# Fundamental of Computational Materials Modelling
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## Lecture 20
## Statistic Mechanics - 2

So good afternoon, let us continue from where we left off.

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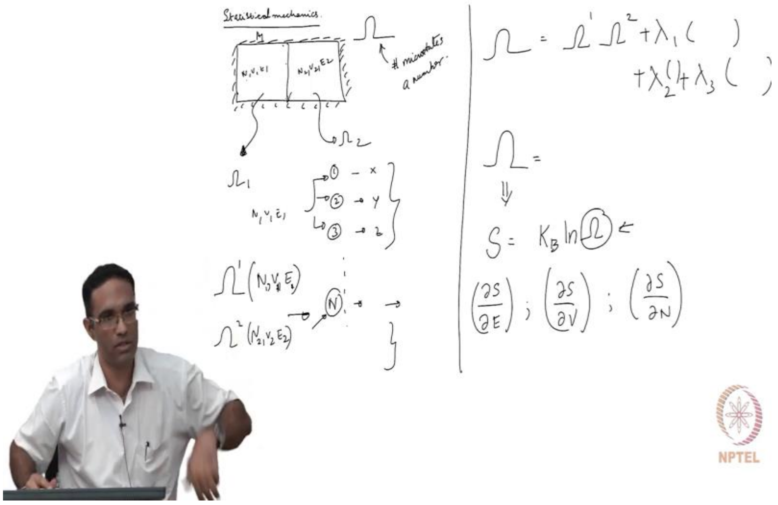

Before going ahead with the new topic I think we will have a quick recap of what we did in statistical mechanics so far. What we were talking about is essentially a certain quantity which we called as omega and we called omega as the number of microstates is basically a number. The total number of ways the system can actually arrange itself when it is at equilibrium.

So if a system is, there are two systems completely isolated from the surroundings and from each other then they will arrange themselves at equilibrium, there will be a certain number of ways they will attain a microstate in such a way that there will be a certain number of ways in which they arrange themselves. Now, it so happens that the manner in which they arrange themselves the is such that the total number of ways by which they can reach their microstate is actually a very very large number.

For example N1, V1, E1 may be reached in say one particular microstate, in say X ways, another microstate in Y ways, maybe another microstate in Z number of ways and so on until say a very large number of possibilities exist. But actually there will be one particular pattern in which it arranges itself say N for which this number, the number of ways it can actually take this microstate is actually extremely large, and it is so large when the total number of molecules is high that all these microstates are simply masked.

So at equilibrium, it is this microstate which appears most frequently or the system spends maximum time in that particular microstate, so most probable microstate. So we are generally concerned with that omega here. So when we say omega in this particular example, when we were talking about this particular example, when we set omega as a function of (N,E,V) what we are saying is, if you substitute N,V and E in this function it is going to give us that particular number the maximum number of ways it is capable of arranging itself in that microstate.

And this is omega 1 for this particular subsystem and there is a omega 2 for the other subsystem and then what we said was, we said that we you know we open this up we said that these two systems can actually be in thermal contact with each other and then we said if the final thing if the final thing has also to be in equilibrium that can only happen if this product omega 1, omega 2 is extremely large with respect to the variables E1, V1 and N1, E2 V2 and N2 and subject to several constraints.

So there were three different constraints here, so this was the final thing that we did where we allowed the central portion of this particular thing to move to exchange material at the same time to exchange energy as well. Consequently we were able to show that once you knew omega, then it is possible for us to define the entropy which is actually a macroscopic quantity as KB log omega and once this is done, then all the other properties of the system such as say the temperature or the pressure or the chemical potential can actually be obtained from this function S.

So our important quantity here is this omega, the total number of ways you can actually attain a particular microstate, and then we went until this the discussion did not involve anything about how we actually obtain that microstate and then we started talking about how we can actually find this out. So this is where you know some there were some questions and this parameter phi started coming in and was a little bit confusing and it is a good idea to actually take a look at it quickly.

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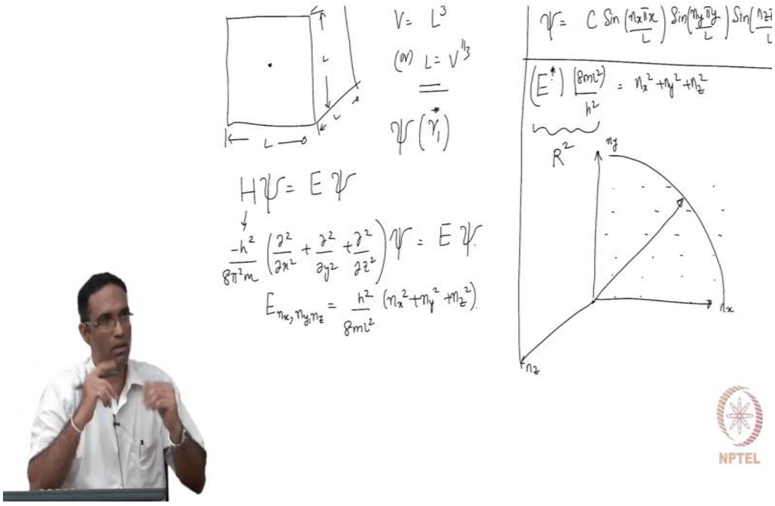
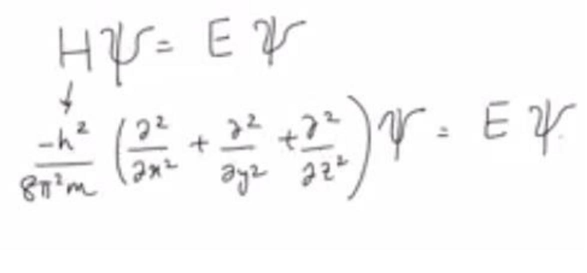


So what we did was, we took the quantum mechanics perspective and considered one particle first there is actually inside a box a 3-dimensional box of length L by L by L. It has a volume V is equal to L cube or L is equal to V to the power 1 upon 3.

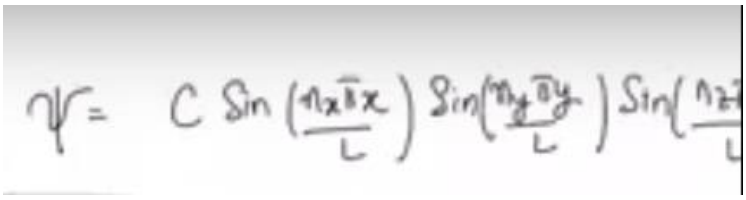
Now when we are looking at it from quantum mechanical perspective, we had to actually solve the Schrodinger wave equation for this particle. Xi is basically the wave function which is a function of the position of that single particle and H is basically the Hamiltonian which happens to be minus h square by 8 pi square m or something like that times dou square by dou X square plus dou square by dou Y square plus dou square by dou Z square.



$$H\Psi = E\Psi$$

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi = E\Psi$$

Now this happened to be a eigenvalue problem and we get E as a function of nx, ny and nz and it turns out to be something like H square divided by 8 mL square and the corresponding value of Z is nothing but some constant times sin nx pi x over L.



So in order to motivate and see how many different ways the energy E of the system can be reached. We assigned a specific energy E star to this value E here, and then said that you know if we were able to look at this value as the radius of a sphere square, then we can actually plot, we have a lot a large number of equispaced points in nx, ny and nz space and if we were able to draw a sphere in the first quadrant of the nx, ny, nz because nx, ny, nz are all positive numbers, such that the radius happens to be equal to square root of E star 8 ml square by h square. Then those and if you count all the points that are actually lying exactly on the surface of this particular sphere of this one eigth of a sphere, you would essentially be getting omega. You would know how many ways this system can have the energy E star. Is that aspect clear? So, we then went ahead and said that particular quantity is kind of difficult to obtain, its kind difficult to obtain and so we took a slightly different approach. What we said was, let us calculate the ... first let us calculate the total number of points that is present for all values of energy less than E star which is nothing but which is going to come from the volume of this particular sphere.

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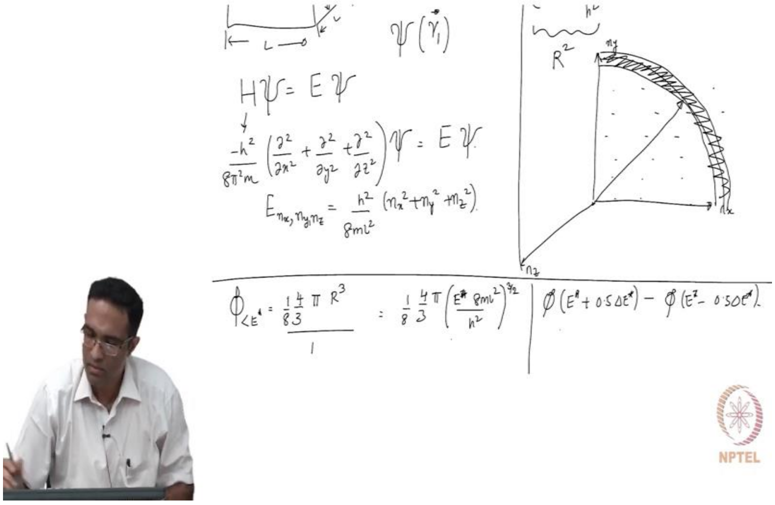

And then we calculated, you know what would be the volume in a spherical shell that is around E star, that is what we did. So this is basically going to introduce this quantity phi where we call this phi less than E star to be equal to 4 by 3 pi R cube divided by volume of one unit in the nx, ny where n is a space which happens to be 1 by 1 by 1 because these nx, ny and nz values are all separated by integer numbers. So this is 1 and this turned out to be 4 by 3 pi and R is nothing but, sorry 1 by 8 of this because it is one eighth of the thing.

So you get here E star, so this would essentially be the total number of points which have energy less than E star.

$$\Phi_{<E^*} = \underline{\frac{1}{8}\frac{4}{3}\pi R^3} = \frac{1}{8}\frac{4}{3}\pi\left(\frac{E^* 8mL^2}{h^2}\right)^{3/2}$$

Now in order to obtain the total number of points in the small spherical shell around E star, what did we do? We did phi of E star plus 0.5 delta E star minus phi of E star minus 0.5 delta E star and that would essentially give us a total number of points that is lying in that belt delta E star and that turned out to be something about that.

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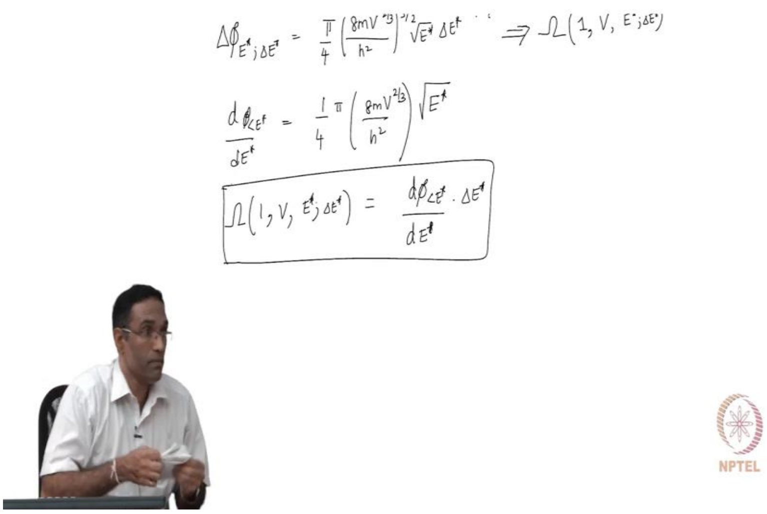

$$\Delta\phi_{E^*;\Delta E^*} = \frac{\pi}{4}\left(\frac{8mV^{2/3}}{h^2}\right)^{1/2}\sqrt{E^*}\,\Delta E^* \Rightarrow \Omega(1, V, E^*;\Delta E^*)$$

$$\frac{d\phi_{<E^*}}{dE^*} = \frac{1}{4}\pi\left(\frac{8mV^{2/3}}{h^2}\right)\sqrt{E^*}$$

$$\boxed{\Omega(1, V, E^*;\Delta E^*) = \frac{d\phi_{<E^*}}{dE^*}\cdot\Delta E^*}$$

So, I shared with you this document also, I hope you received it. Things are a little bit more elaborately explained here in case you have some doubts. It turns out 4 by 3 pi ... we kind of indicated two things, we showed you two graphs, one is that of phi less than E star and showed you the total number of points the order of magnitude of the points.

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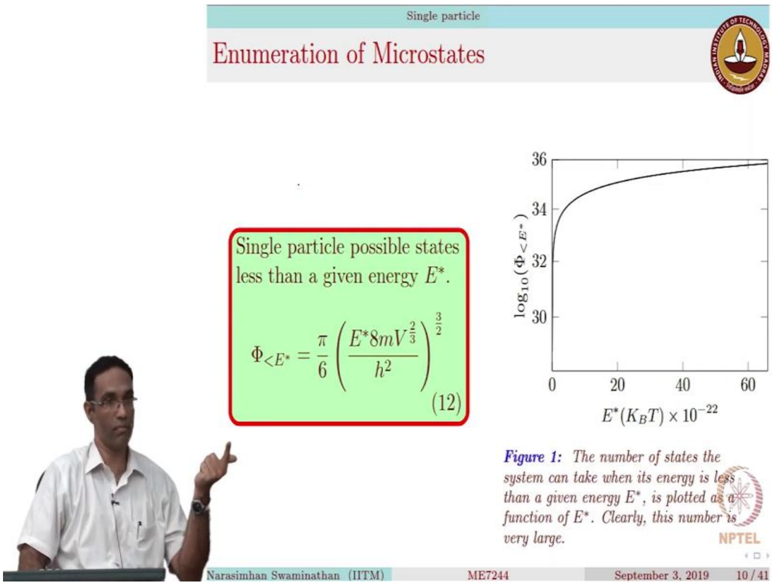

Single particle

Enumeration of Microstates

Single particle possible states less than a given energy $E^*$.

$$\Phi_{<E^*} = \frac{\pi}{6}\left(\frac{E^* 8mV^{\frac{2}{3}}}{h^2}\right)^{\frac{3}{2}} \quad (12)$$

**Figure 1:** *The number of states the system can take when its energy is less than a given energy $E^*$, is plotted as a function of $E^*$. Clearly, this number is very large.*

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for typical values of E, E star, M, L and they all the total number of points that you can have when the energy is less than E star for various values of E star is plotted here and it is in the order of 10 to the power 35 or 36 extremely large, like when compared to the total number of stars in the universe those huge number these are really huge numbers that you get even for moderate values of E star.

Then you can take a look at the quantity and this will turn out to be something like you can just convince yourself that this is indeed true.

Now this is nothing but your omega with some error, this is nothing but your omega except that now I am going to write it as for one particle system the volume is V but the energy is E star with some small error

Student: You said, no. of point at a surface of a particular E

Professor: Yes.

Student: This what ? (And student pointed an error in the equation...)

Professor: sorry, there should not be a E here, ... actually it is, ...

$$\Delta\phi_{E^*;\Delta E^*} = \frac{\pi}{4}\left(\frac{8mV^{2/3}}{h^2}\right)^{3/2}\sqrt{E^*}\,\Delta E^* \Rightarrow \Omega(1, V, E^*;\Delta E^*)$$

$$\frac{d\phi_{<E^*}}{dE^*} = \frac{1}{4}\pi\left(\frac{8mV^{2/3}}{h^2}\right)\sqrt{E^*}$$

this is nothing but your omega.

And if you compare these two equations, you can convince yourself that mistaking the ratios of these two quantities,

$$\boxed{\Omega(1, V, E^*;\Delta E^*) = \frac{d\phi_{<E^*}}{dE^*}\cdot\Delta E^*}$$

it is okay if you are not doing the derivation in detail here in class. You can actually this is just basic algebra, you can just try it out and you will get it. I just do not want to they send some of these expressions are little complicated it is better for me to look at it and do it.

Now, let us try to obtain the same quantity omega, not for a single particle system, but when the box has many particle and these many particles are not interacting with each other, consequently they are referred to a ideal gas, you do exactly the same thing.

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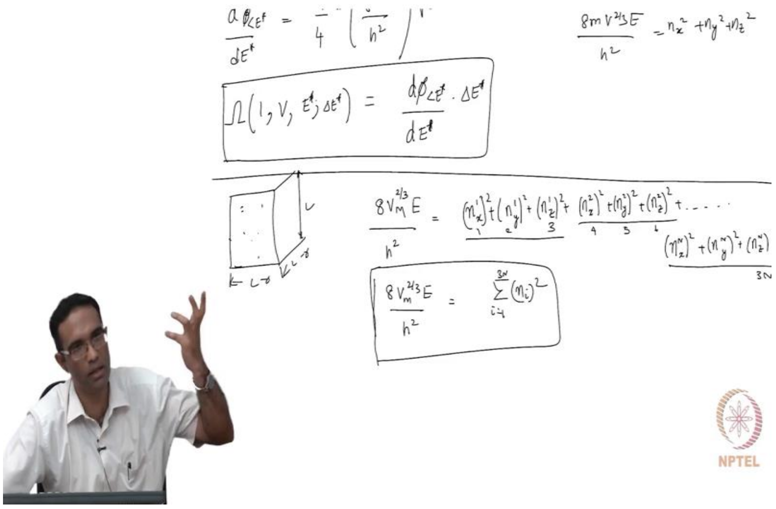


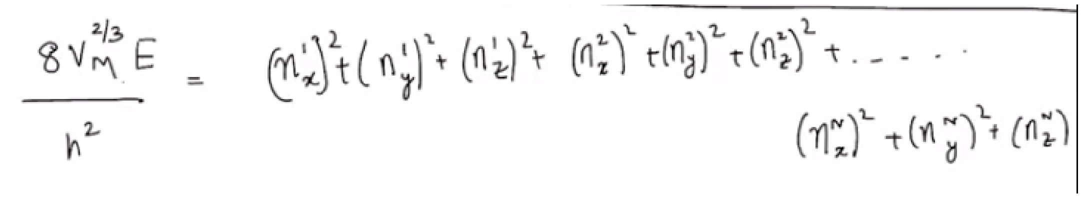
$$\boxed{\Omega(1, V, E', \Delta E') = \frac{d\phi_{<E'}}{dE'} \cdot \Delta E'}$$

$$\frac{8mV^{2/3}E}{h^2} = n_x^2 + n_y^2 + n_z^2$$

$$\frac{8V_M^{2/3}E}{h^2} = \underbrace{(n_x^1)^2 + (n_y^1)^2 + (n_z^1)^2}_{1\ 2\ 3} + \underbrace{(n_x^2)^2 + (n_y^2)^2 + (n_z^2)^2}_{4\ 5\ 6} + \dots \underbrace{(n_x^N)^2 + (n_y^N)^2 + (n_z^N)^2}_{3N}$$

$$\boxed{\frac{8V_m^{2/3}E}{h^2} = \sum_{i=1}^{3N} (n_i)^2}$$

So you have a box many particles length L, length L, L and you have to solve this Schrodinger wave equation, but now at this point of time you are not really interested in the wave function what we are interested in the energies. For the single particle system it turned out that you have 8mV to the power 2 by 3 E divided by h square being equal to nx square plus ny square plus nz square. For the many particle system what happens is the following you have 8. This is what you would have.



$$\frac{8V_M^{2/3}E}{h^2} = (n_x^1)^2 + (n_y^1)^2 + (n_z^1)^2 + (n_x^2)^2 + (n_y^2)^2 + (n_z^2)^2 + \dots (n_x^N)^2 + (n_y^N)^2 + (n_z^N)$$

Student: Last term ?

Professor: what is it?

Professor: Ok? Where this corresponds to particle one, this corresponds to the second particle, this corresponds to the third particle and so on. So this reduces to some term that looks like this.

$$\frac{8V_m^{2/3}E}{h^2} = \sum_{i=1}^{3N}(n_i)^2$$

So you know if I say n2 it means that it is the ny of the first particle and so on. If I say it is n3 then it is the nz of the first particle, if I say n4 then it is nx of the second particle and so on. You can easily see that this is in fact true. Now we use exactly the same methodology that we did for the single particle, you have a question?

Student: In real system, there is going to be some interaction ?

Professor: There is going to be some interaction, right now there is no interaction, it is just an ideal gas.

So now,

Student: Why is it from 1 to 3N?

Professor: why it is from?

Student: Why is it from 1 to 3N?

Professor: Yeah I am just calling this as 1, this as 2, this as 3, this is 4, this as 5, this has 6 of this would essentially be 3N. That is why I am calling it as 3N. So this equation is once again the equation of a sphere in three n-dimensional space. So if we are able to if you have a formula just like how we are the formula for 4 by 3 pi R cube for a sphere and three dimensional space. If we have a corresponding formula for 3 n dimensional space then our work is basically simplified to a large extent.

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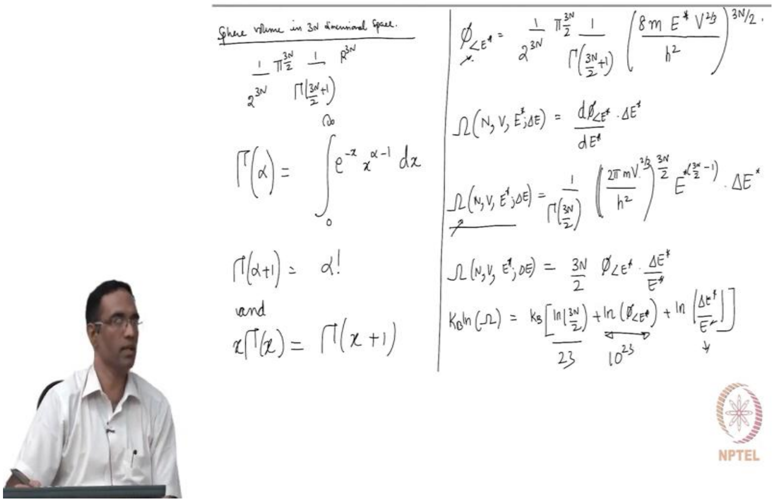

Sphere volume in 3N dimensional space.

$$\frac{1}{2^{3N}} \pi^{\frac{3N}{2}} \frac{1}{\Gamma\left(\frac{3N}{2}+1\right)} R^{3N}$$

$$\Gamma(\alpha) = \int_0^\infty e^{-x} x^{\alpha-1}\, dx$$

$$\Gamma(\alpha+1) = \alpha!$$

and

$$x\Gamma(x) = \Gamma(x+1)$$

$$\phi_{<E^*} = \frac{1}{2^{3N}} \pi^{\frac{3N}{2}} \frac{1}{\Gamma\left(\frac{3N}{2}+1\right)} \left(\frac{8mE^* V^{2/3}}{h^2}\right)^{3N/2}.$$

$$\Omega(N, V, E^*; \Delta E) = \frac{d\phi_{<E^*}}{dE^*} \cdot \Delta E^*$$

$$\Omega(N, V, E^*; \Delta E) = \frac{1}{\Gamma\left(\frac{3N}{2}\right)} \left(\frac{2\pi m V^{2/3}}{h^2}\right)^{\frac{3N}{2}} E^{*\left(\frac{3N}{2}-1\right)} \cdot \Delta E^*$$

$$\Omega(N, V, E^*; \Delta E) = \frac{3N}{2} \phi_{<E^*} \cdot \frac{\Delta E^*}{E^*}$$

$$k_B \ln(\Omega) = k_B\left[\underbrace{\ln\left(\frac{3N}{2}\right)}_{23} + \underbrace{\ln(\phi_{<E^*})}_{10^{23}} + \ln\left(\frac{\Delta E^*}{E^*}\right)\right]$$

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So sphere volume in 3N dimensional space, turns out that the formula is the following. That is the formula for a sphere in 3N dimensional space, where gamma is basically the gamma function, so what is gamma function? It has some interesting properties. Where you have gamma x into gamma of x is equal to gamma of x plus 1 and gamma of x is equal to.... sorry gamma of , yeah this is all the properties I think we have studied this in different places. So we do not want to prove all these things, but we will just accept this.

So this happens to be the volume of the 3N dimensional sphere. So in our case for phi less than E star turns out to be 1 divided by 2 to the power 3N phi to the power 3N by 2 1 divided by this function gamma and this R to the power 3n where R was our 8m E star V to the power 2 by 3 divided by h square the whole root, so you have here 3N divided 2.

We had square root of R, so that is why you have this 2 in the denominator and this was taken to the power 3N, so we have this 3N here. So once you have phi less than E star, we can calculate our omega for N particle system occupying the volume V which has the energy E star around delta E to be equal to d phi less than E star divided by dE star times delta E star, just like how we did for the 1 particle system.

This is exactly the same expression that we had for our single particle system.

Student: N particles, ???

Professor: N particles, 3N degrees of freedom. So this quantity turns out to be something like this.

$$\Omega(N, V, E^*; \Delta E) = \frac{1}{\Gamma\left(\frac{3N}{2}\right)} \left(\frac{2\pi m V^{2/3}}{h^2}\right)^{\frac{3N}{2}} E^{*\left(\frac{3N}{2}-1\right)} \cdot \Delta E^*$$

So this is all delta E star, this would be the total number of complexions, total number of ways the system can actually arranges itself at equilibrium this ideal gas. So we obtained this omega for an ideal gas as a function of V, N and the energy E that you can actually have.

But still we are left with this delta E kind of quantity and we really do not know what to do about it, but we can actually do something more and show that show something really interesting. For example, if you wanted to find out the entropy of this gas now, what would you do? Take KB log E.

So this one is again before doing that this particular expression can once again be written in the following form. This happens to be equal to if you do a little bit of manipulation you can show that this is equal to 3N by 2 phi less than E star times delta E star by E star. omega, if you compare this expression and this expression right here, you can actually show that this omega is nothing but 3 n by 2 times this expression times delta a star by E star.

If you are not convinced, you can just take the ratio and see for yourself that it will in fact be true. Now when you want to calculate the thermodynamic quantity entropy you would essentially do KB log of this quantity omega.

So what happens when you take KB log omega on both sides you get this to be ln of this entire term here which is ln of 3N by 2 plus ln of phi less than E Star plus ln of delta E star by E star. What can you say about this expression? Which of the three terms on the right hand side is actually going to be important to us?

So N, what is N in the order for an ideal gas? May be in the order of 10 to the power 23 n is in the order of 10 to the power of 23. So this term is going to be in the order of 23, It is going to be some 23 or something like that 23. This term is the ratio of energies, it is going to be a very small quantity it is not going to be very significant. Look at this term, this term is actually having power N or power 3N by 2, so this term is going to be of the order of 10 to the power 23.

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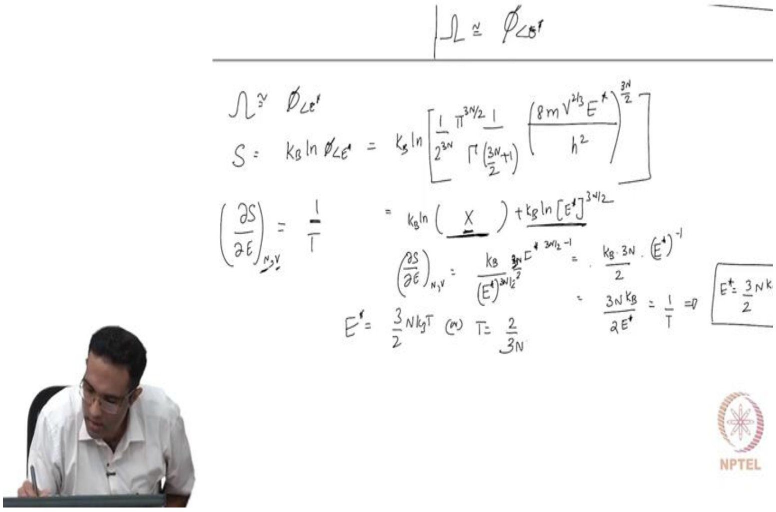

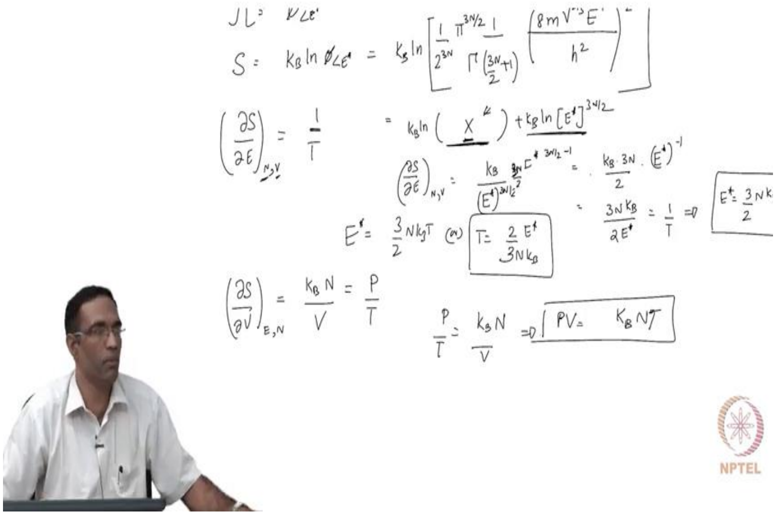

The central term is going to be of the order of 3 n by 2, what this essentially means is KB log of omega is approximately equal to KB log of phi less than E star. Essentially what is this is telling us is when the number of particles is extremely large, whether you consider the total number of particles that is right around E star or whether you consider all the particles beneath it, it is not going to affect our results significantly.

Because of the sheer number of particles that you are having and the number of ways the system can actually arrange itself in that particular microstate. So from now on like what is done in most places our omega is replaced with phi less than E star, I think this is actually a very interesting result I do not think we would have seen it coming.

So omega is approximately equal to phi less than E star, therefore our entropy S is nothing but Kb log of phi less than E star is equal to Kb log of this quantity right here which is this is our entropy expression for entropy for an ideal gas in terms of N, V and E.

$$\Omega \simeq \phi_{<E^*}$$

$$S = k_B \ln \phi_{<E^*} = k_B \ln \left[ \frac{1}{2^{3N}} \pi^{3N/2} \frac{1}{\Gamma\left(\frac{3N}{2}+1\right)} \left( \frac{8 m V^{2/3} E^*}{h^2} \right)^{\frac{3N}{2}} \right]$$

Now I am going to give you an exercise.

Can you find out what the pressure is and the temperature is? So you know that dou S by dou E when you keep N and V a constant, you are supposed to get supposed to be 1 by T according to thermodynamics. Can you tell me what that is? You are supposed to differentiate only with this E star or E. So you can actually club everything and get rid of everything and have only the term which is log E to the power 3N by 2. Perform the differentiation, do it.

Find the pressure temperature, you have seen this before? Kinetic theory of gases. So did you all get this expression? Did you know it is not very complicated, it is just this expression for S looks big but you are only going to differentiate with the E star. So Club all the terms that does not have the E star here and just write it as plus KB log E to the power 3N by 2 and then take the derivative with respect to E.

From the definition of temperature itself you know that you have to keep N and V constant, since N and V are going to appear on his X, they are going to be constant. So it would be 0 if you differentiated that anyways. So you just have to differentiate this with respect to E star and you get this expression 1 by T is equal to 3 by 2N KBT, sorry E star, the energy of this ideal this gas is 3 by 2N KBT or the temperature is nothing but 2N.

$$\boxed{T = \frac{2 E^*}{3 N k_B}}$$

Can you find out the pressure? Dou S by dou volume keeping the, energy and the number of species are constant, yes this?

Student: How are you differentiating ?

Professor: It does not, see when you are differentiating the entropy with respect to energy, you have to keep N and V a constant. Keeping that a constant is important, that X that I have written here is going to depend only on N and V.

So I am differentiating with respect to energy so that it will not turn of. What does this turn out to be dou S by dou V? I do not know I am going to trust you, so tell me that what is it KB into, that is equal to what? That is equal to P by T. So you have P by T is equal to KB times N over V which implies PV is equal to Kb times NT.

$$\frac{P}{T} = \frac{k_B N}{V} \Rightarrow PV = K_B N T$$

You have seen this before? The relationship between pressure and volume for an ideal gas. I think so far in thermodynamics this relationship was probably told you. P for ideal gas PV is equal to NRT or NKBT, but here from the knowledge of the number of ways you can arrange this system, you are able to re-derive it. So this is giving you one additional level of depth into the thermodynamics of the system by which you can actually prove these relationship.

Which is the whole purpose of this exercise was to show you that something like this is possible from Omega nothing more it does not matter if you are not able to actually you know write down these equations without seeing, but the idea was to show that this PV is equal to NKbT was obtained from a slightly more fundamental principle from the fact that this omega exists for a system at equilibrium, I think that is really amazing.

So the whole thing is once you obtain omega, you can actually get everything from the system. This should be clear that once you know how to write omega for all systems suppose you were able to write omega for all systems then you are basically done with the whole problem is omega is not so easy to write down even for ideal gas it took us all these complicated formulas for sphere 3N dimensional space and all that.

But there is still a small problem with this expression, because I will just illustrate that expression I want you to go and check whether what I am telling you is true. There is a little bit of algebra here, so I cannot it is too much for me to do it do it here.

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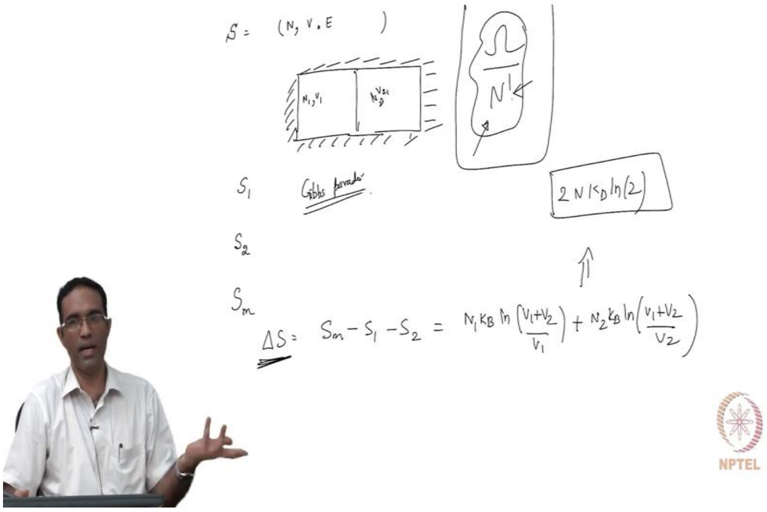

So if you take the entropy expression you have some big expressions here and you consider gases in two chambers. This one is N1, V1, E1 and N2, V2 and E2. So you have some expression here in terms of N, V and E, this is isolated. You can get S1 for the system1 by substituting the value of N1, V1, E1 S2 when you substitute the value of N2, V2 and E2.

Now, I am allowing the two gases to mix up, obviously this is actually an irreversible process, it is an irreversible process, consequently the entropy of the mixture can be obtained by substituting in this expression N as N1 plus N2, V as V1 plus V2, E as E1 plus E2 or the total energy of the system and he would get the entropy of the entire system.

However, the change in entropy that has taken place after this mixing process which is Sm minus S1 minus S2, must actually be a positive number because it is a irreversible process. Is that right? This term provided the particles are of the same mass, turns out to look something

$$\Delta S = S_m - S_1 - S_2 = N_1 k_B \ln\left(\frac{V_1+V_2}{V_1}\right) + N_2 k_B \ln\left(\frac{V_1+V_2}{V_2}\right)$$

like this. Please try it out, there is little bit algebra that is all, it turns out to be like this, which is positive quantity, which is fine telling us that the change in entropy during irreversible process of two gases mixing is supposed to be irreversible process.

But now what happens V1 is equal to V2, N1 is equal to N2 what happens? This turns out to be what? 2N kb ln 2, when I say N1 equal to N2, V1 equal to V2 and I say that they are mixing they are basically it is a irreversible is a reversible process, they are this you are just inserting this thing back in again here, consisting of the same gas do you see that. I am saying N1 equal to N2, V1 equal to V2 everything is equal.

When I am simply allowing the two gases to mix they are, of course there I want them to be in thermal equilibrium with each other, they are in thermal equilibrium with each other…

Student: E also?

Professor: Yes, E is also equal. So then if you do this process what happens is, you are essentially saying that there are you are just inserting a partition between already mixed gases, it is not already in equilibrium, but our expression for the change in entropy is turning out to be positive, but it should be 0.

So we have actually committed some sort of an error in calculating our omega it turns out that this omega is supposed to be divided by this term part N factorial because simply because of the fact that we have considered each of these particles to be distinguishable that means, you are able to catch one atom and say this is atom A and this is atom B and this is atom C. But in reality there is no difference, you cannot make out the difference.

The particles are actually indistinguishable when you account for this indistinguishability of the atoms then, it so happens that the total number of complexions have to be divided by N factorial and when you divide omega or equivalently less phi than E star also the N factorial calculate the entropy and calculate this number it turns out to be 0. So the, ... so every time you will see this n factorial appearing in the denominator.

So I just the reason why I am introducing this is to point out the fact you will always see this n factorial appearing in the denominator of many statistical mechanical expressions, and this is essentially because you want to account for the fact that the particles are actually indistinguishable. It is a correction factor again I have there is more detail as to how exactly it turns out in this notes that I have shared with you, just take a look at it and if you have any questions or corrections to it you please let me know.

But I think I have made some effort in explaining all these intricacies there. So this entire thing is called as a Gibb’s paradox. Basically, if you mix the two gases then you get a positive entropy even though the gases then are the density of the gases on either sides of the compartment are essentially the same, we just wrong.

So, division by N factorial is important, are there any questions? So the whole idea of this very brief introduction to statistical mechanics was, to quantum statistical mechanics was to show that once you know omega, you kind of know a lot of you kind of know almost everything about the system, if you are able to write down omega properly.