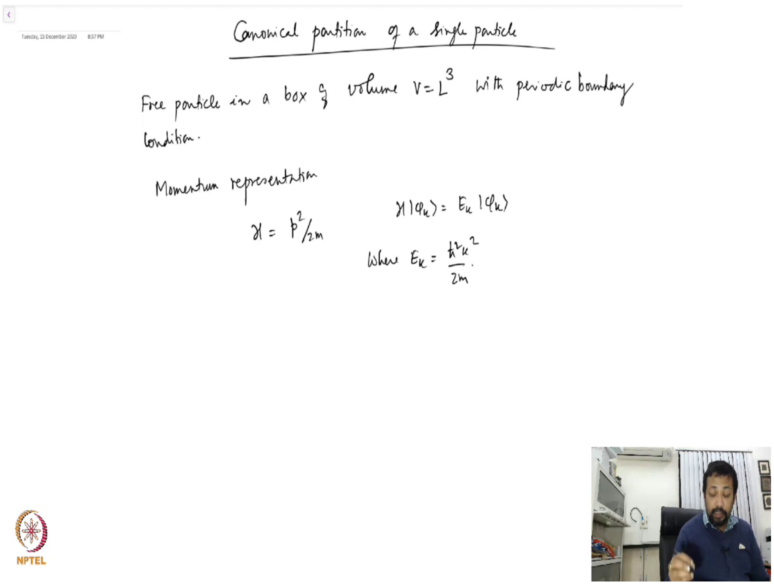

So, we now want to calculate the partition function. Let us say the canonical we will start off with Canonical partition function of a single particle and our first case that we are interested in is a free particle in a box of volume V is equal to L cube with periodic boundary condition right.

So, the task is now very simplified if we look at the momentum representation right. So, in the momentum representation I have the Hamiltonian which is just a single particle is p square over 2m and H of phi k is E k phi k, where the energy eigen value is h square k square over 2m.

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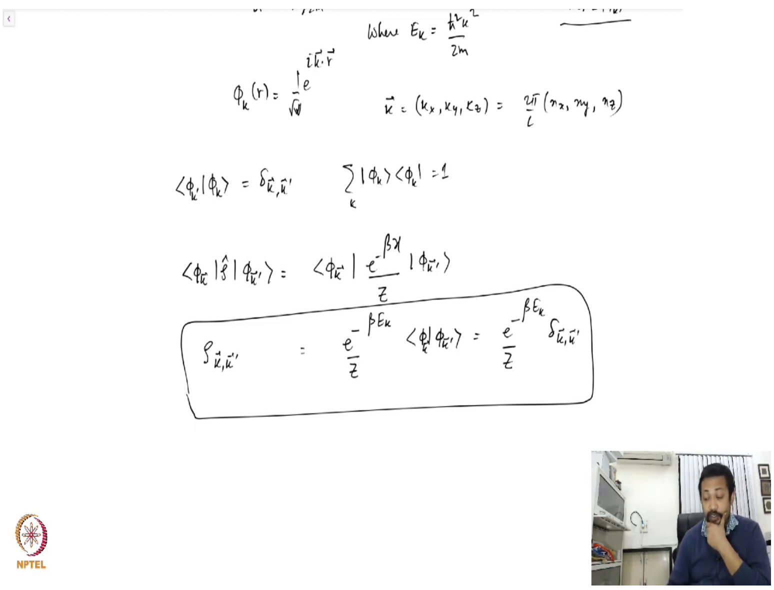

The coordinate the wave function the coordinate representation of the wave function I know that it is i k dot r 1 over square root V and this follows from the box normalization where the vector k x a vector k is k x k y k z which is 2 pi over L n x, n y, n z right. Now, assuming that this box is large enough, so, these eigen values are typically discrete right and it depends on 1 over L.

So, if 1 over L is small which means a box is large enough then you can see that these eigen values they lie very very close to each other right. So, you can imagine that. So, you can consider them to be a continuous spectrum of energy eigen values that you have. Now, the eigen functions are orthonormalized which means phi k prime phi k is delta k k prime and they form a complete set right.

So, now I want to calculate the density matrix in this momentum representation and I know how to do that. So, I have essentially rho hat phi of k prime which is phi k e to the power minus beta h over Z phi of k prime.

And this is going to be minus beta E k over Z phi of k phi of k prime which is E k to the power minus beta E k over Z delta k comma k prime which means that this matrix elements are diagonal in this. So, rho of k k prime is diagonal in this energy representation which is not very very surprise right.

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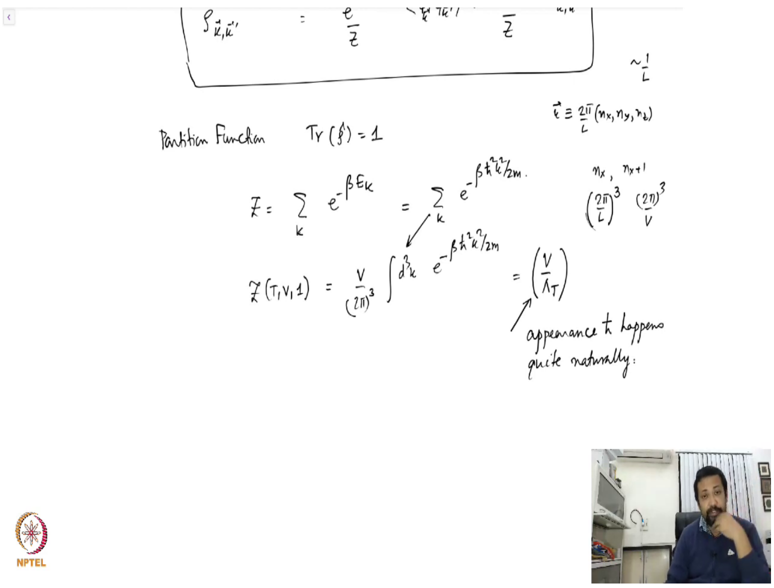

So, therefore, the partition function follows from trace of rho is equal to 1 that is the normalization condition and one gets therefore, Z is equal to sum over k e to the power minus beta E k which is sum over k e to the power minus beta h square k square over twice m.

Now, up to this is fine, but now in order to evaluate the sum I realize that this vector k is equal to 2 pi over L n x, n y and n z discrete values, but it goes as 1 over L. So, clearly if I have a large box that I am considering then this energy values are spaced very very closely. So, one can imagine that for a large box I have a continuous spectrum of energy value.

So, since the energy values are very very closely packed I can convert this into integral. I will write down Z as explicitly Z T comma V comma 1, I have just one particle and this is going to be V over 2 pi whole cube. This discrete sum gets converted into this into d cube of k e to the power minus beta h bar k square over twice pi m.

This you can realize this conversion happens because you know that in let us say you take x direction then n x and between n x plus 1 there is only one mode. So, 2 pi by L contains only one mode right. So, therefore, from that conversion you see that this is in three dimensions this is going to be 2 pi whole cube over L.

So, that is 2 phi whole cube over V this has only one mode therefore, this integral comes out to be if you go from the sum to an internal you are going to use this. And if you do the integral it is not very difficult to do you are going to get V over lambda T, which is exactly the classical partition function for a single particle that we had evaluated.

However, the difference is here lambda T will naturally appear and lambda T contains h bar. So, the appearance of h bar happens quite naturally, it is not introduced in any ad-hoc manner that you can imagine, it is appears because of this form of integral that is it. In classical statistical mechanics we had to kind of introduce it rather ad-hocly saying that well my micro number partition function I am going to take a love of that.

Therefore, Z must be dimensionless, but for such a system hydrostatic system or even for a single particle free particle I know that the partition function is an integral over momentum and coordinates. Therefore, it is dimension full and therefore, I divided by 2 pi h bar because p and q are p times q has a dimension of action and h bar also has the dimension of action right, good.

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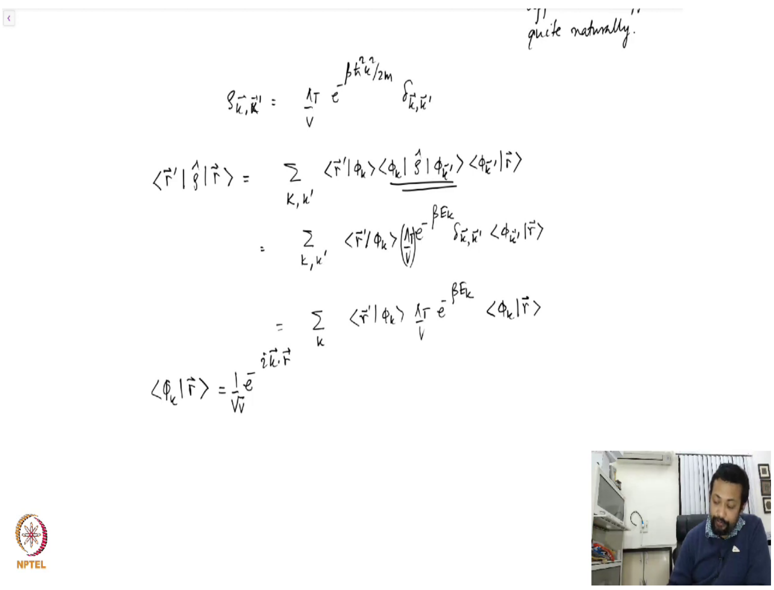

But now so, essentially therefore, I have rho k k prime is lambda T over V e to the power minus beta h bar square k square over twice m delta k comma k prime right. Now, the idea is that I want to evaluate the same density matrix in the coordinate representation. So, in the coordinate representation would mean that I have r prime rho hat and then I have r right.

So, this I can write down k k to I will write down r prime phi k phi k rho hat phi k prime phi k prime r right. So, I introduce the completeness of this and this quantity I already know right.

This quantity is at least this quantity I know is k k prime r prime phi k e to the power minus beta E k we will just use that 1 over z or rather let us explicitly use it lambda T sorry.

So, many stupid mistakes lambda T over V e to the power minus beta it is a k E k delta k comma k prime and then I have phi of k prime r. So, I can carry over ones sum over k and take care of the delta function. So, that I am going to have sum over k r prime phi k lambda T over V e to the power minus beta E k phi k times r right. Now, phi k is minus i k dot r 1 over square root V.

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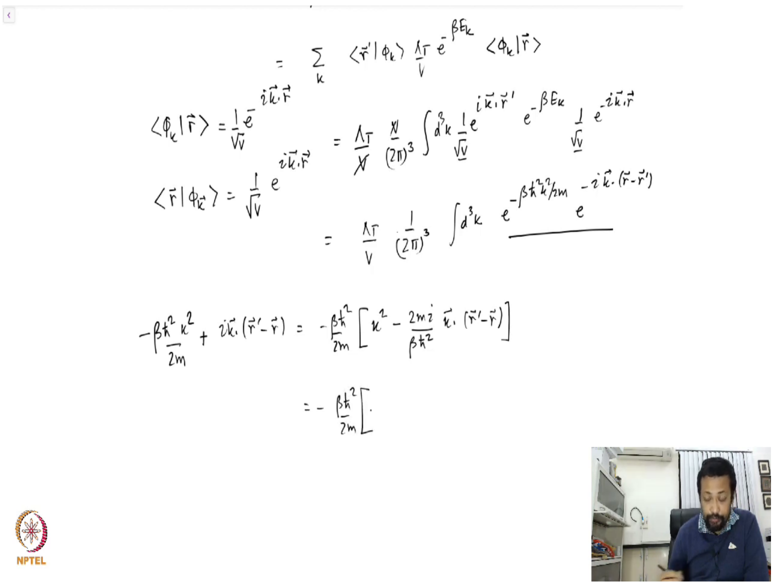

And phi k is 1 over square root V e to the power i k dot r right. So, that this sum is sum over k; so, I have lambda T over V times the sum becomes an integral d cube of k e to the power i k dot r prime 1 over square root V e to the power minus beta E k and then I have 1 over square root of V e to the minus i k dot r right.

So, you see all of this I have a factor V then I have 1 over V here. This, this cancels square root V square root V gives me a V. So, I have 1 over lambda. So, lambda T over V integral d cube of k e to the power minus beta h square k square over twice m e to the power i k minus i k dot r minus r prime.

Let us look at the argument of the exponential. I have minus beta h bar square k square over twice m plus i k dot r prime minus r which I take it as minus beta h square over twice m k square minus 2m twice mi over beta h bar square k dot r prime minus r.

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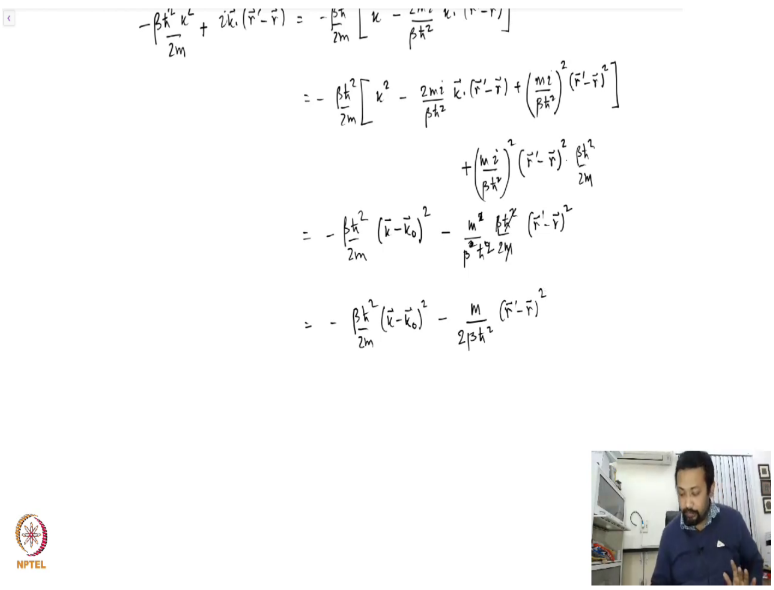

Which is minus beta h bar square this is the standard manipulation of a Gaussian integral and k square minus twice m i beta h bar square k dot r prime minus r plus m i beta h bar square whole square r prime minus r. So, that this argument becomes a complete square and then you are adding this term you have to subtract mi over beta h square whole square r prime minus r whole square times beta h bar square twice m.

So, therefore, this integral, so, this becomes k square. So, we will write down straightforward as k minus k 0 whole square, this gives you an i square as minus right. So, this is going to be (Refer Time: 13:38) one has to be careful over here. This gives you an i square, i square is minus 1 and then there is overall minus.

So, this becomes a plus and therefore, this is going to be minus m square beta square h bar 4 beta h bar square twice m r prime minus r whole square. So, this becomes minus over twice m k minus k 0 whole square. I cancel with the m, one beta goes out, one h square goes out. So, I have m beta h bar square half r prime minus r whole square. So, it will be involved algebra, but nothing which you cannot do; nothing which is not do able.

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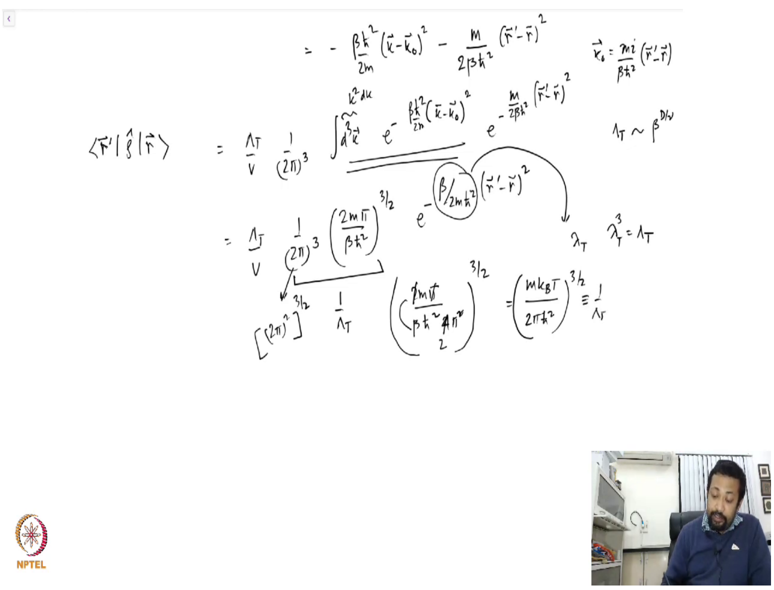

So, your integral over here now is very nicely, your the matrix in the coordinate representation the density matrix now takes the form as lambda T over V 1 over 2 pi whole cube integral d cube k e to the power minus beta h bar square over twice m k minus k naught.

And note that k naught is m i over beta h bar square r prime minus r right; whole square times e to the power minus m over 2 beta h bar whole square r prime minus r whole square. Now, this integral is exactly doable, now it is in a Gaussian form and note that this measure is actually k square d K.

And if you evaluate this integral, so, this is just square root pi by a for one dimension I know, but this is now k square multiply, therefore, this is going to be twice pi whole cube. You are going to get 2m pi over beta h bar square raise to the power 3 by 2 times e to the power minus beta 2mh bar square r r prime minus r whole square.

Now of course, it involves certain limit of amount of algebra. If you carefully look at this then this is just 1 over lambda T right. Just simplify this then you will see that this is going to be 1 over lumber T and this quantity that you see over here is going to be lambda T where lambda T whole cube is going to be capital lambda T.

So, just simplify this. This becomes twice m pi beta h bar square and this term I can write 2 pi whole square times raise to the power 3 by 2. So, this becomes 4 pi square raise to the power 3 by 2 and this is very easy to calculate now.

Beta takes a k B T, m k B T and then you have this gives you 2, this gives you pi. 2 pi h bar square raise to the power 3 by 2 which is exactly your 1 by lambda T, right. Recall in the classical statistical mechanics when we did calculate your define this de Broglie wave length, we said that this quantity goes as beta to the power d by nu. In our case it is beta to the power 3-half and therefore, you have this as 1 over lambda T.

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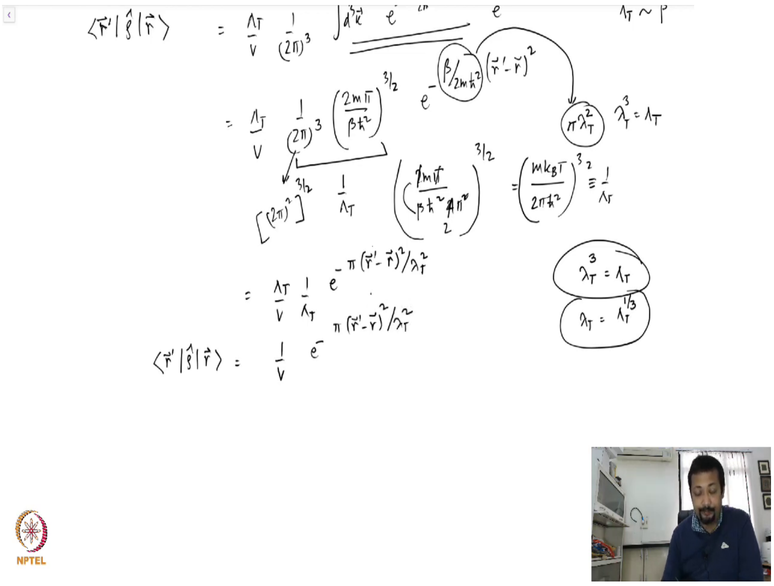

And if you look at this quantity this becomes pi times lambda T square and therefore, this is lambda T over V 1 over lambda T e to the power minus pi r prime minus r whole square divided by lambda T square where lambda T whole cube is equal to capital lambda T and lambda T is lambda T raise to the power one-third; capital lambda T raise to the power one-third.

So, that the expression for the density matrix in the coordinate representation takes a very neat form, which is 1 by V e to the power minus pi r prime minus r whole square divided by lambda T square.

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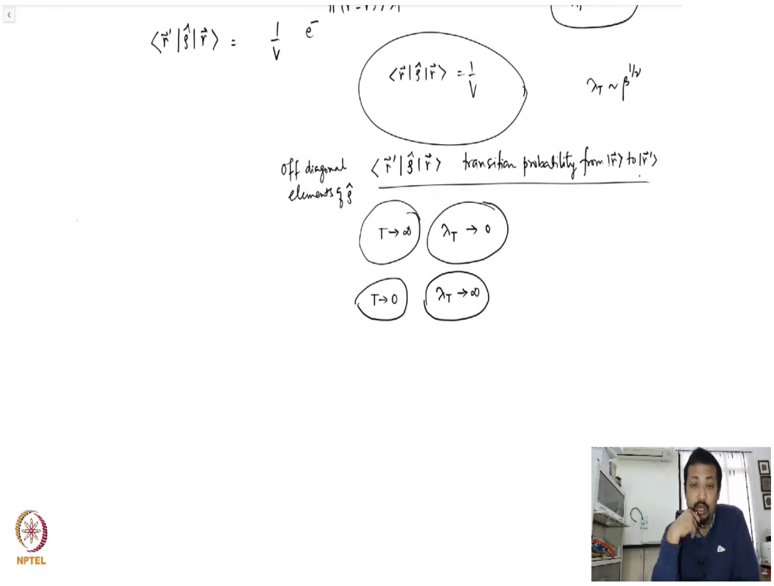

Now, if you look at it carefully then you see that the diagonal elements, which is r rho hat r is equal to 1 by V. And this quantity so, one particle in a volume V and this quantity is nothing but the classical density is a classical density. The transition this off diagonal elements denote the transition probability from r to r prime and these are your off diagonal elements of rho hat in the coordinate presentation.

Now, as T tends to infinity, you know that lambda T go vanishes because lambda T goes as beta to the power 1 over nu. So, in the limit of this when lambda T in the limit of large temperature, when lambda T vanishes you see the off diagonal elements of this also vanish right. So, you only have the coordinate you only have the diagonal elements. When T tends to 0, your lambda T tends to infinity and that is when your off diagonal elements starts appearing and you talk about a transition probability from r to r prime.

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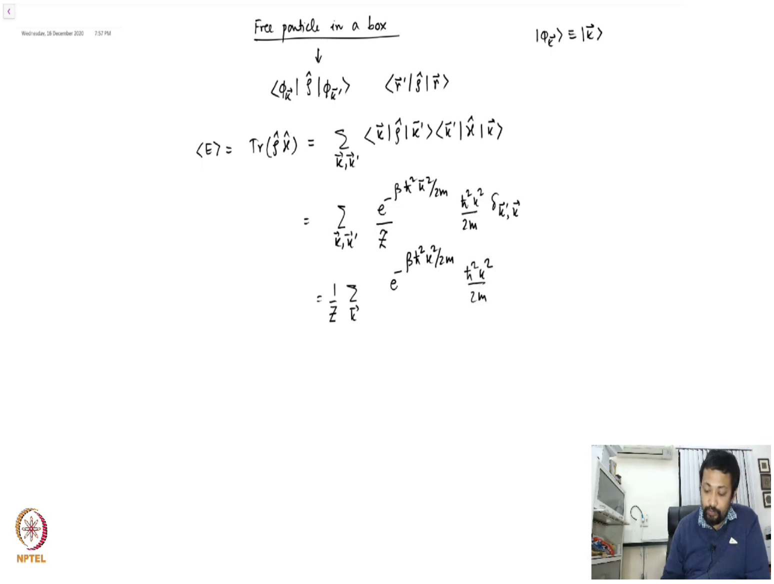

So, we have looked at the ideal gas, free particle in a box and for this particular case we computed the density matrix in the momentum representation as well as in the coordinate representation. So, we calculated phi k phi of k phi of k prime as well as r prime rho hat r. Note that this representation phi k is identical to this presentation and we will use this inter changing.

So, the average energy is given by trace of rho hat h hat which is going to be sum over k k prime k rho hat k prime k prime h hat k and this is e to the power minus sum over k k prime and there is a vector sign on top. Since we are looking at three dimensional system, h square k square over 2m.

The Hamiltonian is h square k square over twice m and I have a Z which comes from rho and I have delta k prime K. So, I can use one of the sums to take care of the delta function and I have 1 over Z e to the power minus beta h bar square k square over twice m h bar square k square over twice m.

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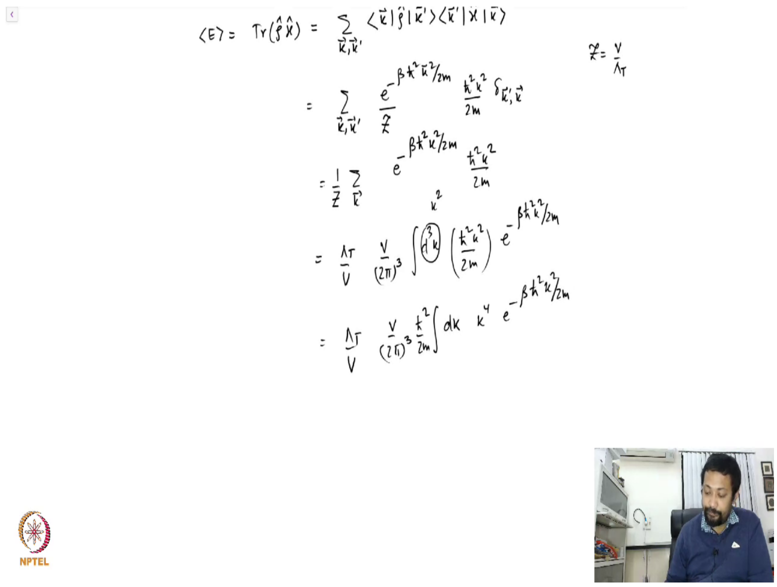

This I know that the single particle partition function is V over the lambda T. So, this becomes lambda T over V. The integral over k can be again converted d cube of k and I have h bar k square over twice m times e to the power minus beta h bar k square over twice m.

So, which means, I have lambda T over V, V over 2 pi whole cube h bar square over twice m dK, this gives me a factor k square and there is already a factor k square. So, this is e to the power minus beta h bar square k square over twice m.

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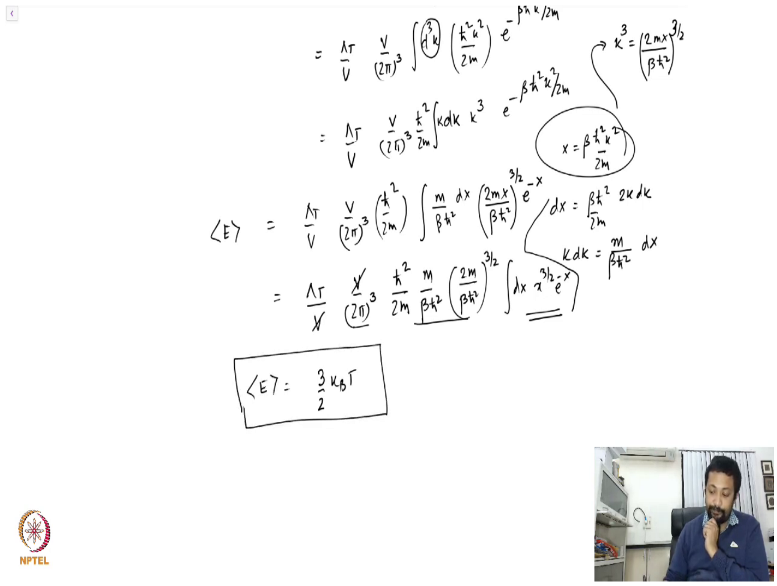

If you substitute x as beta h bar square a square over twice m then dx is beta h bar square twice m times 2 k dK. So, that k dK is going to be m over beta h square bar square times dx. So, average of the energy is going to be lambda T over V, V over 2 pi whole cube h bar square over twice m dK.

So, I can use it as k dk times k cube. So, we will just write it down as k times dk times k cube and k dk is m over beta h bar square times dx. From this relation substitution I know that k is going to be twice m X over beta h bar square. So, raise to the power half. So, k cube is going to be this raise to the power 3 by 2. So, I have twice mX beta h bar square raise to the power 3 by 2 e to the power minus X right.

So, everything comes out now. The lambda T V, V over 2 pi whole cube h bar square over twice m, m over beta h bar square and then I have twice m beta h bar square raise to the power 3 by 2. I have dx x to the power 3 by 2 e to the power minus X.

This I can express it in terms of a gamma function and is going to be and will give me a square root pi. So, if I now simplify this V, V is going to cancel out, all these factor if you simplify you will finally, get that this is going to come out to be 3-half k B T in accordance to the classical result.