Statistical Mechanics
Prof. Ashwin Joy
Department of Physics
Indian Institute of Technology, Madras

Lecture – 13
Classical Ideal Gas (Microcanonical Ensemble)

Good morning to all of you. Today will case of a Microcanonical Ensemble.

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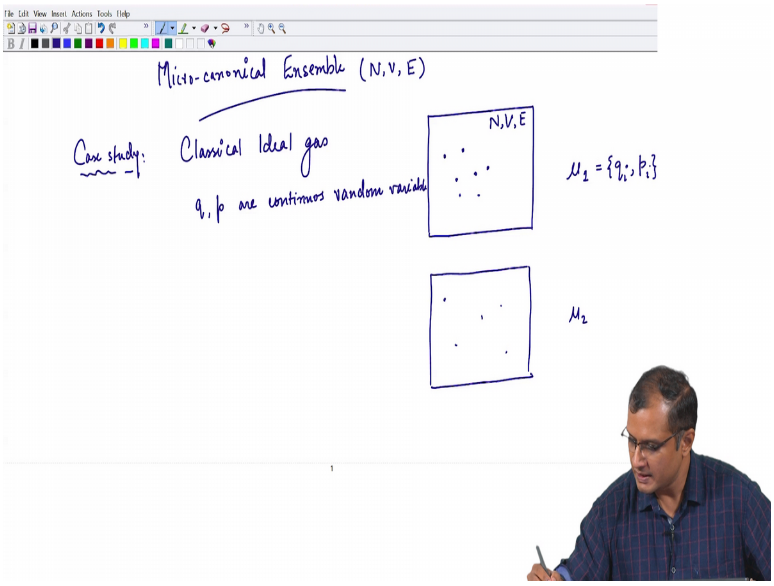

And I am going to take a case study of a Classical Ideal Gas a fixed number of particles volume and energy. So, the case study is that of classical ideal gas ok. So, when I say an ideal gas this is an example of a system with degrees of freedom that are continuous ok. So, if I take a gas inside a box of volume V and there are N particles in this box at the total energy E. So, these particles here basically a free to move anywhere in the box and the moment is also continuously varying.

So, I can say that particular microstate that I have shown here, let us say this is a microstate mu 1 ok of the macro state N V E it is basically of these coordinates r I, I can take the coordinates as position coordinates as q i and momentum coordinates as p i. So, q and p are continuous random variables and so, this is a system with degrees of freedom that are continuous. So, I can also take for example, the same macrostate N V E for a different arrangement of particles ok.

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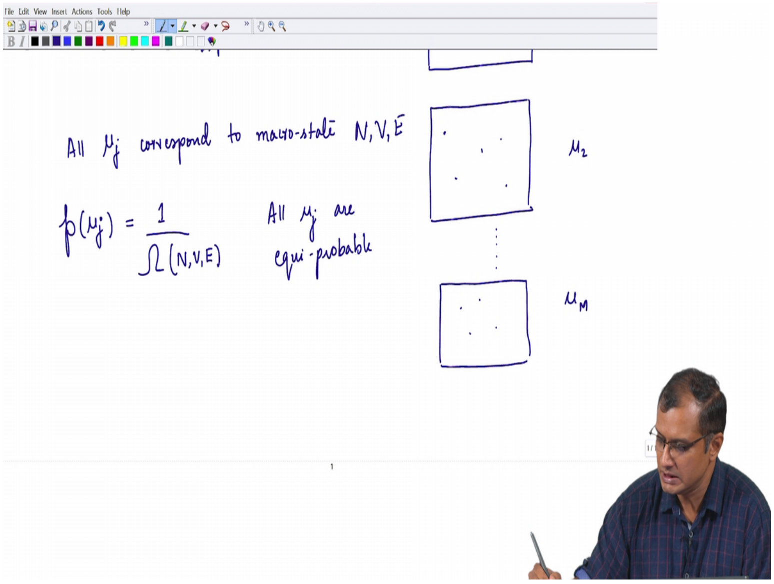

Let us called as mu 2 and this way I can construct a large number of microstates very large number all corresponding to let us say very large number M all corresponding to a macrostate N V E ok. So, all microstates correspond to the same macro state N V E the specified values of N V and E. So, which brings us to the next question what is the probability of finding my system in any j-th microstate. Well, that is of course, 1 upon the total number of microstates assessable to my system at this specified condition of N V and E because all microstates are equiprobable by the Boltzmann assumption.

So, if there are omega number of microstates all of them are equiprobable the probability of getting my system in one of these microstates is certainly 1 upon omega ok.

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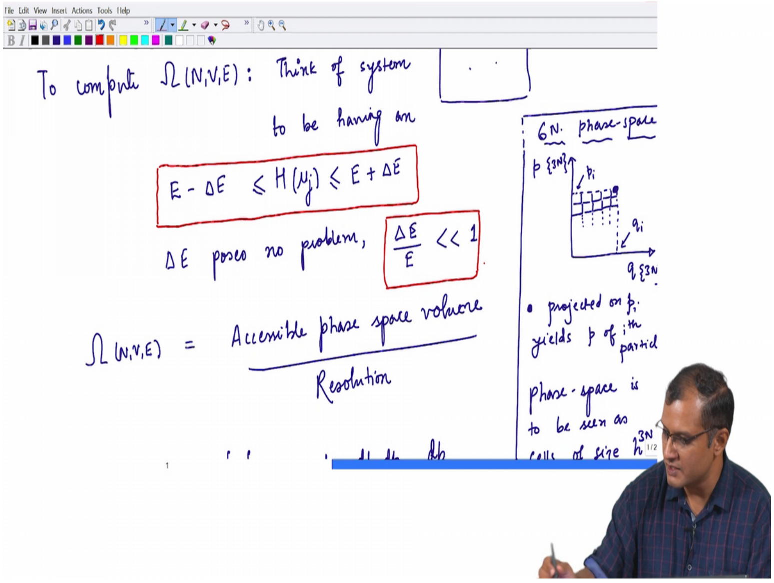

Now, I must compute omega, because that is how I will develop thermo dynamics of the system ok. Because, once I compute omega I can do a lot of things I can compute entropy by taking a logarithm of this omega, from entropy I can compute energy, chemical potential, pressure so and so forth. All thermo dynamic quantities can be computed once I have in my hand the expression for entropy by invoking derivatives of appropriate type. Which means for any thermodynamic calculation to perform I must first compute number of microstates, because that is how I connect statistical mechanics to thermodynamics in the system.

So, to compute the number of microstates you need to understand the following. We can think of our system to be having an energy and I am calling the energy of the system as the Hamiltonian. Let us pick up any Hamiltonian any microstate mu of j and we say that the energy of the system which is basically the Hamiltonian is not exactly constraint to be E, but is allowed to vary between E plus delta E and E minus delta E.

So, as you can see already there is some relaxation of the constraint that the energy has to be strictly E. And I will show you why this relaxation was necessary because, it allows me to compute the number of states in the following way.

Now, if you are worried about the fact that have taken a small spread delta E, you know it poses no problem because I can take delta E to be so small that the ratio of delta over the actual energy of the system is a very small number. So, it is like almost constant energy surface the width is so small that the ratio width over energy is essentially 0 or a very very smaller and number much smaller than 1.

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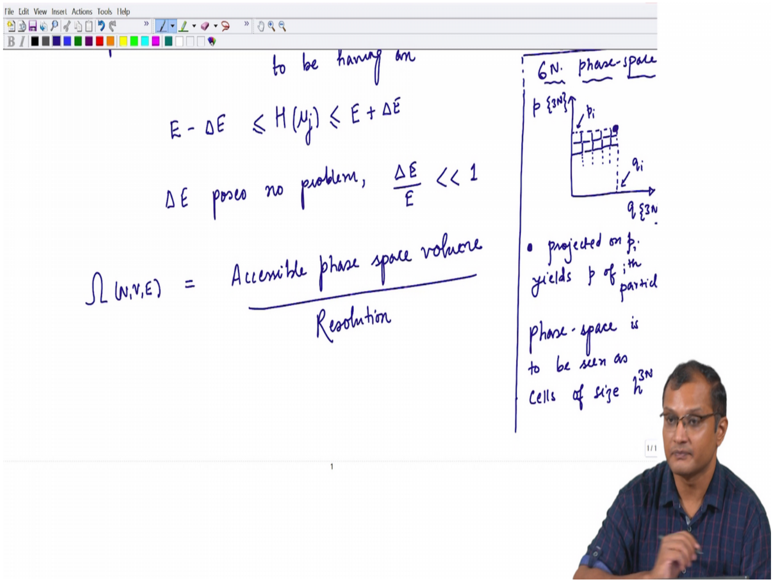

This small relaxation sphere spherical surface to a spherical shell allows me to compute omega as the accessible phase space volume divided by some resolution. Now, what is meaning of assessable phase space volume and resolution? Well, you can think of the following our system has access to is basically you know it can be represented as a single point in a 6 N dimensional phase space. So, I am going to draw phase space here ok. So, I am going to draw a phase space and this is 6 N dimension phase space. So, basically what I have done here is I have taken momentum and I have taken 3 N momentum axis and I have taken positions and I have taken 3 N position axis because, I have a 2 dimensional surface I am constraint to show only 2 axis here, but you must imagine 3 N momentum axis and 3 N position axis.

And in this 6 N dimensional phase space my entire system of N particles is represented by one point which means if I project my point here on some access p of i so, if it is projected on p i. So, basically what I get is the moment of the i-th particle. And similarly if I project it on the q axis then it gives me momenta of i-th particle; this will give me momenta of the p-th i-th particle. Suppose I project this point on p p x of 5th particle it will give me the x component momentum of the 5th particle in the system.

So, what I can do here is compute the assessable phase space volume to my system and divided by the smallest compartment in the phase space accessible to my system. So, I can be divide phase space into small cells; and these cells here are to be you can do this construction of this phase space in as an net of cells of the size ok. So, the phase space here is to be seen as you know cells of size h the power 3 N ok.

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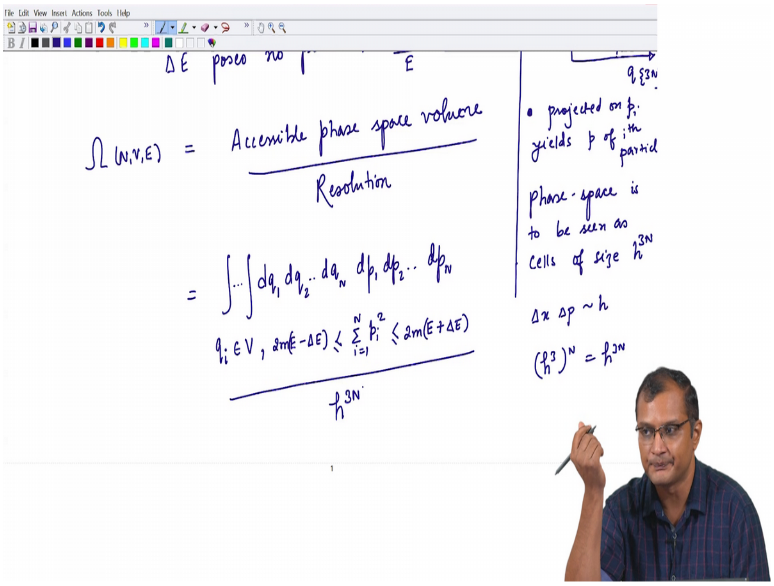

So, the smallest compartment in the phase space has a size h the power 3, which simple reason be for a single particle the moment and the position are uncertain by an order h. Now this is an 1 direction, in 3 directions you will be uncertain by of this product by an amount h cube, for N particles the system point in the phase space is uncertain by an amount h cube to the power N which is basically h the power 3 N. So, this is the smallest resolution or this is the highest resolution you have in this phase space.

So, you can think of the phase space volume as integral over all the position coordinates an integral over all the momentum coordinates subject to the constraint that each position coordinate was inside the volume V. And the momentum coordinates are constrained to have a sum of squares between twice m E minus delta E and twice m E plus delta E ok. So, that is my numerator and the resolution which is basically the smallest cell in my phase space is h to the power 3 N ok.

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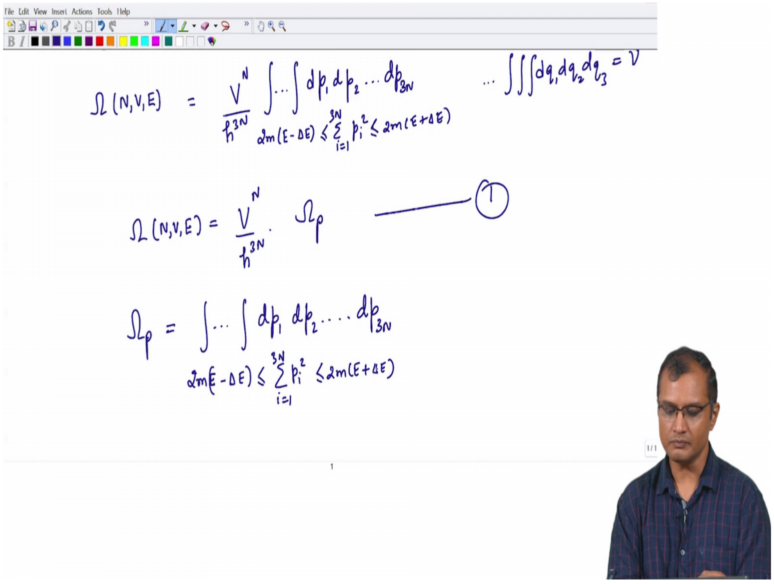

Now, if you integrate the position degrees of freedom each position degree of freedom will give me a volume V because, that is the integration of dq i there are N such position integrals give me V raise to N. And this is multiplied to the leftover which is these momentum integrals 3 N of them actually this is going up to 3 N ok. So, subject to the constraint that: my sum of squares of momentum is between divided by h to the power 3 N ok.

In fact, I will going to write down this h to the power 3 N here ok, what I have done here is just the fact that an integral triple integral of this type is basically volume V and there were 3 N such integrals it has given me V to the power N ok. So, this is what I have used here and now this is given me the number of states accessible to my system macro state N V E. So, let us call this as equation 1 ok.

So, I am going to refer to this integral momentum integral as omega P; omega P and I am going to define it as a. So, I am going to write down let me call this as omega which is my total number of states as V raise to N upon h the power 3 N into omega P and I am going to call this as equation 1. Where, this omega P is just the contribution of omega contribution to omega coming from this momentum spherical shell in 3 N dimension, again the constraint is that the sum of squares of the is momentum degrees of freedom is constraint to be lying between values twice m E minus delta E is going to 3 N here ok.

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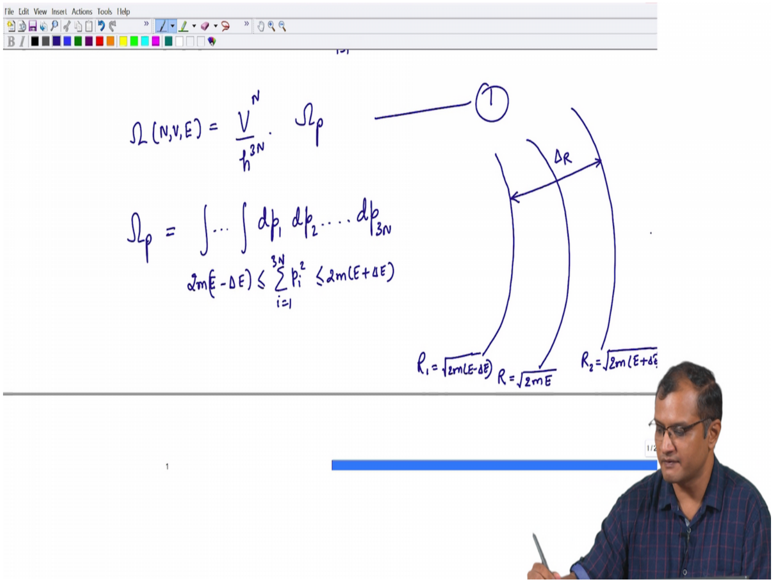

So, you could think of it the following way. So, this is like, you can think of the momentum spherical surface at radius R which is nothing but square root for twice m E and I have called that the radius is a square root twice m E because, the equation of spherical surface is summation over i going from 1 to 3 N p i square equals to R square; the equation in spherical surface and I know this is equal to twice m Es. This is equation of a spherical surface in 3 N dimensions.

So, I can take a one more spherical surface at radius R 2 which is at square root of twice m E plus delta E ok. So, let me write to sort of save the space I am going to write it I have little space available this is a spherical surface at radius square root of twice m E I am going to write down another spherical surface at radius twice m E plus delta E. And, I am going to write down an inner spherical surface with radius R 1 equal to square root of twice m E minus delta E. So, these are the 3 spherical surfaces I have taken.

And width of this shell I am calling it as delta R remember this is the shell that I have taken in the beginning. This shell corresponds to an what I have taken here is a shell of twice delta E ok. So, it is a reminder that I have already taken a shell of thickness twice delta E that simply corresponds to this thickness delta R, ok.

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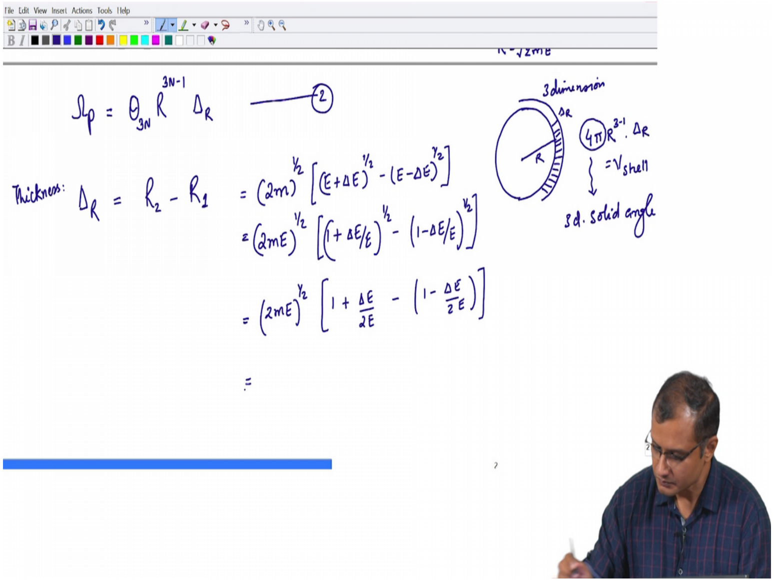

So, this surface is at E plus delta E and the inner most is for E minus delta E. Now clearly I can write down this omega P as, because its spherical shell volume; as some kind of solid angle 3 N dimensional solid angle some kind of a solid angle I am going to refer solid angle by an expression a symbol theta. Let us say theta is a solid angle and just to remind that this is a 3 N dimensional solid angle I am going to raise just put as superscript 3 N for let us say since it is a label that is use a subscript. So, that you do not confuse it as a power. So, this is a 3 N dimensional solid angle multiplied to the radius to the power 3 N minus 1 into thickness which is delta R.

It is very easy because, if you had taken a sphere in sphere in 3 dimensions. Let us say in 3 dimensions, if we have taken a sphere of radius R and you are asked to compute the volume of a spherical shell at radius R and of thickness d R. Well, you could have computed the volume this shaded region as simply 4 pi R square which is 3 minus 1 into delta R this was the volume of the shell ok. So, this 4 pi that you taken is basically the 3 d solid angle into R raise to 3 minus 1 3 is basically number of dimensions delta R; that is what I have done here we have instead of 3 dimension momentum shell I have a 3 N dimensional momentum shell which means instead of 4 pi I have to take a solid angle which is 3 N dimensional that is this guy.

And instead of R to the power 3 minus 1 I have taken R to the power 3 N minus 1 because now the number of dimension 3 N that is the second guy and the thickness that I have taken is delta R which is this guy ok. So, I am going to compute each of them separately ok. So, let us label this as some equation 2 and now proceed. The easiest thing to compute first is delta R thickness of the 3 N dimensional shell. Now this is nothing but R 2 minus R 1 if you look at the figure, R 2 is the outermost R N is the innermost. So, the thickness delta R is R 2 minus R 1 which is nothing but I will take the pre factor square root of 2 m as common, and write it as E plus delta E square root minus E minus delta E square root I am going to take square root E also outside. And this will give me simply 1 plus delta E by E square root minus 1 minus delta E by E square root.

This is where approximation will come to a rest, I have already taken E to be very large and delta E to be small if you recall your observation here or your assumption here I am going to. So, delta E by E is already taken to be a much smaller than 1, which means if I expand it in a Taylor series and a retain terms of only first order then this expansion straightaway gives me each one of these terms inside the square brackets as an Taylor expansion. So, to linear order I can write it as delta E over twice E and I am going to drop terms of the order delta E square minus here I will get 1 minus E by 2 E again I am going to drop terms of the order delta E square here.

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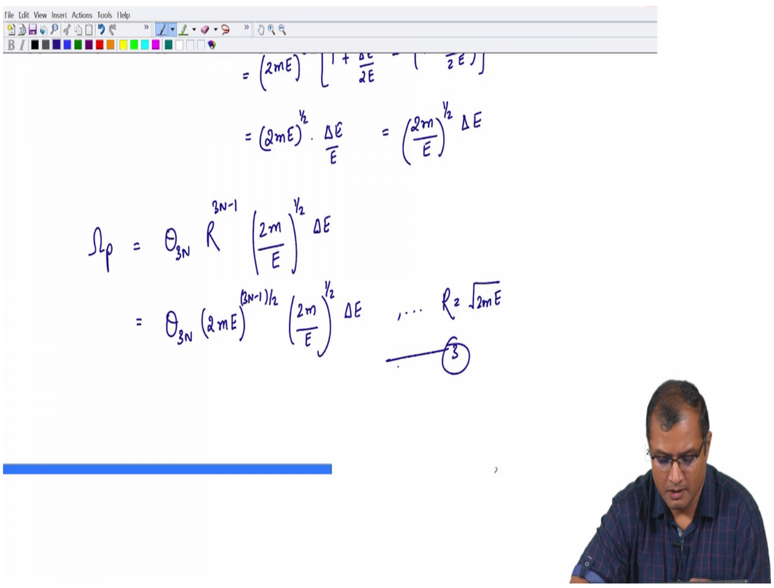

So, this is basically just twice m E square root into delta E by E which is nothing, but twice m by E square root into delta E because delta E is much smaller than 1. So, I will not be taking terms beyond order 1 in delta E. So, delta R is computed very simple. So, let us plug this delta R in equation 2 what we get now is omega P as the 3 dimensional solid angle into R to the power 3 N minus 1 into delta R which is already computed twice m by E square root into delta E and let us plug the value R also R as we already know a square root of 2 m by E 2 m E.

So, I will I can write this as I can simply write it as 2 m E to the power 3 N minus 1 the whole divided by 2 into 2 m by E to the power half into delta E since, I have used R as square root of 2 m E let us call this as equation 3. Now, you can see that the only thing remaining is to compute 3 dimensional solid angle that is the only thing remaining.

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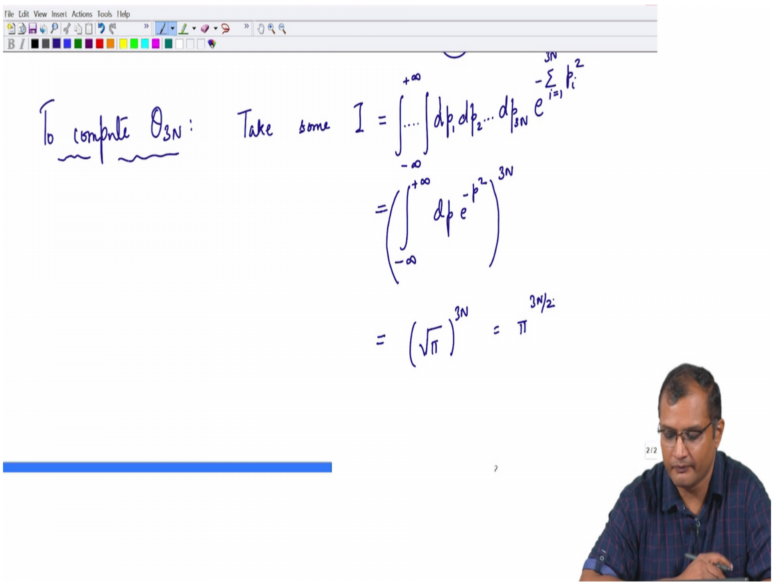

So, here we take a small digression; small digression is needed here I am going to compute different integral disconnected from a problem. So, take some integral this is a pure mathematical construction I which is nothing but the N dimensional integral or sorry 3 N dimensional integral of this Gaussian ok. So, I have got a Gaussian integral an N dimensional.

Now, since all the moment as are independent I can write it simply this integral is between minus infinity to plus infinity each integral on each degree of freedom p i goes from minus infinity to plus infinity and there were 3 N of them. And since, each degree of freedom is independent of the other I can write it as a single integral going from minus infinity to plus infinity of some variable p its a dummy variable. Because, you have definite integral here E to the power minus p square the entire thing raise to power 3 N and you know the guy inside the bracket this is nothing but square root of pi to the power 3 N, because I know that the Gaussian integral is square root of pi.

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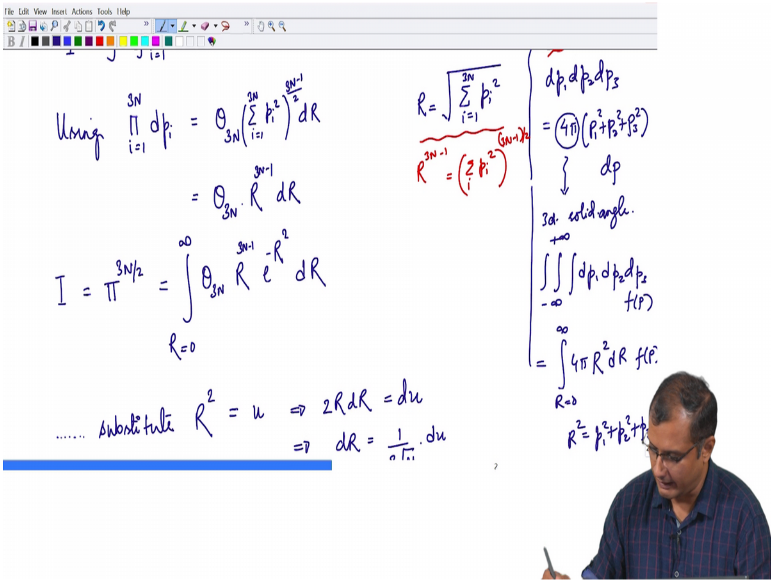

So, I am going to write it as pi to power 3 N by 2. So, I have just computed this integral I as which was defined as these N integrals of this is a product this is the summation this is not a simple pi this is the product of d p i e to the power minus summation overall i going from 1 to 3 N p i square and we have just computed this result as pi to the power 3 N by 2 ok.

I am going to re write this integral, because using the fact I am going to re write integral using the fact that this volume element this volume element is nothing but the 3 dimensional solid angle into my summation over p i square into dR or d ok. So, this is basically I have to define what is the meaning of this R here R here is nothing but square root of summation I going from 1 to 3 N p i square, because summation overall p i square is nothing but R square ok. So, this is because if you have been just 3 dimensions ok.

So, I am just going to show in 3 dimensions dp 1 dp 2 and dp 3 is the volume element I can write it as 4 pi p square which is nothing p 1 square plus p 2 square plus p 3 square into dp where p is nothing but the square root of sum of p square that is what I have written this 4 phi is a nothing but you know 3 d solid angle. So, instead of 4 pi I have taken our 3 N dimensional solid angle which is this term, instead of just p 1 square p 2 square and p 3 square I have taken summation over all p i square which is nothing but my R square.

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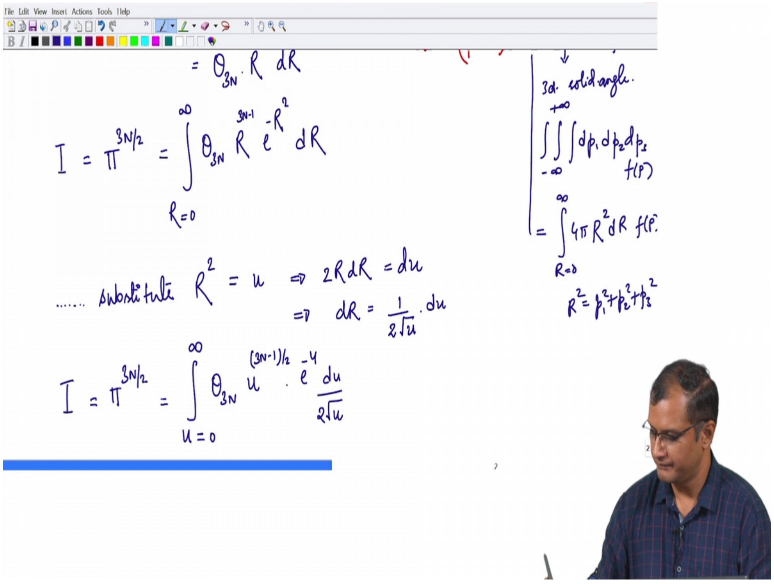

So, this is nothing, but theta to the power 3 N into R square into dR ok.

So, I can write down my integral I as which is already is calculated to be as phi raise to 3 N by 2, but now the I am going to rewrite my integral as simply instead of individual co-ordinates going from minus infinity to plus infinity I have taken now the magnitude which is R. Now, R can only go the radius can only go from 0 to infinity for example, analogy with 3 dimension would be if I take this volume element and sum function of p. This integral if I make p 1 p 2 p 3 all go from minus infinity to plus infinity I can rewrite this as a you know R going from 0 to infinity 4 pi R square d R into f of p where, R square is nothing but p 1 square plus p 2 square plus p 3 square ok.

So, in the same analogy I am going to write down this as ok. So, I am going to use is a analogy with 3 dimensions. So, our integral now becomes theta to the theta 3 N 3 dimensional solid angle into R square and this function. Now our function E raise to minus R square into d R, because we are integrating this I where E raise to minus summation p i square is simply E raise to minus R square, right.

So, I can substitute R square as some u ok. So, this will give me twice R dR as du and which will finally give me my d R as 1 upon 2 into square root of u du correct. So, I am going to substitute this in my integral which is already pre computed to be phi to the power 3 N by 2. But now, this will transform to an integral in u where, the limits on u will go as usual from 0 to infinity theta 3 d 3 N dimensional solid angle R square is already taken as u and E to the power minus u and d R is taken as 1 upon 2 square root of u d u ok. So, let me just check everything here ok.

So, I have made a small error here. So, this is a small correction here this cannot be R square it has to be R to the power 3 N minus 1 ok. So, this has to be basically 3 N minus 1 by 2, because the in 3 dimension you have to take 4 phi R square d R which is R to the power 3 minus 1. So, in 3 N dimensions you have to take radius to the power of 3 N minus 1.

Now, radius itself is summation p i square raise to 1 half as I have written here this is my radius ok. So, R to the power 3 N minus 1 would still which is be this summation i pi square to the power. So, this is this is already 3 N minus 1 by 2 the square root is 1 by 2 correct. So, with the small error this becomes 3 N minus 1 and here this becomes u to the power ok.

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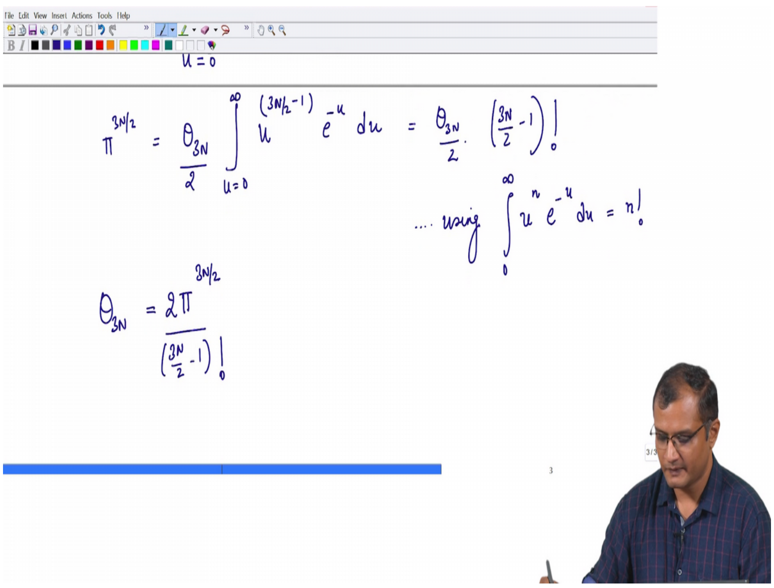

So then, this becomes I can write down pi to the power 3 N by 2 equals to solid angle is a constant this simply becomes integral 0 to infinity in fact I can take 1 by 2 as outside this simply becomes u to the power 3 N by 2 minus 1 into E raise to minus u d u and this is nothing, but the definition of 3 N by 2 minus 1 factorial. So, this gives me nothing, but 3

N by 2 minus 1 factorial whereas, use this result integral 0 to infinity some u to the power N E raise to minus u du is nothing but N factorial ok.

So, I can now compute my 3 N dimensional solid angle as simply pi raise to 3 N by 2 into 2 divided by 3 and by 2 minus 1 factorial.

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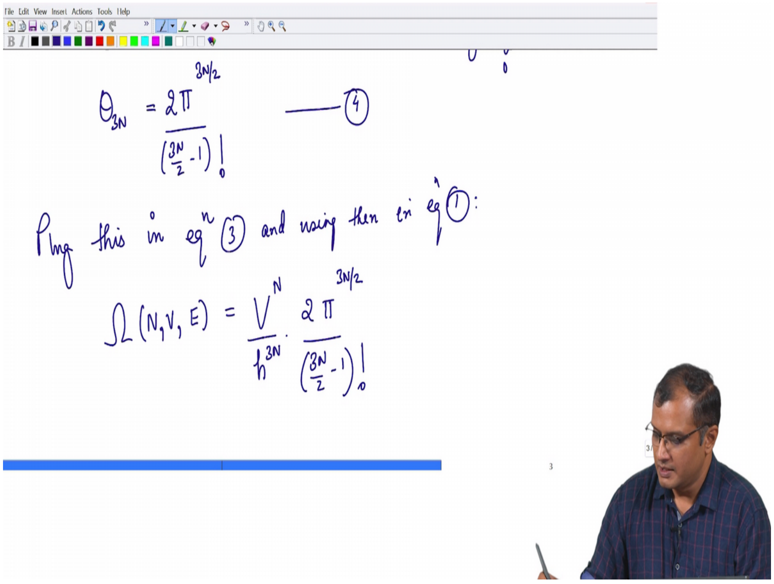

So, let us call this as equation number 4 and you plug this in our equation 3 and that will give you the enumeration of omega or enumeration of microstates. So, our omega p omega number of microstates for our system simply becomes. So, our equation 3 if you see in fact I am going to plug it in equation 1 ok. So, basically to get the final answer somewhat write it as we were to plug it in equation 3 and using then in equation 1 finally we want the omega. So, this we had V to the power N upon h the power 3 N into component coming from momentum space for which we have just computed the solid angle that is 2 phi to the power 3 N by 2 divided by 3 N by 2 minus 1 ok.

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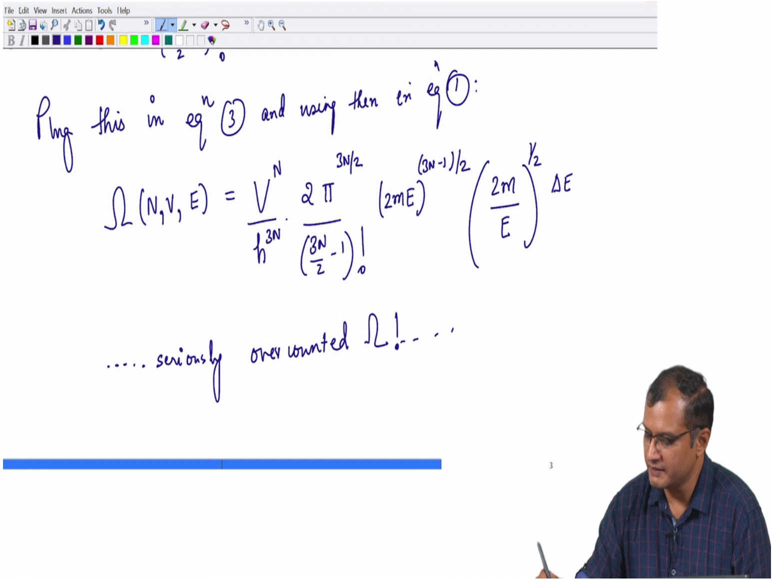

And this component 2 m E to the power 3 N minus 1 by 2 in to let us see something else is pending into square root of 2 m by to delta E fine So, this is the final form of the entropy of the number of states, but there is still a problem here. So, this problem is basically due to the fact that we have seriously over counted the number of microstates I have explained why do we need to correct this.

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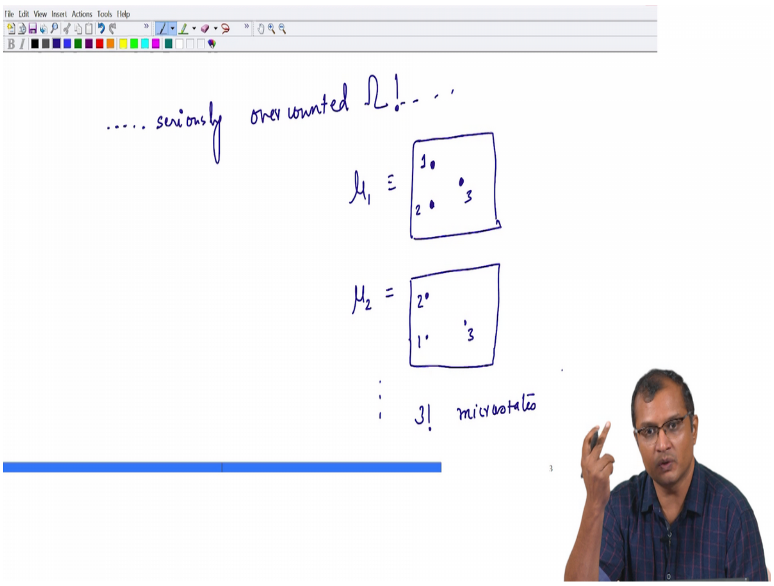

The fact that we have taken a microstate mu a 1 which is basically you know a particles arranged like this someone will show only 3 particles to make the case simple. So, I will take the first particle here second particle here. And the third particle here what you have just computed also includes a microstate precisely with the same arrangement, but particle 2 here, particle 1 here, and particle 3 here without changing the location of 1 2 relative orientation and you can just permute this labels 1 2 3 in 3 factorial ways. So, this is basically there are 3 factorial microstates for just you know 3 relative orientations of 1 2 and 3. Now with N particles clearly there are N factorial microstate that are over counted ok.

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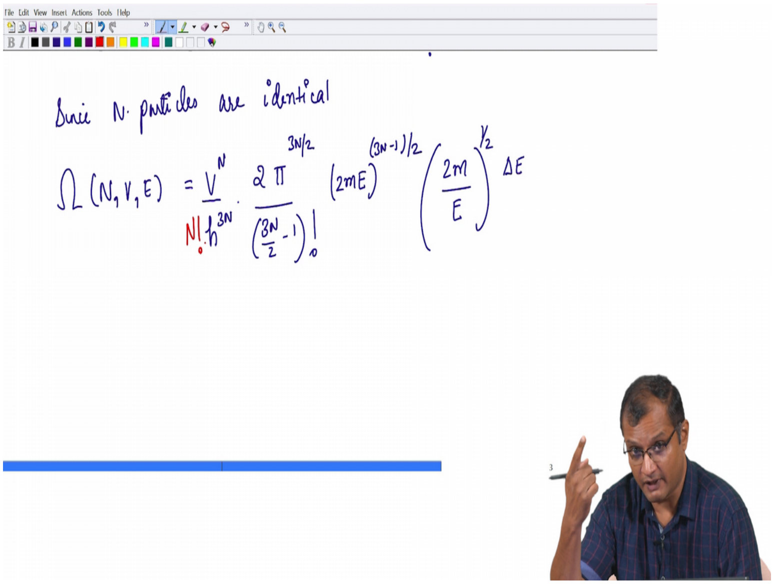

So, I can say that I must correct this over counting, because the particles are indistinguishable since N particles are identical we need to compute the omega number of states by removing all those N factorial permutation that you can do on these N particles. So, our final expression is just this expression that we have computed and I want to correct it forward counting by by simply dividing it by N factorial ok.

So, this N factorial is very necessary and I am going to just remind a user that what you have done here by simply highlighted correction ok. So, this N factorial is correction necessary to remove the over counting of the microstates, because precisely for N particles I can shuffle the positions without changing the relative orientations or relative positions in N factorial ways.

So, each micro state that was computed in omega were basically over counted by a factor which is N factorial.

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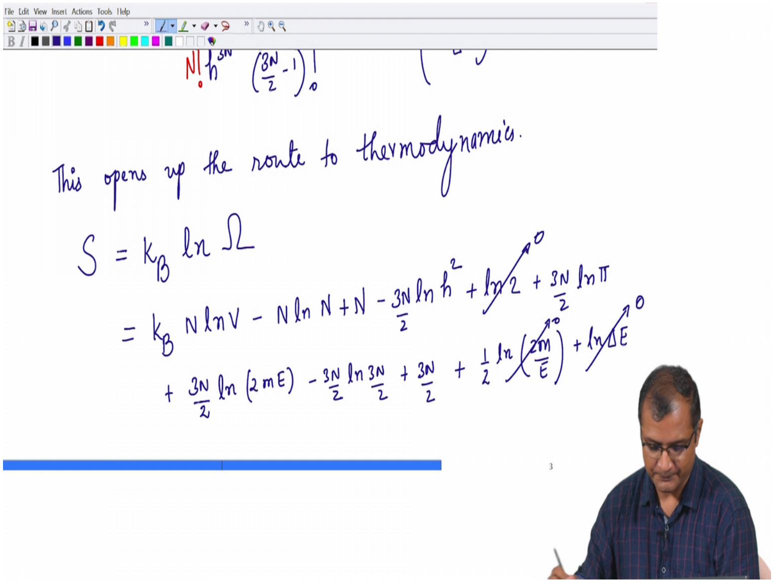

So, I have to correct for that and now I have a correct expression for omega. So, this is the route, so this end the you know or this ends discussion on computation of micro states well it also opens up the route to thermodynamics. And route thermodynamics opened up by simply computing entropy by taking the logarithm of omega by both Boltzmann's formula and I can simply write down take their logarithm using the fact that N is large ok.

So, I can approximate 3 N by 2 minus 1 as 3 N by 2 and write down the entropy as N ln V minus N ln N factorial plus N minus 3 N ln h ok. But I can write it as minus 3 N by 2 ln h square and plus ln 2 plus 3 N by 2 ln pi plus 3 N by 2 I am going to write down 3 N minus 1 by 2 as just as 3 N by 2 into ln 2 m E minus 3 N by 2 ln 3 N by 2 plus 3 N by 2 plus 1 half ln 2 m by E plus l N delta E ok.

Now, there are several terms which can be dropped because there of lesser order much lesser order then the other terms. So, clearly I can drop this term because it is of the order l n E this term also can be dropped. And I am going to drop this is well do these qualities are intensive and they not going as extensive going as N or N l N N ln N ok. So, what I get here is just then the following.

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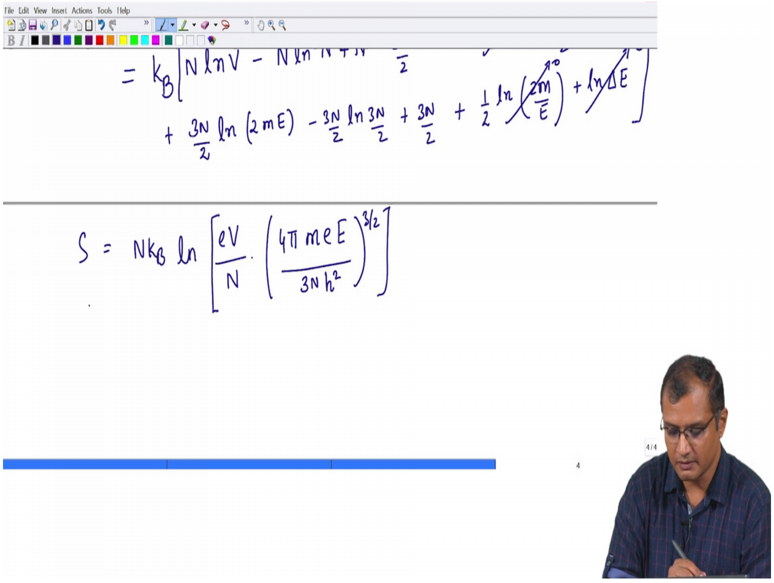

So, I can write this as would entire thing is multiplied by KB. So, this is nothing, but if I take N KB as constant N KB as a constant pre factor and this gives nothing but V by if you re arrange the terms you can write it as e V by N into 4 pi m e E by 3 N h square to the power 3 by 2.

So, this is the definition of entropy. And in the next class we will compute other various thermodynamic quantities starting from this expression for entropy. So, we will break here and we meet in the next class.