Foundations of Computational Materials Modeling
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Lecture 19
Statistical Mechanics-1

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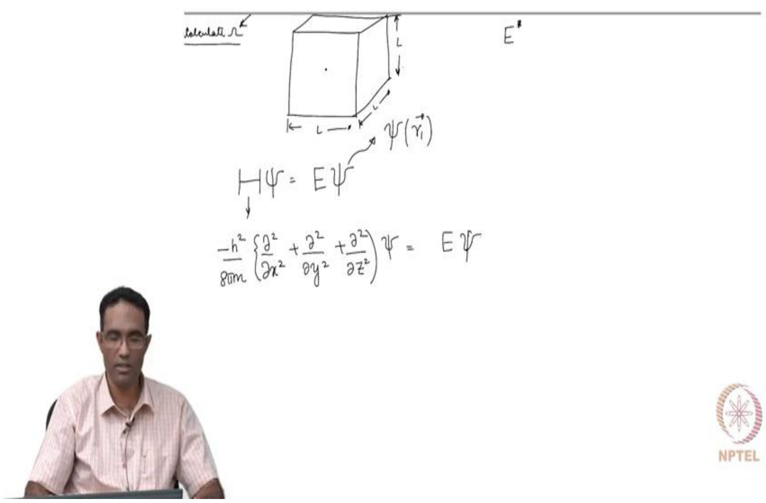
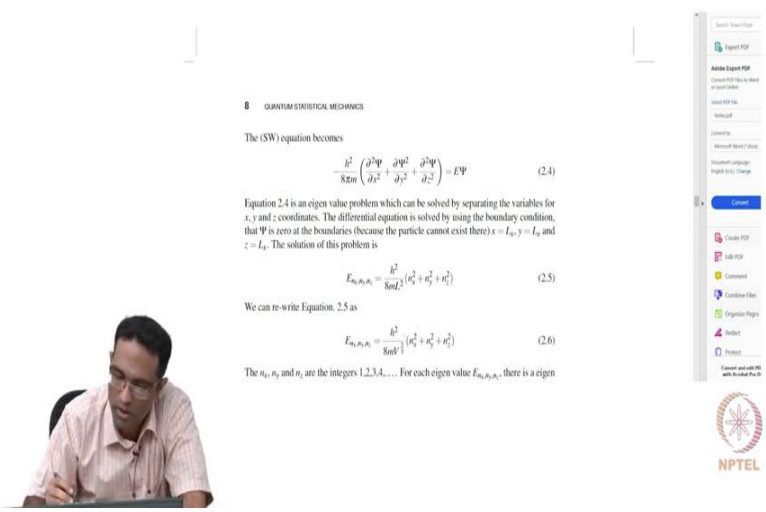
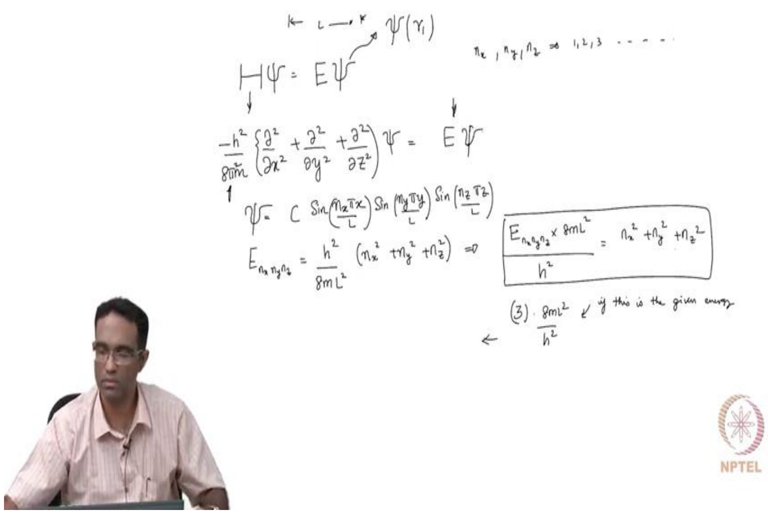
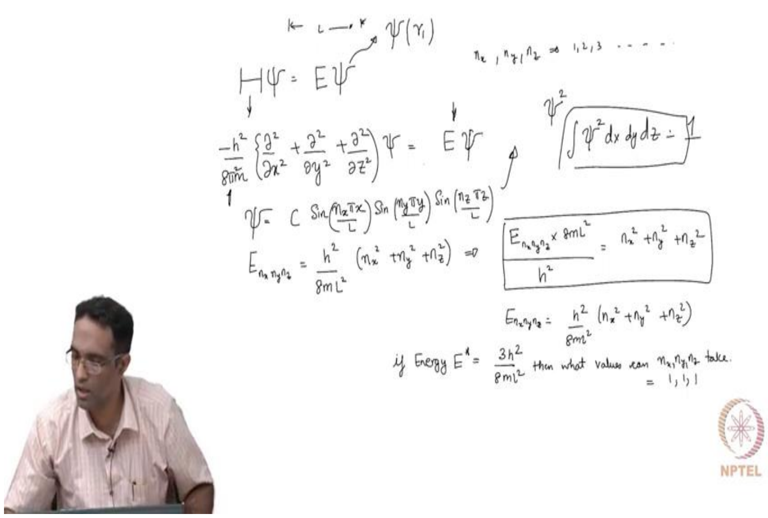






ψ(r₁)
nx, ny, nz = 1, 2, 3 . . . .
Hψ = Eψ
−h²/8π²m (∂²/∂x² + ∂²/∂y² + ∂²/∂z²) ψ = Eψ
ψ = C Sin(nxπx/L) Sin(nyπy/L) Sin(nzπz/L)
E nxnynz = h²/8mL² (nx² + ny² + nz²) ⇒
E nxnynz × 8mL² / h² = nx² + ny² + nz²
(3) · 8mL²/h² ← if this is the given energy
NPTEL



ψ(r₁)
nx, ny, nz = 1, 2, 3 . . . .
Hψ = Eψ
−h²/8π²m (∂²/∂x² + ∂²/∂y² + ∂²/∂z²) ψ = Eψ
ψ²
∫ψ² dx dy dz = 1
ψ = C Sin(nxπx/L) Sin(nyπy/L) Sin(nzπz/L)
E nxnynz = h²/8mL² (nx² + ny² + nz²) ⇒
E nxnynz × 8mL² / h² = nx² + ny² + nz²
E nxnynz = h²/8mL² (nx² + ny² + nz²)
if Energy E* = 3h²/8mL² then what values can nx, ny, nz take.
= 1, 1, 1
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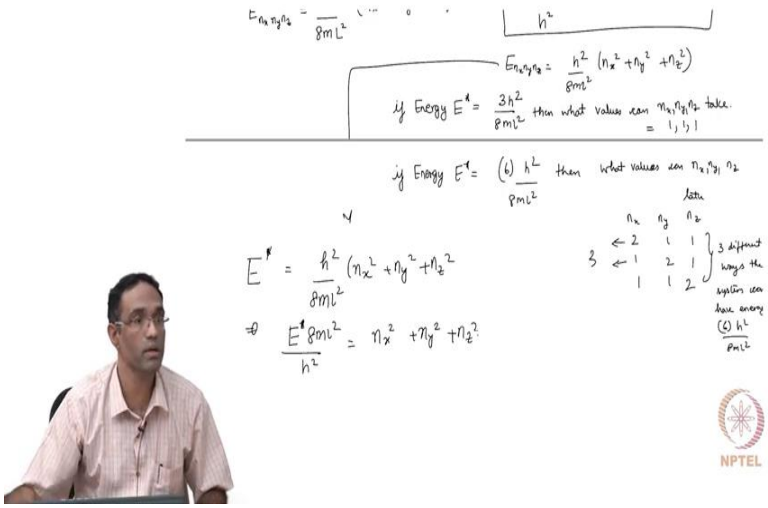

So, now let us try to calculate this omega. Like I mentioned, calculation of omega cannot be done for any arbitrary system. It becomes very complicated, but I want to show it to you for a particle inside a box, you almost have at least seen this particle inside a box problem from quantum mechanics. Whenever you are studying or started to study quantum mechanics, the first thing that you actually study is what happens to a particle inside a box.

So, we will start with quantum mechanics and show you the, what is the approximate number order of magnitude of this particular number. The total number of ways or the energy levels of the total number of complexions possible for a single particle inside a box. We have to start from the quantum mechanical perspective that will make certain things very clear and make illustrate the fact that this is actually a very very large number even for a single particle inside a box. And obviously for more particles, it is going to be even more larger.

So, the idea is to illustrate that particular concept. So, we have to do a little bit of quantum mechanics, but not too much. I think most of you will be familiar with the preliminary quantum mechanics stuff that I am going to do here. So, let us take a box. And there is a single particle 3 dimensional box and it is dimensions are all L. Now, when we talk about quantum mechanics, you have to solve the, what equation?

Student: Schrodinger wave equation

Professor: Schrodinger wave equation, Schrodinger's wave equation has to be solved for this particle and what the Schrodinger's wave equation give you, this is the Schrodinger's wave equation written in a very simple form. What does Schrodinger's wave equation will give you? Is this psi, and what is psi?

Student: wave function.

Professor: wave function and the wave function happens to depend in this case only on the position of the particle. So, I am going to write this as r1, we do not need a whole lot of quantum mechanics, certain things that I want to illustrate will come out automatically once you see what I am getting at.

Now, this is also an Eigen value problem, this is also an Eigen value problem. So, this H is actually called as the Hamiltonian and the Hamiltonian is, so, the Hamiltonian is minus h square by 8 by m times dou square by dou x square plus dou square by dou y square plus dou square by dou z square. And therefore, the wave equation can be written as follows, all right? H is basically the planks constant and m is a mass of the particle.

So, this is the Schrodinger's wave equation. And if you solve this, you basically trying to find out what possible states the particular particle can exist, but the states are not as important to us as the values of the energy that it will take. We want to find out, so, we are considering this to be our nve, there is a volume, there is number of particles is one, and it has some energy, the energy that it has say some e star.

I do not know what energy some e star. The idea is like as I mentioned, this exercise is done to show you what this omega number is, how it looks like for a simple case.

Student: Sir, there will be like in the denominator should contain a pi square?

Professor: There will be a pi square?

Student: yeah, because it is minus h cross by 2 pi.

Professor: okay, fine. So, there is a pi square. So, let us there is some detail missing there. So, it is probably equal to pi Square. Is that right? I do not know, I do not remember the exact form, but there is not really important to us for this derivation.

So, when you solve this. What do you get? You can solve this using what? How would you solve this problem? Using separation of variables? You can solve this problem using separation of variables and you happen to get psi to be equal to c into sin nx pi x by L, sin ny pi y by L, sin nx pi z by L is your psi and the corresponding is are the Eigen values.

And that turns out to be, this. So, h square by 8 mL square, so this implies so if we are given a certain E star, if you are given a certain energy, say for example the energy is maybe three times 3 mL square by h square. If this is a given energy, then what values can nx, ny and n is it can take? What values can I take nx, ny, nz are all positive numbers.

So, nx, ny, nz are all 1, 2, 3 and so on, there is integer values. So, this is a solution for the Schrodinger's wave equation and these are the various ways it can have energy E nx, ny, nz. So, the energy depends on these integers nx, ny, nz. Suppose I am saying that the imposed energy on the system is actually three times 8 mL square by h square is the energy.

Energy is 3 E nx ny is 3. So you can, how will you get this energy? This will have to be what? Well, if it is, so it is. Well, okay. I think I need to be a little bit careful, so, I think I should post the question a little bit carefully here. So, if energy is equals 3 h square by 8 mL square, then what values can nx, ny, nz take?

What can they take? 1, 1, 1, Right? Can it take anything else? Can it takes anything else. So there is only one way of getting this energy. There is only one way of getting this particular energy. And the corresponding psi of the wave function will be c sin one pi x by L, c sin pi y by L and so on. And of course, while psi by itself does not have any specific physical meaning, psi Square apparently can give you the probability per unit volume of finding a particle in some region in the space.

Therefore, it is possible for you to find this constant c by requiring that integral of psi square dx, dy, dz equal to 1. So, I think this things might be familiar to you. So, by requiring that psi square satisfy this condition, it is possible for you to find C. And it turns out to be something in this problem, but now let us come to the energy. Now let the energy that I am imposing is not, say it is something six.

For example, the energy is 6 h square by 8 mL square. Then what values can nx, ny, nz take? 2, 1, 1 right? Then 1, 2, 2 sorry 1, 2, 1 and then 1, 1, 2, right? So, basically there are three different ways the system can have, energy 6 h square divided by 8 mL square. And if I increase this number 6 to something else, then I will have a larger number of ways, the system can actually have this particular energy.

Now remember, for each nx, ny, nz the corresponding psi is going to be different, in the first case in 2, 1, 1, so you had sin 2 pi x by L, sin pi y by L sin pi z by L, in a second case there is going to be a 1 here, 2 here and 1 here. And in the third case, it is going to be the other one. So, there are three different values of psi which have basically the same energy, right? So, the 3 different three different quantum states the particle can have with the same energy, and I can keep going on and on and demonstrating that the number of ways in which you can achieve these energy levels is going to increase as you increase the energy level of the system.

Now another thing that you have to notice is that between 1, 1, 1 and 2, 1, 1 there are not any other energy level, there is no other energy level between these two levels, there is nothing in between this 3 h square by 8 mL square and 6 h square by 8 mL square, simply because these energies have to be dependent, dependent on these nx, ny, nz which are basically integer numbers, which essentially is what quantum mechanics is basically telling with the energy levels of the system are actually discrete. They jump from one value to the other without anything in between like what is happening here.

Now suppose we have, so this is demonstrating we know how different states can exist with the same energy level. Is there any question there anything?

Student: Is n equal to zero ?

Professor: n is not 0, n is 1, 2, 3, 4 as the solution of this differential equation requires. And if it is trivial, then e is 0, so, n cannot be zero, okay. Anything else? Okay.

Student: If nx is 0, psi also comes out to be 0, if that.

Professor: That is all. So, you cannot have 0, either integer nx, ny,nz the integers that you get cannot be 0. Now, the question is if some arbitrary energy is imposed on the system, how will I find out the total number of ways it can get? How will I find out this? Now you saw that this was three, how will I find out for any arbitrary energy is a question? So that is somewhat a hard problem to solve.

So, what we can do is we can actually look at this equation a little bit more carefully. So, let E star be the energy and that is actually equal to h square divided by 8 mL square divided by nx square plus ny square plus nz square, which essentially means E star times 8 mL square divided by h square is equal to nx square ny square plus nz square. In order to try to find out the total number of ways the system can actually have the energy E star what we do is we look at this equation and realize that it is an equation of a.

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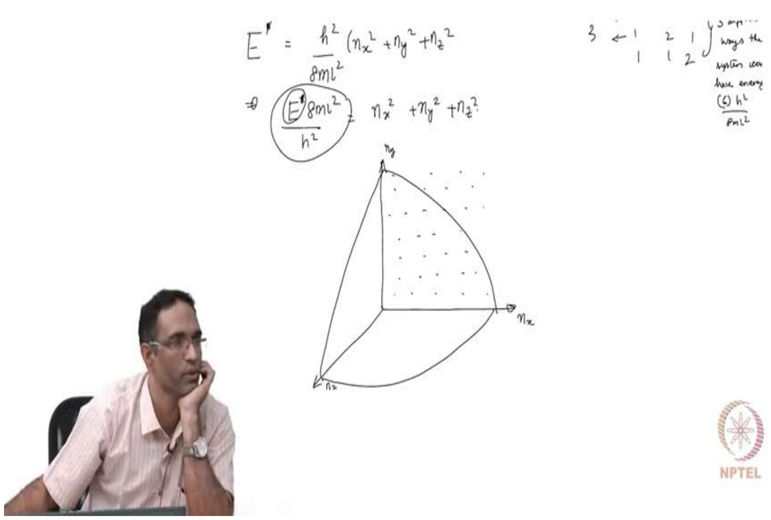

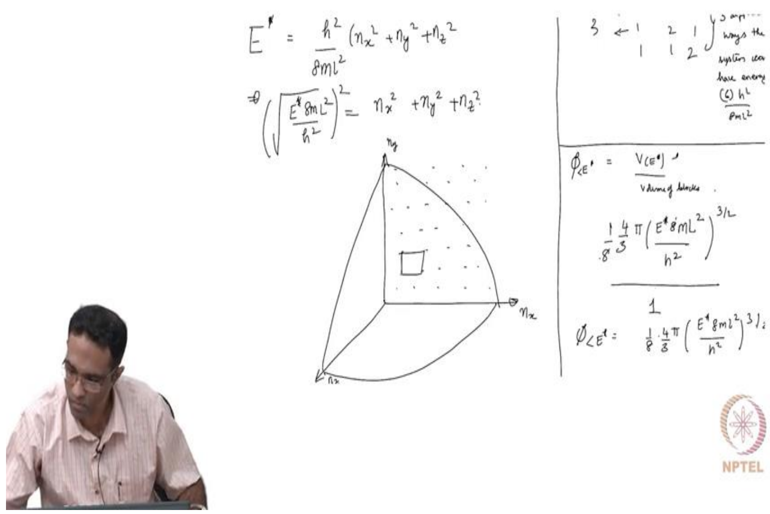

Suppose this is nx axis, ny axis and this is nz axis, this actually is a equation of a.

Student: sphere.

Professor: sphere, since nx, ny, nz are all positive, then it is basically the equation of a we are only considering the one octant of a one eighth of a sphere in the positive x, y, z quadrant. And the actual set of all possible ways, so, if this is the sphere, this is one 8th of a sphere and there are many of these points here and so on. They just filled with these points, if you want to find out how many points are there with this as the energy, then you will have to find out how many points are laying on the surface of the sphere with square root of this as the radius, is that clear?

Student: Just E star is the energy ?

Professor: Yeah, because it is exactly that energy I want the total number of points at that energy, if I if I take the square root of this I mean, if I if I know the total number of things on the surface of this thing, now it is again, not possible for us to find out that number either. What we can do is, we can actually look at it in the following manner. So, let us write this down again, so, let us know see we can do this so let phi.

Let phi less than E star be the total number of points. Which are total number of points, which are less than E star. Total number of points, which are all having energies less than E star. So, how would you calculate that? You can basically do the following, you can calculate the volume of this entire sphere, volume of the sphere at this energy corresponding to each star 8 mL square by h square h, h square and divided by the volume of each individual blocks.

That is actually making up the sphere, making of this sphere, and that would basically tell you how many points are there with energy less than E star 8 mL square by h square. Is that, are you following that? So, this is very simple, it is nothing but 4 by 3 pi r cube where r is my E star 8 mL square divided by h square power 3, that is the volume.

And if I have extremely large number of points, then the error that I would be committing in actually dividing this by 1, where 1 is basically the volume of 1. So, this would be one, because all these numbers are increasing only by 1. So, either in the nx direction is 1, in ny direction is 1, in nc direction is 1, so the minimum volume element that is comprising the sphere is actually 1 by 1 by 1.

So, if I divide the total volume by 1, I would essentially be getting the total number of points which have energy less than E star, yes or no? No, not following, not following.

Student: If we take the entire sphere, are we including the negative points ?

Professor: no, we are not taking that, we are not, so, the question is, if I take the entire sphere I am also including the negative points. Correct, correct. So, I need to multiply it by 1 by 8, is that okay? Now it is okay. Is that the issue? Okay. I have to multiply by 1 by 8 here because I am only interested in 1 8th or one octet of the sphere. Yes.

Student: In which case, the value of radius is very small, this would not work.

Professor: This would not work, this value of the radius or the energies are extremely small this approximation does not work. It only works if the energies are somewhat very high, but we will plot and quickly show you that for very very quickly, as the energy just increases a little bit, from 0.01 KBT, you can actually quickly see the total number of nx, ny, nz will become very large, it will just become huge.

So, now what we do is.

Student: Sir the radius is the square root of the LHS, so…

Professor: What is that?

Student: sir the radius is square root of the lhs, so.

Professor: correct, correct I agree. 3 by 2 is square root, right? This is nothing but this square,

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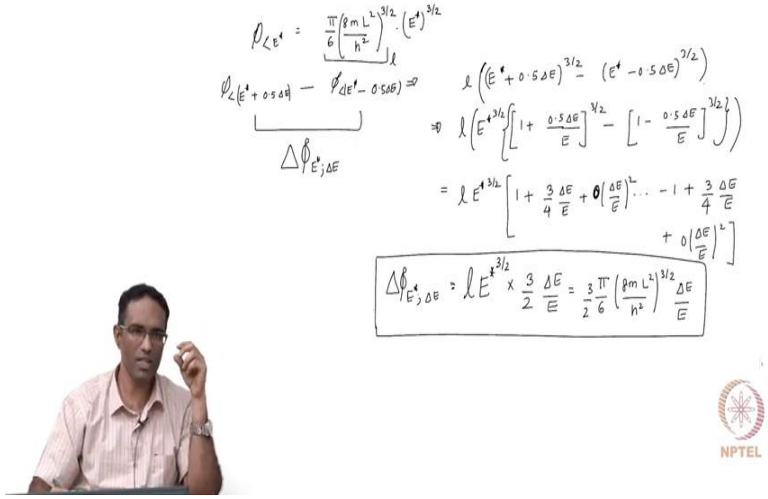

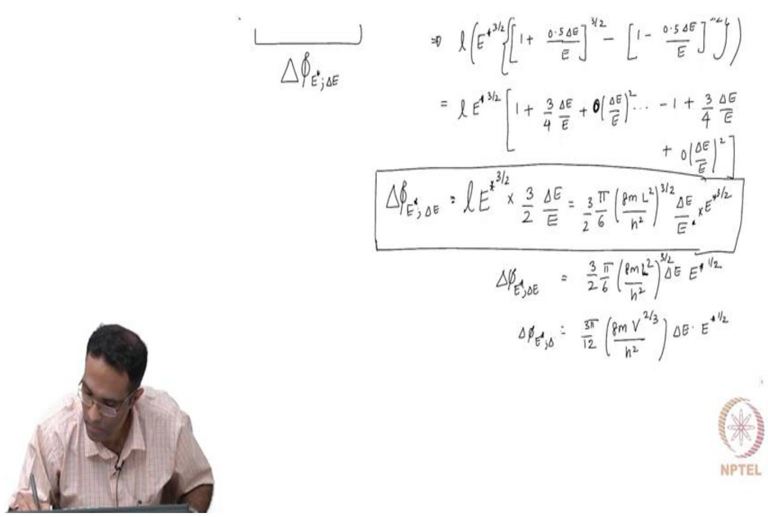

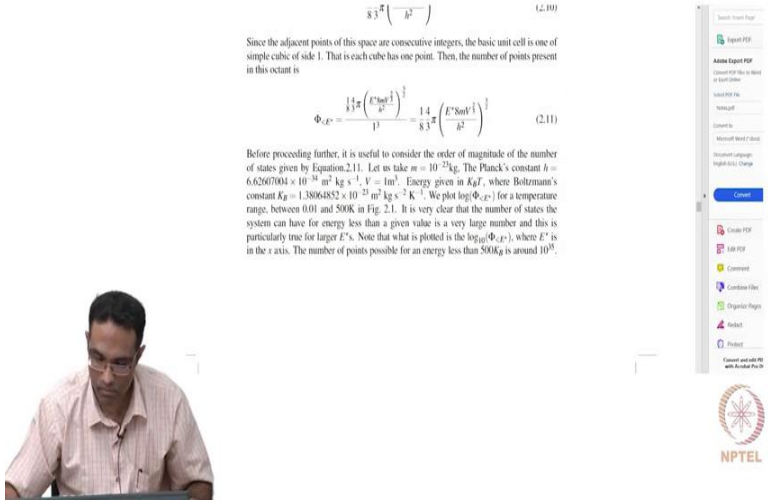

so, what was the expression I need to rewrite the expression now. So, now we have to find out, this is not the number that we want, we want the total number of points that is going to exist at E star, that is what we are looking for. How many points are that at E star is what we are looking for.

So, that is again, very difficult to get, however, we can do some small approximation, what we can do is we can calculate phi of E, E star plus 0.5 some small energy subtracted from, can we do this? This will give us the total number of points that is going to be present in that shell around E star. We are of course, making an approximation that our this shell thickness is going to be of the size of delta E, so we will see what that gives us.

Student: Sir how should delta E be..

Professor: You can do anything you want as long as it is delta E or something like that. So, I am going to call this entire thing as some L. So, I have L times E.

Student: sir in the bracket there is a mistake

Professor: okay, so good point. So l now we just take this E star power 3 by 2 outside 1 plus I can expand this terms will be the order of delta E by E the whole square minus 1 plus.

What you get? So what we call this let us call this thing as and l is your. So, this is the total number of points that is going to lie in a shell of thickness delta E around the energy level delta E, the E star. Now what you have done is actually not very wrong because when you are talking about a closed system, we are talking about a closed system but or isolated system, no system is actually isolated, even the act of if we are trying to measure something from the system, you are actually going to interact with it and it has to exchange some amount of energy from.

For example, if you are measuring the thermometer, you need to allow the system to exchange heat with the thermometer so that you can measure temperature. So the energy E is always going to be fluctuating a little bit about E of E star. So in a sense, what we have done is not very far from reality and you will get some number of states about the energy E star of width of delta E. Now what you can do is let us calculate the quantity.

Student: Sir I have a question on the equation above

Professor: okay. Yes.

Student: Sir is E correct there..

Professor: What is wrong? Did I miss something here? There is a E star, E star times I think I missed E star power 3 by 2, Right? Yeah, that is why that, that is a good point, that is important. There is a E star power 3 by 2 here. So, this becomes a 3 by 2 pi by six 8 mL square by h square delta E, E star power 1 by 2, is that right?

Student: Sir considering the volume term is it there..

Professor: yes, this is that right here, here in terms of l you can write the volume, right?So, this can be again written as if you want to write it in terms of, again, did I missed something this 3 by 2 and this will be volume power 1 by 3, so 2 by 3 divided by h square. So, now let us see, any doubts something confusing?

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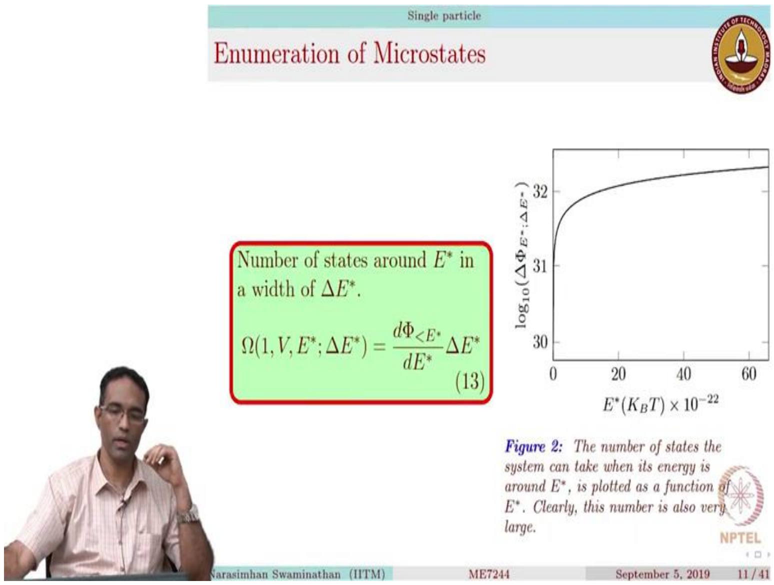

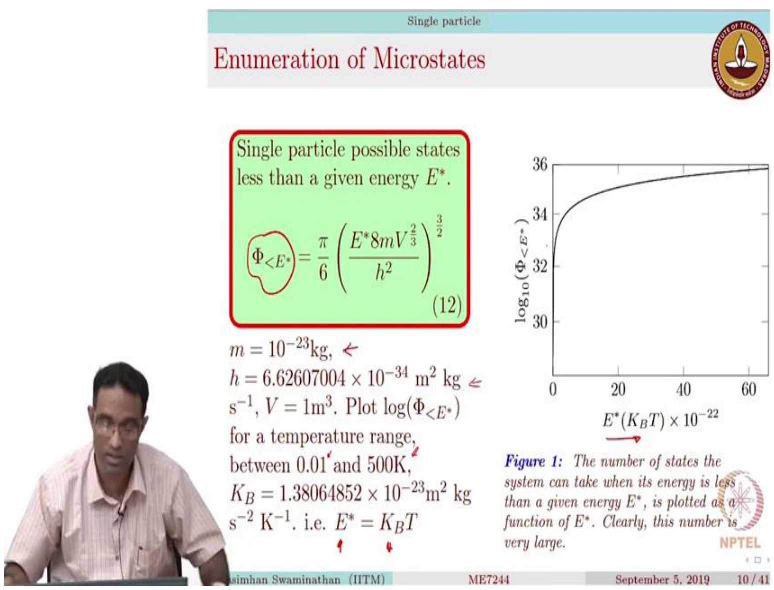

Well, before we proceed any further, let us try to see how many states, what is this total number phi for given energy E star let, what is phi less than E star, this particular quantity right here, that we just calculated. So, I took m to be 10 to the power minus 23 kilo grams, H is the planks constant volume is about 1 meter cube and for a temperature range between 0.01 and 500 kelvin taking E to be say KBT ranging between 0.01 and 500 kelvin is a temperature taking T to be in that range.

If I take E star to KBT and substitute in this expression and calculate phi less than E star for every single case and I plot it, I get this curve on the right hand side. Is the last bench can you see the slide? Yes, so this on the x axis is basically the energy and I have plotted phi less than E star, total number of points which will give you energy less than E star. So, considering that, which basically consists of all the points inside the entire volume of the octet.

So, it is plotted in a log based ten scale, you see the total number of points that you are having here. So, for very quickly, the total number of points increases and reaches something close to 10 to the power 34 total number of points 10 to the power 34 and we are still looking at only one particle inside the box. Now, is this a large number of states? Is this clear? If I take a particular energy E star and plot the total number of ways basically total number of ways that are existing up to E star and I plotted for various energies, I get this for various energies.

For some typical mass and you know temperature range. The states is 10 to the power 34 and 35, so to give you an idea as to whether the number is large or not, the total number of stars in this universe is how much, do you know? Some estimate 10 to the power 21 stars in the universe for a single particle inside a box. The total number of complexions that you get, not complexion, the total number of states which have energy less than E itself is 10 to the power 35 huge number.

So, that octet of the sphere contains an extremely large number of particles. Now, what I did I plotted, okay. Now I just need to do a little bit more to talk about the next slide. So, you agree that there is a large number, it is a very large number for just one single particle inside a box. And it is obviously going to increase if you have more particles.

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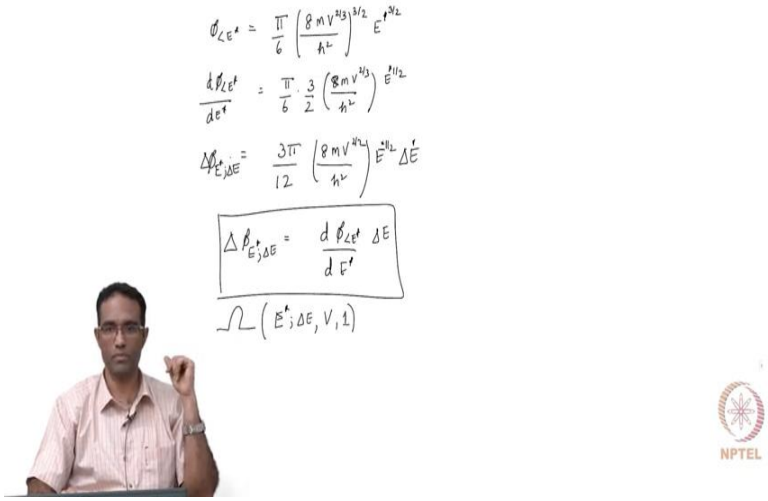

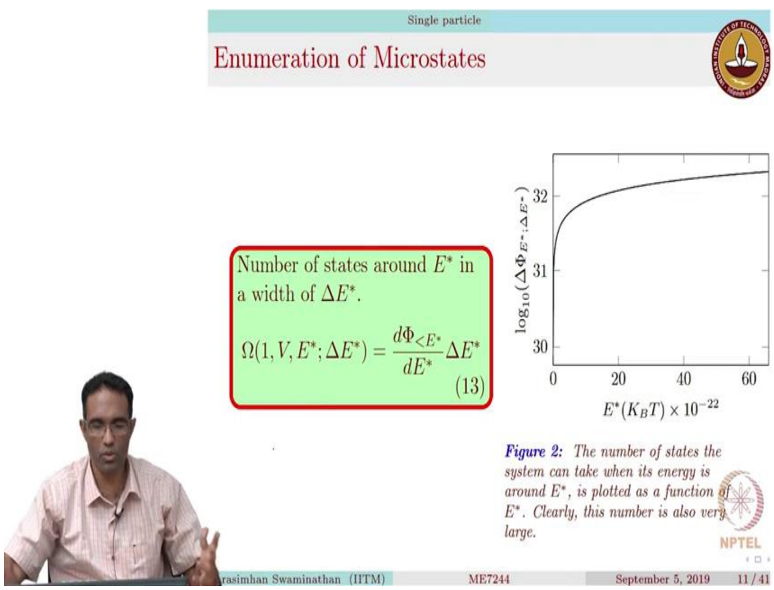

Now, let us calculate the function, so, I need to rewrite something. So, if you are note it down can you please tell me what is phi less than E star, so that I do not have to keep.

Student: pi by 6 into 8 mL square by h square whole to the power 3 by 2.

Professor: Times?

Student: times E star

Professor: E star to the power 3 by 2 let us calculate the quantity that would give you, now, what was our delta phi less than E star? Can you tell me what was our delta phi less than E star.

Student: 3 pi by 2

Professor: 3 pi by 2, 3 pi by 12

Student: 8 M times V.

Professor: E to the power half times delta E, so E star all that is interchangeable, so now. So if you look at these two expressions, what can you say? They both are just, you can write one. You can write it like this, you can write, you will get this. The thing I should be careful in writing this. So, this delta E star about delta E about with a thickness delta E is actually our omega the total number of complexions that it can actually have when it has a certain energy E star, except that now it is about some delta E at constant volume and with a number of species being equal to one.

This is actually our omega, except that it is a little approximate we cannot obtain exact values. This is our omega the number of ways the system can actually take that energy E star, we will plot this function. So, this function you can plot d phi by d E star times delta E by assuming some small value of delta E as well, this one also the huge number is in the order of 10 to the power 32.

And I think I assume some small delta E here, here maybe 0.01 KBT or something like that has been assumed to plot this showing you that even delta E, even delta, even omega is actually in the same order of magnitude as omega less than phi star. There are as many points, almost as many points on the surface as there are points within the volume of the sphere, which essentially means as the radius increases, the energy becomes more closely spaced, the energies are getting more and more closely spaced.

That is what this tells you. So, large numbers, so we have just seen how large omega is for a single particle in a box. Now we can do the exact same thing when you have more particles in a box.

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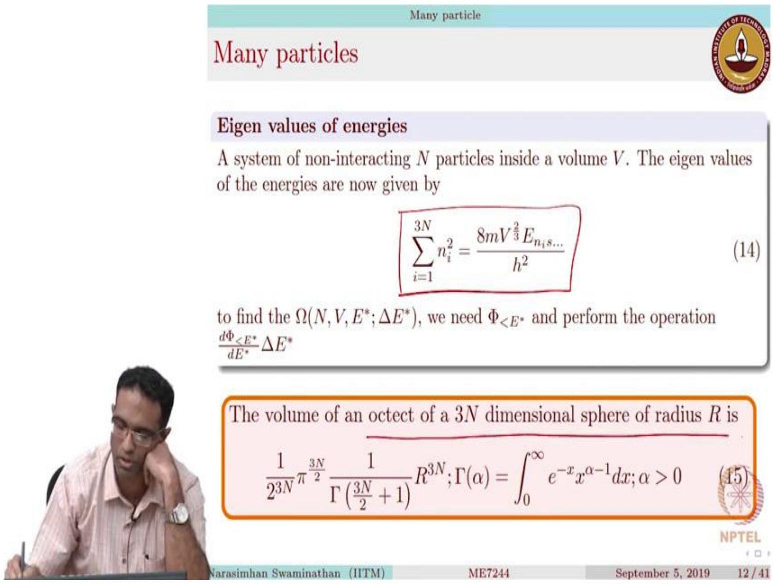
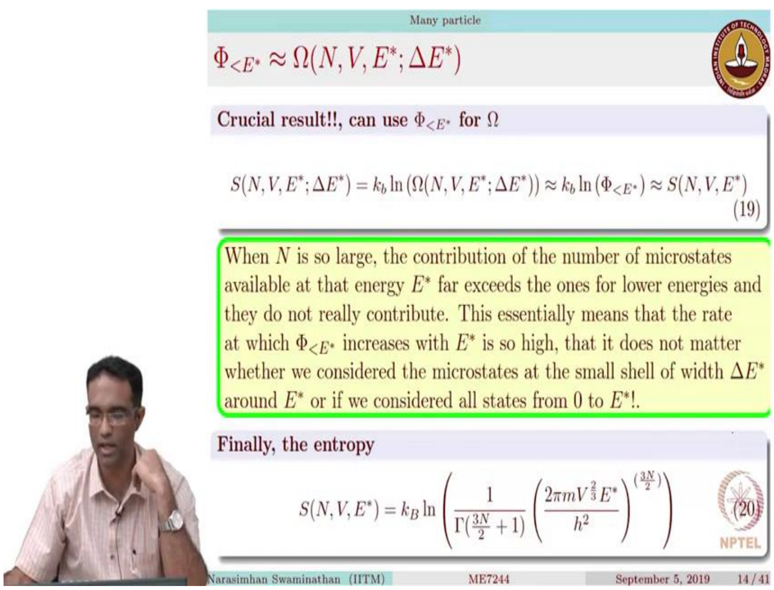




Many particle microstates

Microstates less than E^*

$$\Phi_{<E^*} = \frac{1}{2^{3N}} \pi^{\frac{3N}{2}} \frac{1}{\Gamma\left(\frac{3N}{2}+1\right)} \left(\frac{8mV^{\frac{2}{3}}E_{n_i s \ldots}}{h^2}\right)^{\frac{3N}{2}} \quad (16)$$

Microstates around E^*, width of ΔE^*

$$\Omega(N,V,E;\Delta E) = \frac{1}{\Gamma\left(\frac{3N}{2}\right)} \left(\frac{2\pi m V^{\frac{2}{3}}}{h^2}\right)^{\left(\frac{3N}{2}\right)} E^{\left(\frac{3N}{2}-1\right)}\Delta E = \frac{3N}{2}\Phi_{<E^*}\frac{\Delta E}{E} \quad (17)$$

Entropy

Omitting the constant k_b for brevity:

$$\ln\left(\Omega(N,V,E;\Delta E)\right) = \ln\left(\frac{3N}{2}\right) + \ln\left(\Phi_{<E^*}\right) + \ln\left(\frac{\Delta E}{E^*}\right) \quad (18)$$

$\Phi_{<E^*} \approx \Omega(N,V,E^*;\Delta E^*)$

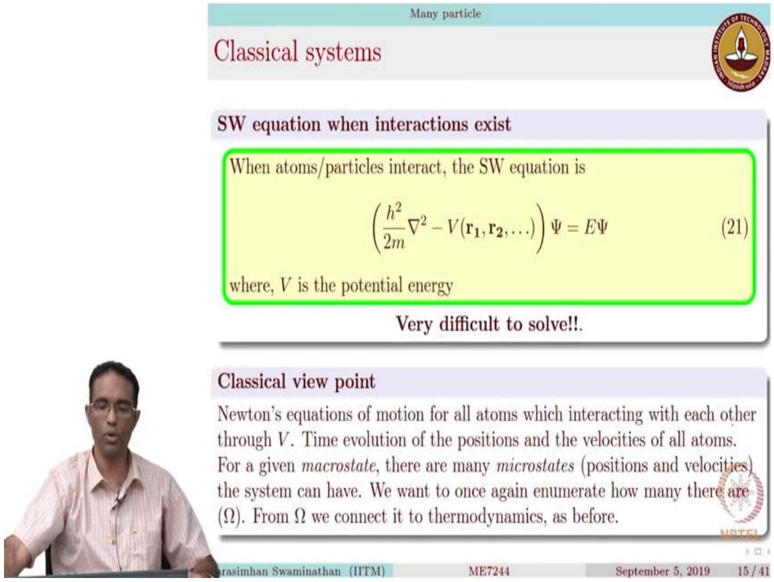
Crucial result!!, can use $\Phi_{<E^*}$ for Ω

$$S(N,V,E^*;\Delta E^*) = k_b \ln\left(\Omega(N,V,E^*;\Delta E^*)\right) \approx k_b \ln\left(\Phi_{<E^*}\right) \approx S(N,V,E^*) \quad (19)$$

When N is so large, the contribution of the number of microstates available at that energy E^* far exceeds the ones for lower energies and they do not really contribute. This essentially means that the rate at which $\Phi_{<E^*}$ increases with E^* is so high, that it does not matter whether we considered the microstates at the small shell of width ΔE^* around E^* or if we considered all states from 0 to E^*!.

Finally, the entropy

$$S(N,V,E^*) = k_B \ln\left(\frac{1}{\Gamma\left(\frac{3N}{2}+1\right)}\left(\frac{2\pi m V^{\frac{2}{3}}E^*}{h^2}\right)^{\left(\frac{3N}{2}\right)}\right) \quad (20)$$



So, that will basically take us to an ideal gas. Now, instead of looking at one octet of a sphere, we look at the same one octets of a sphere however, in a larger dimensional space, we now need to do the entire calculation with by knowing the expression for the volume of a sphere in 3n dimensional space.

So, n is the number of particles we can calculate the you can calculate what the volume would be of all the particles that would turn out to be something like this, this would be the volume of an octant of a 3n dimensional sphere of radius using this idea, you can actually derive omega for a system which has a large number of particles we will do this in the next class and then this, with this we can find what s is because s is nothing but KB log omega.

With that we can show what happens when we take the derivatives with respect to energy and with respect to volume, we will get back the expressions for pressure that you all would have studied in kinetic theory of gases in your 12th grade, right? You will get exactly the same number for the energy, same expressions for the energy and pressure and all that. So it is kind of interesting to see that again, basically trying to illustrate the point that once you know omega, you can get everything else from it, with that we stop.