Statistical Thermodynamics for Engineers
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Lecture 25
The Particle in a Box

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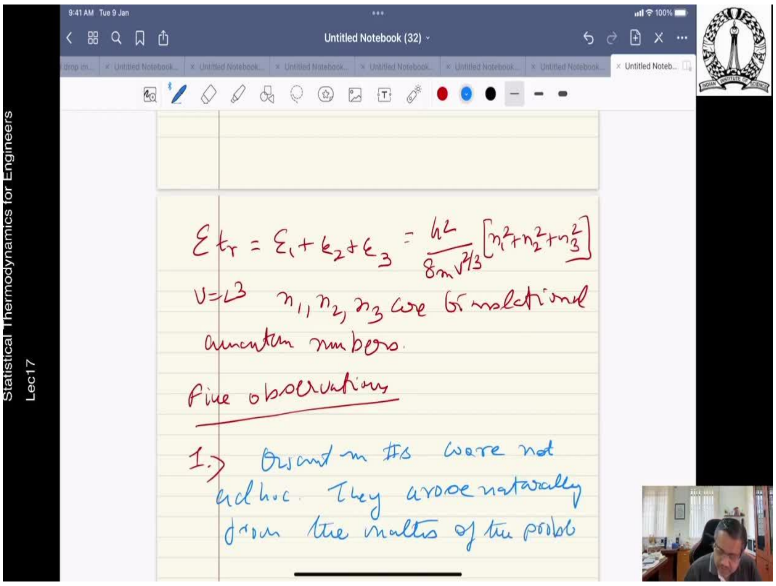
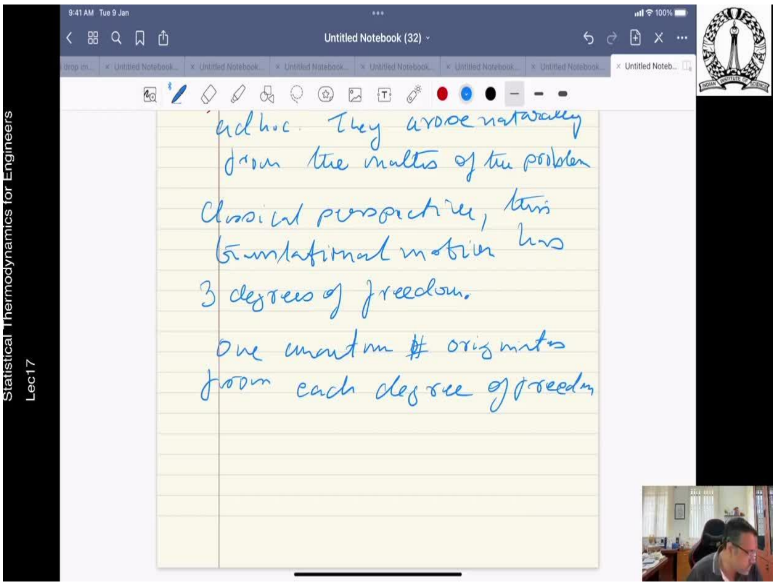


$\mathcal{E}_{tr} = \epsilon_1 + \epsilon_2 + \epsilon_3 = \frac{h^2}{8mV^{2/3}}\left[n_1^2+n_2^2+n_3^2\right]$

$V = L^3$ n_1, n_2, n_3 are translational quantum numbers.

Five observations

1.) Quantum #s were not ad hoc. They arose naturally from the maths of the probl



ad hoc. They arose naturally from the maths of the problem

Classical perspective, this translational motion has 3 degrees of freedom.

One quantum # originates from each degree of freedom

So, welcome to lecture number 17 of statistical thermodynamics for engineers. So, we have now found out what is the translational energy, let us write it down one more time E tr is E1 plus E2 plus E3 which is equal to 8 square 8 mv to the power of two third, n1 square plus n2 square plus n3 square. So, v was equal to L cube, is the volume of the cube and n1, n2, n3 are translation quantum numbers. So, there are 5 important observations as we said in the last class that we can make, 5 observations that we can make.

First observation, we note that these quantum numbers are generated automatically, So, the quantum numbers were not adhoc. They were arose naturally from the mathematics of the problem which is nice. So, there is not adhocism over here. So, as we know from our classical perspective, so this particular motion, this translational motion has 3 degrees of freedoms. So, x, y, z; 1, 2, 3, whatever you call it. So, one quantum number originates from each degree of freedom. So, one quantum number for each degree of freedom, so and each quantum number is used to identify the complete state of the system that are concerned with. So, that is good.

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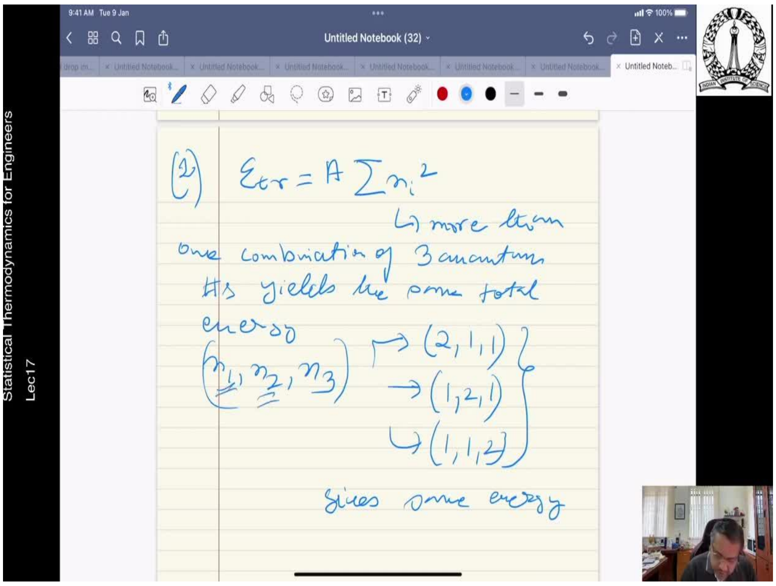

(2) $\mathcal{E}_{tr} = A \sum n_i^2$

↳ more than one combination of 3 quantum #s yields the same total energy

(n_1, n_2, n_3) → (2,1,1) → (1,2,1) → (1,1,2) gives same energy

So, there is a classical little bit of a classical analogue. The second part which is important is that E tr if we write it properly is A, A is that constant ni square. So, you can see more than more than one combination of 3 quantum numbers yields the same total energy. And as an example, so an example say, this combination so total, say for example n1, n2, n3, so let us assume this triplets. So, 2, 1, 1, and 1, 2, 1, and 1, 1, 2, these three gives you the same energy this gives you the same energy, but the individual quantum numbers are different. So, you guessed it right, so this is some kind of a degeneracy of the system.

From the point of view of quantum mechanics, this is a very common feature and we already have an idea of micro-states and macro-state, so the total energy is like a macro-state. And how you possess that total energy in these 3 different ways for example here, this is some kind of the, yes it is micro-state because it does not alter the total energy, but it alters the way that you preserve it you possess some total energy.

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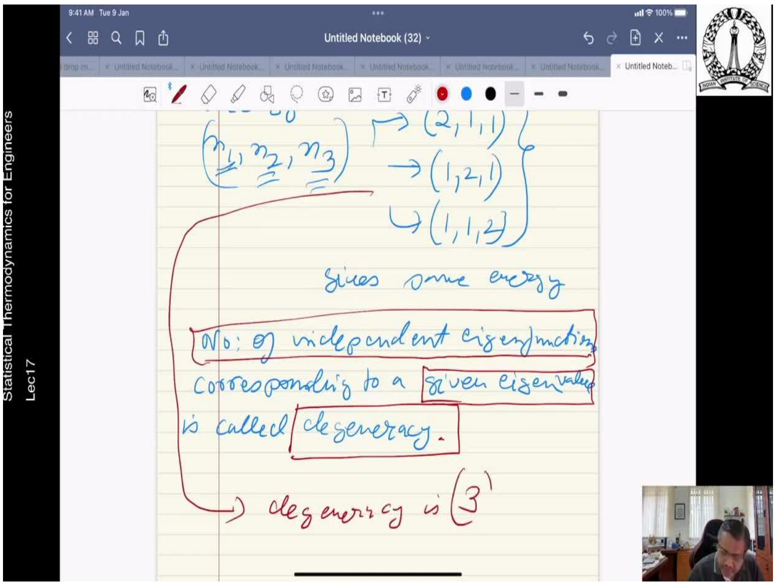
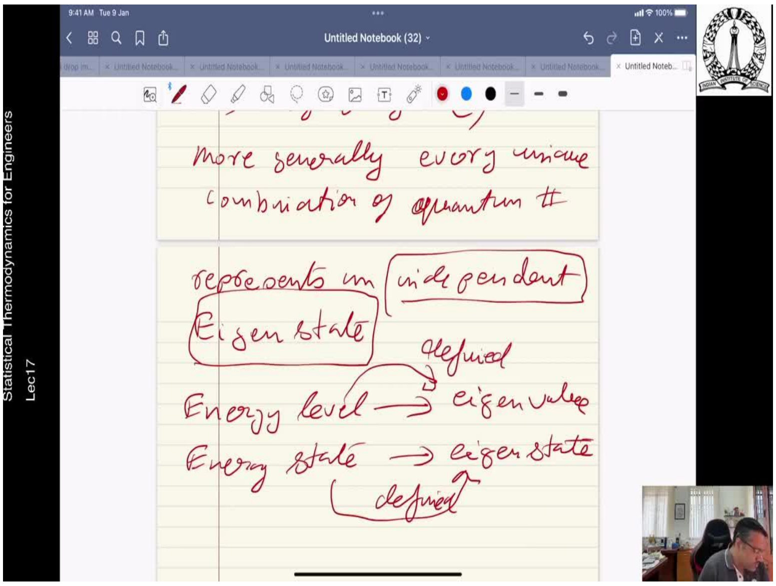


$(n_1, n_2, n_3) \rightarrow (2,1,1) \rightarrow (1,2,1) \rightarrow (1,1,2)$

gives same energy

No: of independent eigenfunction corresponding to a given eigenvalue is called degeneracy.

→ degeneracy is (3)



More generally every unique combination of quantum #

represents an independent Eigen state

Energy level → eigenvalue

defined

Energy state → eigen state

defined

So, point of view of quantum mechanics. So, the number of independent from the point of view of quantum mechanics the number of independent Eigen functions corresponding to a given Eigen value is called degeneracy, the number of independent Eigen functions corresponding to a given Eigen value is called degeneracy. So, for example, in this case the degeneracy is 3, degeneracy is 3 in this particular case. The point of view of quantum mechanics, the number of independent Eigen functions corresponding to a given Eigen values degeneracy in this case for example, the degeneracy is 3.

So, more generally every unique combination of quantum number 3, quantum number represents an independent Eigen state of a system. Each unique combination like 2, 1, 1; 1, 2, 1, these are unique combinations. So, from this perspective what we can say that energy level is like an Eigen value whereas, energy state this is like the microstate these are the Eigen state. So, each energy level is defined by its Eigen value, whereas each energy state is defined by its Eigen state, defined by its Eigen value.

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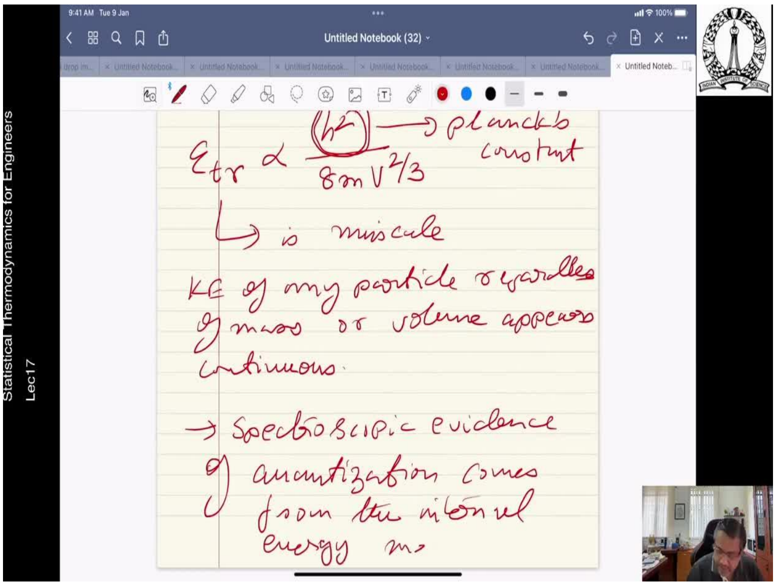

$$E_{tr} \propto \frac{\boxed{h^2}}{8mV^{2/3}} \longrightarrow \text{plancks constant}$$

↳ is miniscule

KE of any particle regardless of mass or volume appears continuous.

→ Spectroscopic evidence of quantization comes from the internal energy mo

Now, the third point is that if you look at it a little bit more carefully. So, the point here say E translation is proportional to h square divided by 8 mv to the power of two thirds. Now, if you look at it this is the Planck's constant very low(())(8:52). So, therefore, this is miniscule due to its dependence on the square of the Planck's constant. For this reason, that kinetic energy of any particle regardless of its size, regardless of mass or volume appears continuous.

So, the spectroscopic evidence, so if you are looking for spectroscopic evidence that means the discreteness of the lines, spectroscopic evidence of quantization comes from the internal energy modes, this is external right this is translation internal energy nodes, vibration, rotation, etcetera. Not through this, not through the translation component at all.

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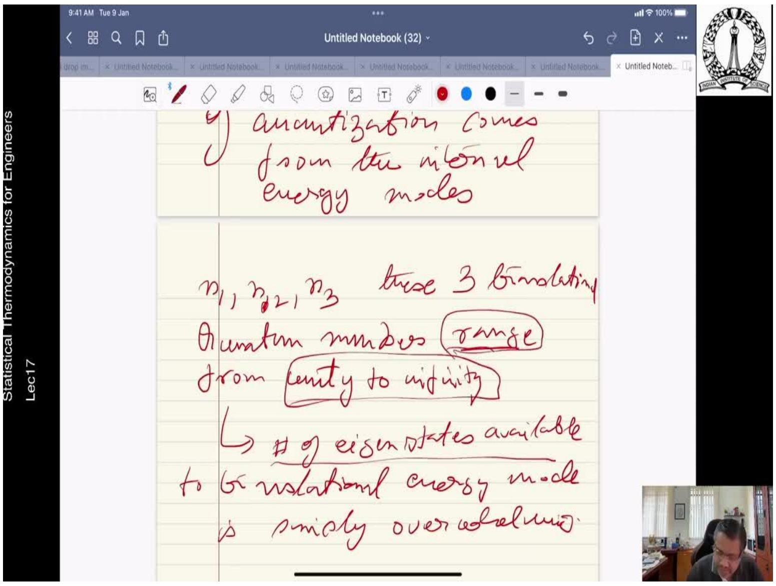

quantization comes from the internal energy modes

n_1, n_2, n_3 these 3 translating Quantum numbers range from unity to infinity

↳ # of eigenstates available to translational energy mode is simply overwhelming.

So, the last one the point that is that these three translational quantum numbers range from unity to infinity, the number of Eigen states. So, since they range from unity to infinity, the number of Eigen states this leads to a number of Eigen states available, accessible to translational energy node is simply overwhelmed. So, if the cube is 3 dimensional as you can see, so it ranges it is got a huge range as a result of that number of Eigen states can also be huge in this particular case.

So, we have got two things like for example, the energy is miniscule and therefore, it appears continuous and therefore, we need to take a look at internal energy nodes for evidence. And we know that n varies from 1 to infinity and the energy levels are like the Eigen values whereas, the energy states correspond to the energy states represented by this quantum numbers are correspond independent Eigen states (())(12:12).

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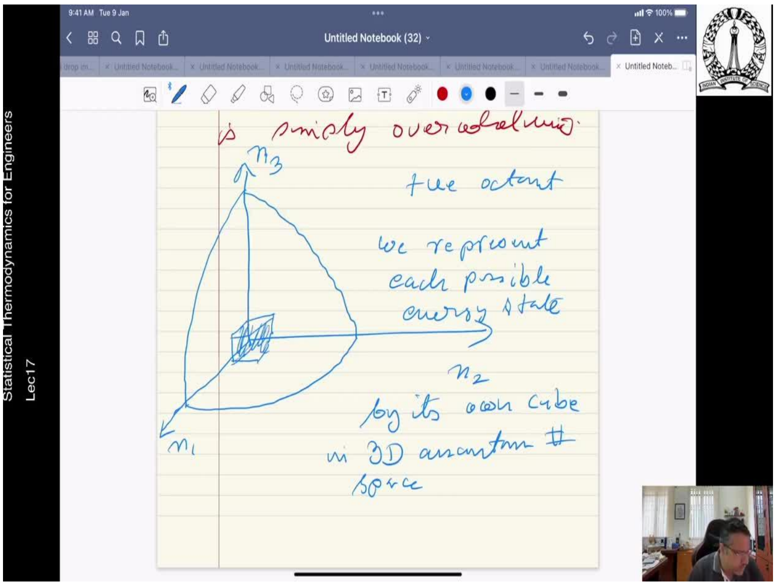
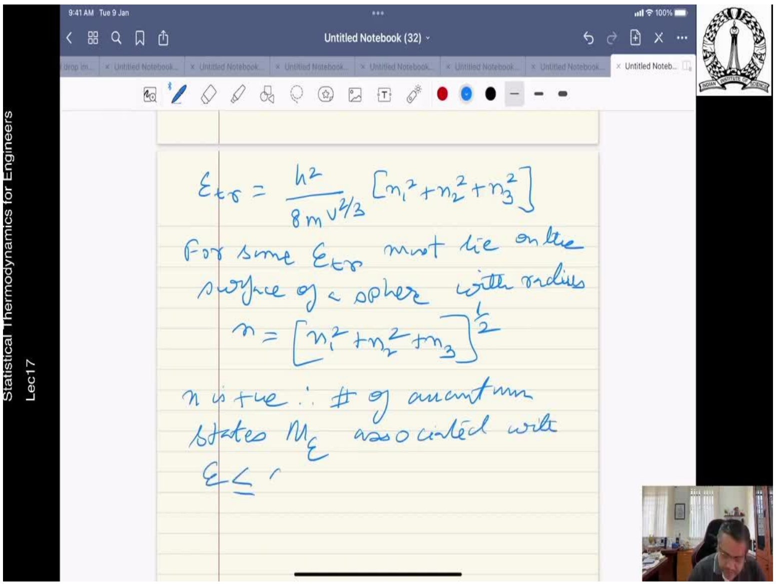


is simply overwhelming.

+ve octant

we represent each possible energy state by its own cube in 3D quantum # space



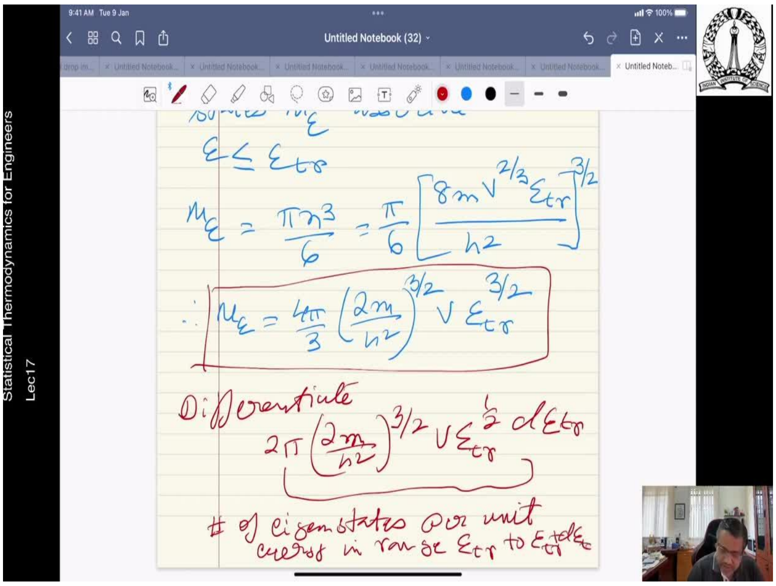
$$\varepsilon_{tr} = \frac{h^2}{8mV^{2/3}}\left[n_1^2+n_2^2+n_3^2\right]$$

For some ε_{tr} must lie on the surface of a sphere with radius

$$n = \left[n_1^2+n_2^2+n_3\right]^{\frac{1}{2}}$$

n is +ve ∴ # of quantum states M_ε associated with

$\varepsilon \leq$



$\varepsilon \leq \varepsilon_{tr}$

$$M_\varepsilon = \frac{\pi n^3}{6} = \frac{\pi}{6}\left[\frac{8mV^{2/3}\varepsilon_{tr}}{h^2}\right]^{3/2}$$

$$\therefore \boxed{M_\varepsilon = \frac{4\pi}{3}\left(\frac{2m}{h^2}\right)^{3/2} V\,\varepsilon_{tr}^{3/2}}$$

Differentiate

$$\underbrace{2\pi\left(\frac{2m}{h^2}\right)^{3/2} V\,\varepsilon_{tr}^{\frac{1}{2}}}\, d\varepsilon_{tr}$$

# of eigenstates per unit energy in range ε_{tr} to $\varepsilon_{tr}+d\varepsilon_{tr}$

So, we can represent each possible energy state by its own cube, cube either in a 3d space, how to do that? Let us take a look at this. So, these are the different quantum of states n2, n3. So, this is a positive octant. So, we represent each possible energy state by its own cube in the 3d quantum number states. So, this is how the representation actually happens. So, we represent each possible energy state by its own cube in 3D quantum number space.

So, if we say that E tr is equal to h square 8 mv two third square. So, for same E tr, because E tr should be the same that is like a macro state. So, the state must lie on the surface of a sphere with radius n equal n1 square plus n2 square plus n3 square raise to the power half. n is positive therefore, number of quantum states ME associated with E less than or equal to is E tr.

So, ME is therefore written as pi n cube by 6 which is also pi by 6 8 mv to the power by two third energy translation divided by h square 3 by 2. Therefore, ME is 4 by pi 3, 2m h square 3 by 2, v translation3 by 2. So, differentiating this we can differentiate those you will get 2 pi 2m h square 3 by 2 v translational energy d E tr. This actually gives you the number of Eigen states per unit energy in the range E tr to E t M r.

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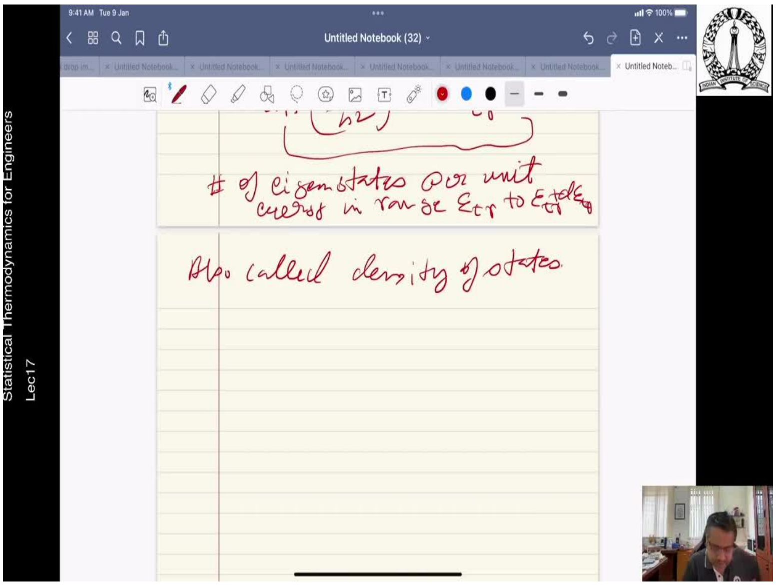
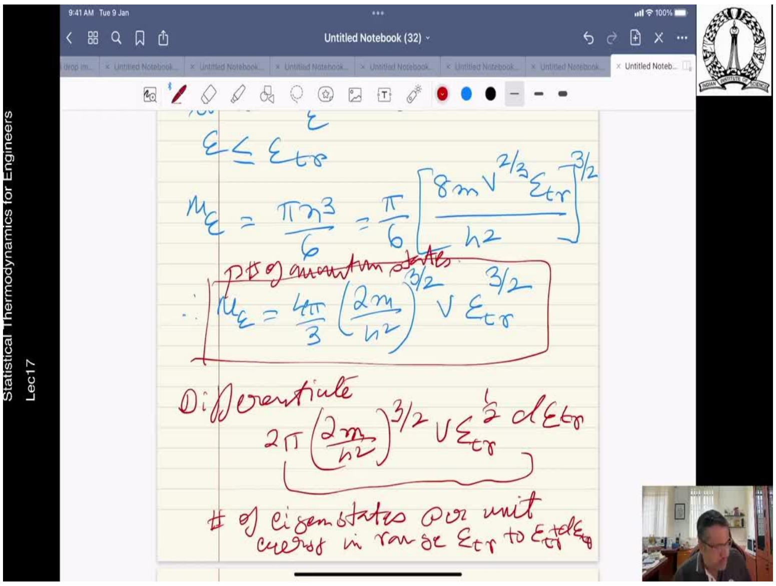


# of eigenstates per unit energy in range E_{tr} to $E_{tr}+dE_{tr}$

Also called density of states



$\varepsilon \leq \varepsilon_{tr}$

$$M_\varepsilon = \frac{\pi n^3}{6} = \frac{\pi}{6}\left[\frac{8mV^{2/3}\varepsilon_{tr}}{h^2}\right]^{3/2}$$

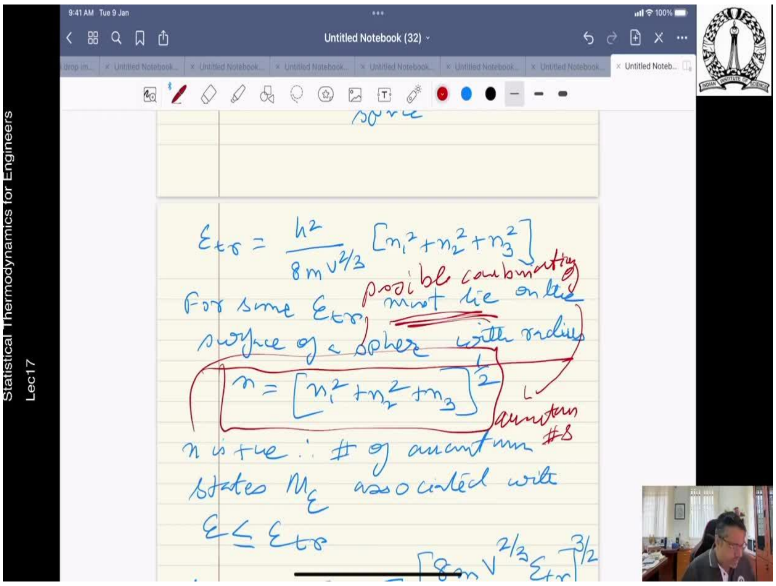
# of quantum states

$$\therefore \boxed{M_\varepsilon = \frac{4\pi}{3}\left(\frac{2m}{h^2}\right)^{3/2} V \varepsilon_{tr}^{3/2}}$$

Differentiate

$$\underbrace{2\pi\left(\frac{2m}{h^2}\right)^{3/2} V \varepsilon_{tr}^{1/2}}\, d\varepsilon_{tr}$$

# of eigenstates per unit energy in range ε_{tr} to $\varepsilon_{tr}+d\varepsilon_{tr}$



space

$$\varepsilon_{tr} = \frac{h^2}{8mV^{2/3}}\left[n_1^2+n_2^2+n_3^2\right]$$

For some ε_{tr}, possible combination must lie on the surface of a sphere with radius

$$\boxed{n = \left[n_1^2+n_2^2+n_3^2\right]^{1/2}}$$

quantum #s

n is +ve ∴ # of quantum states M_ε associated with

$\varepsilon \leq \varepsilon_{tr}$

$$\left[8mV^{2/3}\varepsilon_{tr}\right]^{3/2}$$

So, this is also called density of states, this is also called the density of states. So, therefore, the number of quantum states available is given by this, so this is quantum states and so the numbers must lie on the surface of this possible combination of quantum numbers, must lie on the surface of a sphere with radius this.

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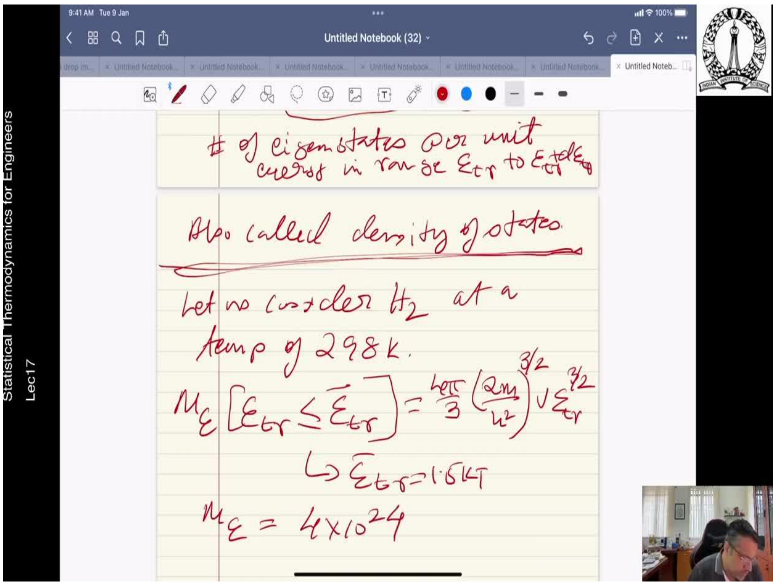


# of eigenstates per unit energy in range ε_{tr} to $\varepsilon_{tr}+d\varepsilon_{tr}$

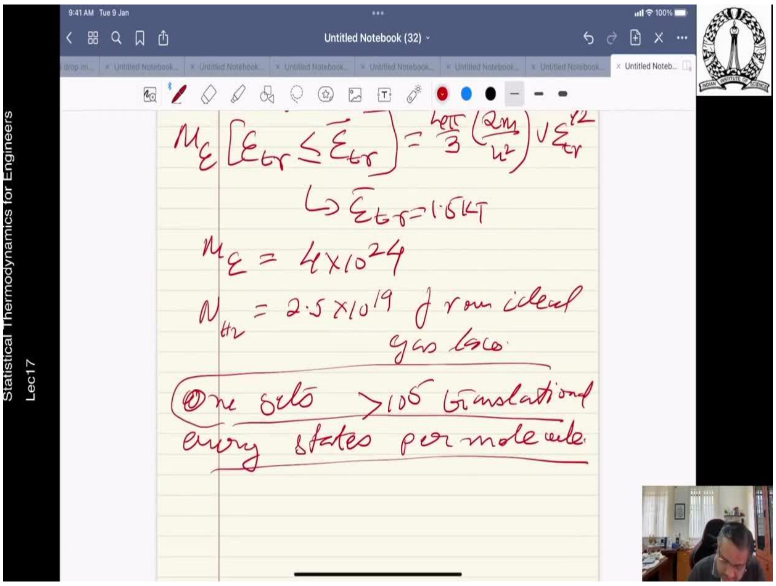
Also called density of states

Let us consider H_2 at a temp of 298 K.

$$M_\varepsilon\left[\varepsilon_{tr} \le \bar{\varepsilon}_{tr}\right] = \frac{4\pi}{3}\left(\frac{2m}{h^2}\right)^{3/2} V \varepsilon_{tr}^{3/2}$$

$\hookrightarrow \bar{\varepsilon}_{tr} = 1.5kT$

$M_\varepsilon = 4\times10^{24}$



$$M_\varepsilon\left[\varepsilon_{tr} \le \bar{\varepsilon}_{tr}\right] = \frac{4\pi}{3}\left(\frac{2m}{h^2}\right)^{3/2} V \varepsilon_{tr}^{3/2}$$

$\hookrightarrow \bar{\varepsilon}_{tr} = 1.5kT$

$M_\varepsilon = 4\times10^{24}$

$N_{H_2} = 2.5\times10^{19}$ from ideal gas law.

One gets $>10^5$ translational energy states per molecule

So, take an state of small example here, let us say hydrogen, let us consider hydrogen at a temperature 298 kelvin. ME E tr less than or equal to (())(18:52), where E tr average energy is about 1.5 KT, this is just an example of hydrogen. So, if you calculate this number, this is actually now therefore equal to 4 pi by 3, 2 m by h square 3 by 2 E tr 3 by 2. So, this will give you the value of ME is equal to 4 into 10 to the power of 24.

So, the number of hydrogen molecules if we look at it, the number of hydrogen molecules this is actually equal to 2.5 into 10 to the power 19, so that is some ideal gas law. So, one can one gets it is more than10 to the power of 5 translation energy states per molecule. This is outrageous, so that is the number of molecules that is the number of translational stages that you are going to get. This essentially almost guarantees that any gas will have its dilute limit(())(20:59) and liability on it. So, many number of translational stages that are available.

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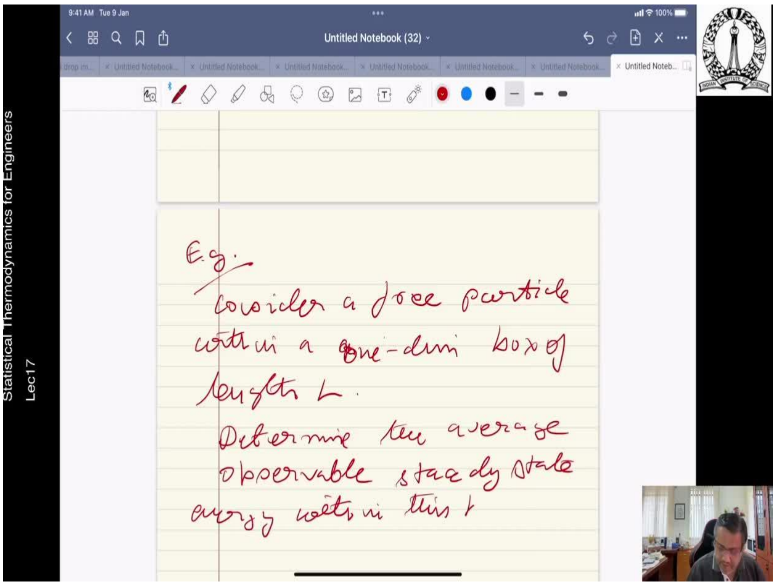
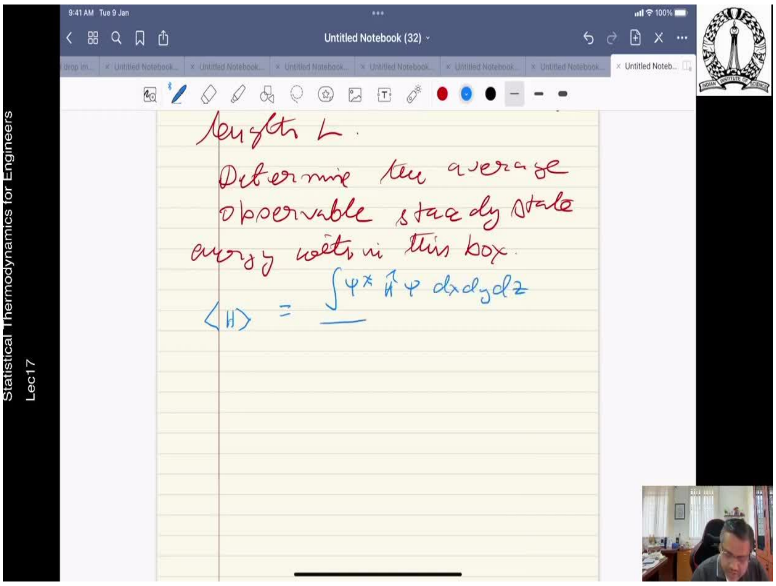


E.g.

Consider a free particle within a one-dim box of length L.

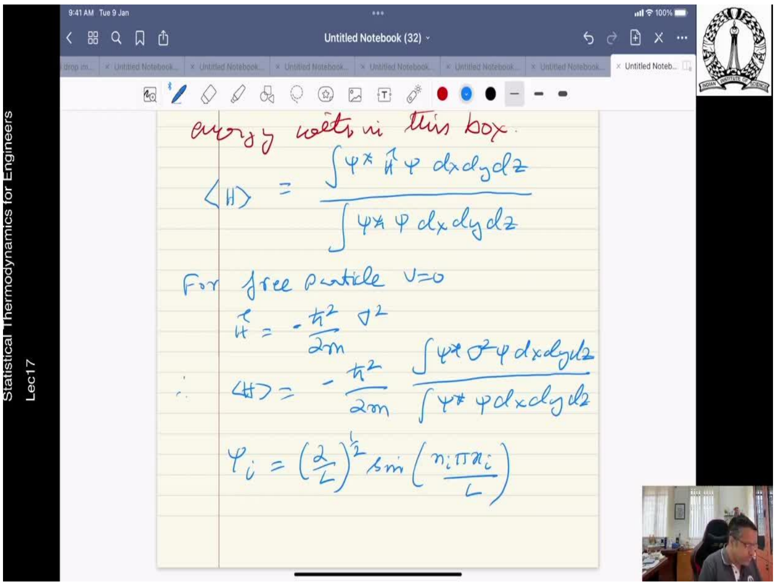
Determine the average observable steady state energy within this b



length L.

Determine the average observable steady state energy within this box.

$$\langle H \rangle = \frac{\int \psi^* \hat{H} \psi \, dx\,dy\,dz}{}$$



energy within this box.

$$\langle H\rangle = \frac{\int \psi^* \hat{H} \psi \, dx\,dy\,dz}{\int \psi^* \psi \, dx\,dy\,dz}$$

For free particle $V=0$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2$$

$$\therefore \langle H\rangle = -\frac{\hbar^2}{2m}\frac{\int \psi^* \nabla^2 \psi \, dx\,dy\,dz}{\int \psi^* \psi \, dx\,dy\,dz}$$

$$\psi_i = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n_i \pi x_i}{L}\right)$$

Now, let us do an example. Consider a free particle within a one-dimensional box of length L. So, you have to determine the average observable steady state energy within this box. So, for any dynamic variables, we already know the rule here for H is for the steady state energy as we know this is given as Psi star H hat time dx dy dz, Psi star dx dy dz.

For a free particle v is equal to 0, so that Hamiltonian operator becomes minus h bar square by 2m into the Laplace. So, therefore H bar becomes minus h square by 2m, Psi star Psi dx dy dz divided by Psi star Psi dx dy dz. So, this is equation if you look at this, if you look wave number Psi i you already found this given by 2 by L to the power half, ni pi by Psi by L. This equation we already made.

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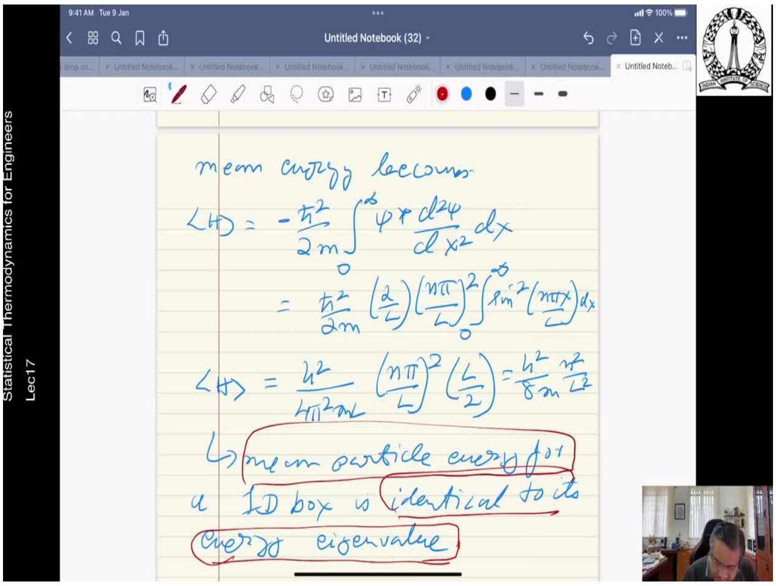


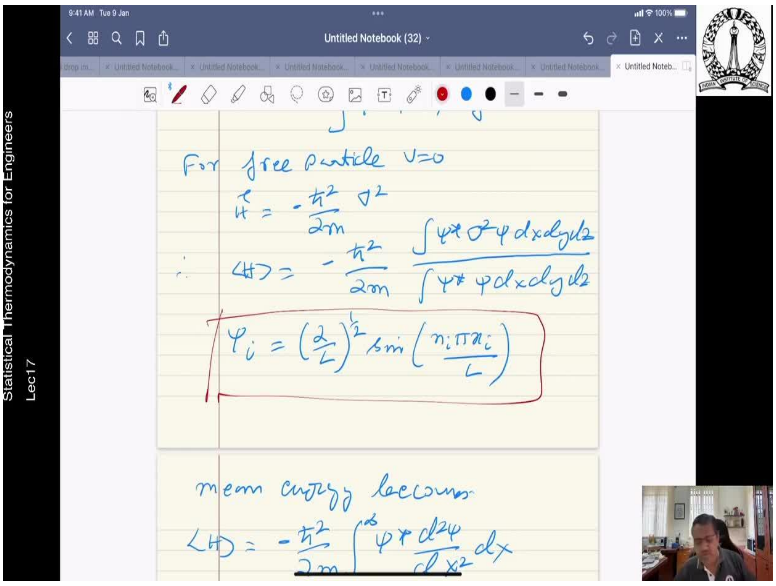
mean energy becomes

$$\langle H\rangle = -\frac{\hbar^2}{2m}\int_0^{\infty} \psi^* \frac{d^2\psi}{dx^2}\,dx$$

$$= \frac{\hbar^2}{2m}\left(\frac{2}{L}\right)\left(\frac{n\pi}{L}\right)^2 \int_0^{\infty} \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$\langle H\rangle = \frac{h^2}{4\pi^2 mL}\left(\frac{n\pi}{L}\right)^2\left(\frac{L}{2}\right) = \frac{h^2}{8m}\frac{n^2}{L^2}$$

↳ mean particle energy for a 1D box is identical to its energy eigenvalue



For free particle $V=0$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2$$

$$\langle H\rangle = -\frac{\hbar^2}{2m}\frac{\int \psi^* \nabla^2 \psi \, dx\,dy\,dz}{\int \psi^* \psi \, dx\,dy\,dz}$$

$$\boxed{\psi_i = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n_i \pi x_i}{L}\right)}$$

mean energy becomes

$$\langle H\rangle = -\frac{\hbar^2}{2m}\int_0^\infty \psi^* \frac{d^2\psi}{dx^2}\,dx$$

So, this is what we found out about the boundary conditions mean energy becomes we have to just plug this in H bar h cut minus h square, 0 to infinity Psi d square Psi by dx square into dx becomes equal to h square by 2m, 2 by L, n pi by L square 0 to infinity, sine square n pi X by L dx. If we evaluate this integral, so this will give you h square by 4 pi square m into L, gives you validate the calculation. Also equal to h square 8 m, n square by L square. So, as expected the particle the mean particle energy for 1D box is identical to its energy eigenvalue. So, this is consistent with our general expectation at this is what it should.

So, we can see so therefore, the mean particle energy is this. So, this is a one-dimensional things we have done it. This can actually draw holes if you want a bit size equal to 1 there is only 1 dimension that is available. So, this is identical to what we have seen from your quantum mechanics as indicated by your earlier versions, so like the turbo image.

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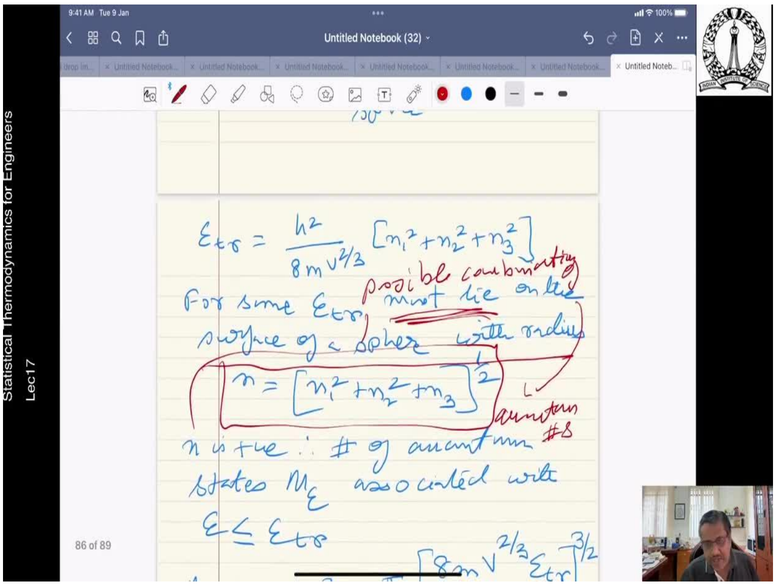


$$\varepsilon_{tr} = \frac{h^2}{8mV^{2/3}}\left[n_1^2+n_2^2+n_3^2\right]$$

For some ε_{tr}, possible combinations must lie on the surface of a sphere with radius

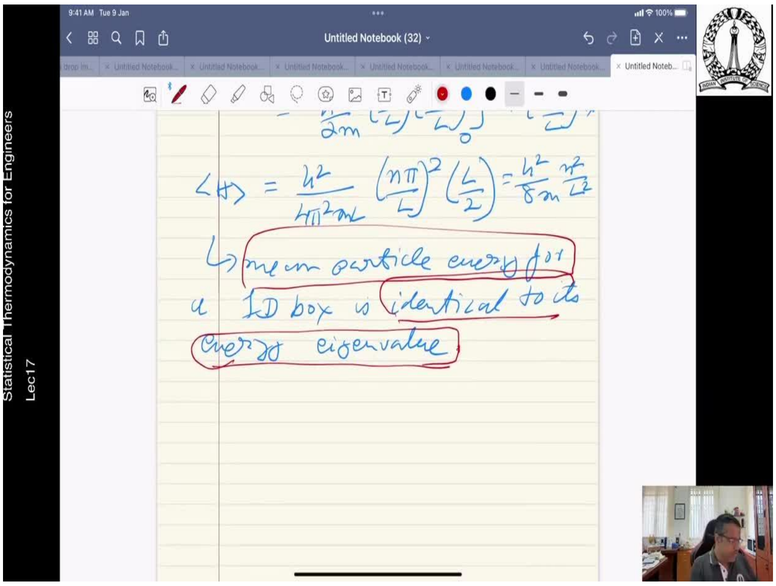
$$\boxed{n = \left[n_1^2+n_2^2+n_3^2\right]^{\frac{1}{2}}}$$

quantum #s

n is the : # of quantum states M_ε associated with

$\varepsilon \le \varepsilon_{tr}$

$\left[8mV^{2/3}\varepsilon_{tr}\right]^{3/2}$



$$\langle H\rangle = \frac{h^2}{4\pi^2 mL}\left(\frac{n\pi}{L}\right)^2\left(\frac{L}{2}\right) = \frac{h^2}{8m}\frac{n^2}{L^2}$$

↳ mean particle energy for a 1D box is identical to its energy eigenvalue

So, this actually completes the translational modes, so we have seen that many translational modes possible, and we have seen that the translational modes can have like these 3 quantum numbers, translational quantum numbers corresponding to its 3 degrees of freedom, there are going to be very large number of energy states that will be available and the energy value is nothing but the Eigen value of this particular system.

But the energy is very miniscule because it is dependent on h square which is a Planck's constant and therefore, we need more need to look at the internal modes if you want to have a good idea that how this would look for specific evidence for the same. So, we will see in the next class where we will go through the uncertainty, start with uncertainty principle in the next class. Thank you.