Statistical Thermodynamics for Engineers

Professor Saptarshi Basu

Indian Institute of Science, Bengaluru
Lecture 49
From Particles to assembly II

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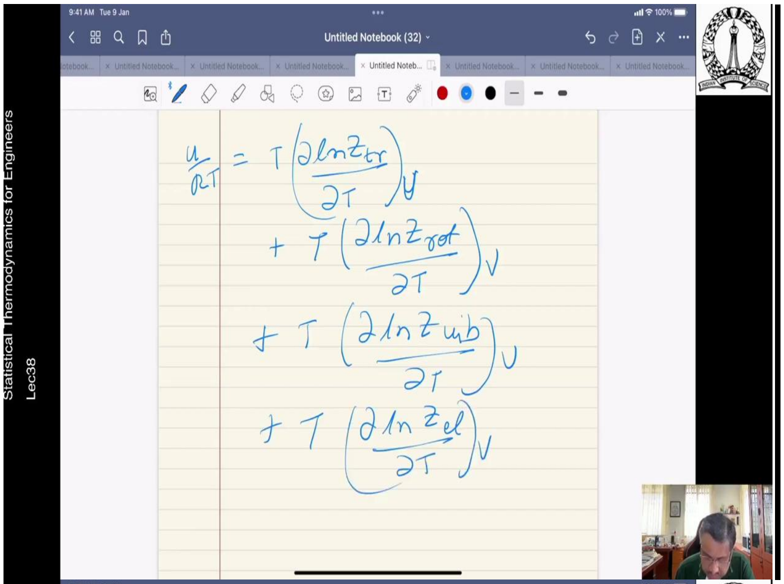
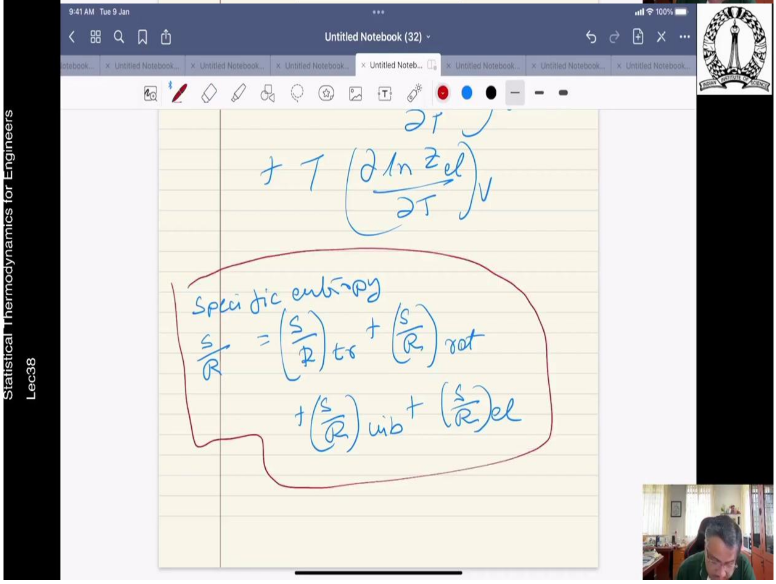


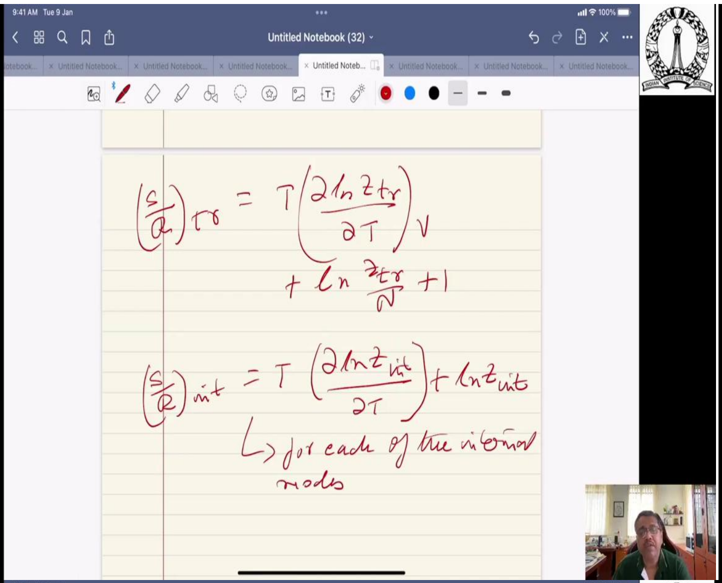
$$\frac{u}{RT} = T\left(\frac{\partial \ln Z_{tr}}{\partial T}\right)_V + T\left(\frac{\partial \ln Z_{rot}}{\partial T}\right)_V + T\left(\frac{\partial \ln Z_{vib}}{\partial T}\right)_V + T\left(\frac{\partial \ln Z_{el}}{\partial T}\right)_V$$



$$+ T\left(\frac{\partial \ln Z_{el}}{\partial T}\right)_V$$

Specific entropy

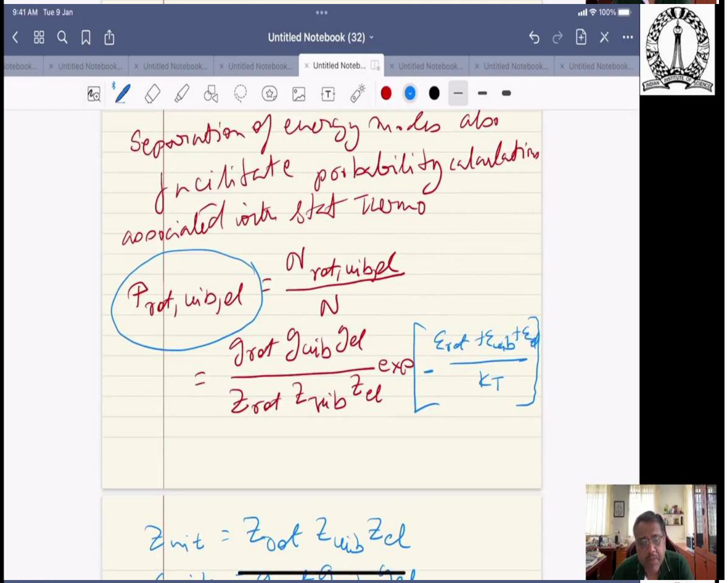
$$\boxed{\frac{s}{R} = \left(\frac{s}{R}\right)_{tr} + \left(\frac{s}{R}\right)_{rot} + \left(\frac{s}{R}\right)_{vib} + \left(\frac{s}{R}\right)_{el}}$$



$$\left(\frac{S}{R}\right)_{tr} = T\left(\frac{\partial \ln Z_{tr}}{\partial T}\right)_V + \ln\frac{Z_{tr}}{N} + 1$$

$$\left(\frac{S}{R}\right)_{int} = T\left(\frac{\partial \ln Z_{int}}{\partial T}\right) + \ln Z_{int}$$

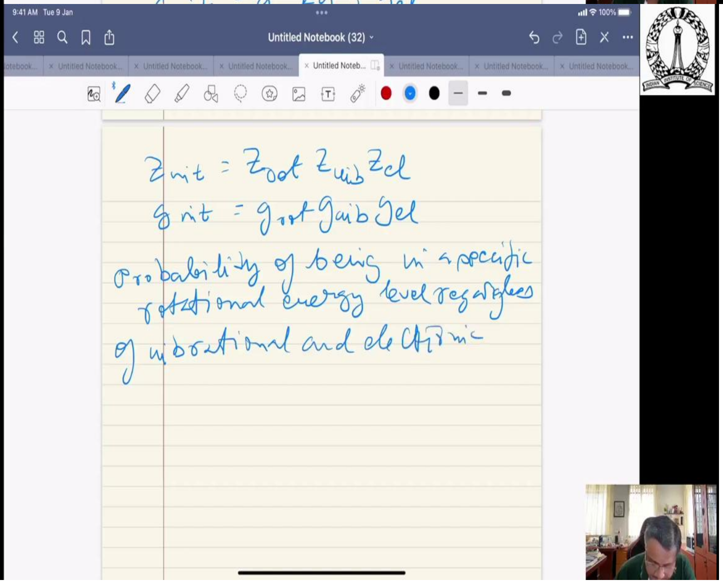
↳ for each of the internal modes



Separation of energy modes also facilitate probability calculation associated with stat Thermo

$$\boxed{P_{rot,vib,el}} = \frac{N_{rot,vib,el}}{N} = \frac{g_{rot}\, g_{vib}\, g_{el}}{Z_{rot}\, Z_{vib}\, Z_{el}} \exp\left[-\frac{\varepsilon_{rot}+\varepsilon_{vib}+\varepsilon_{el}}{kT}\right]$$

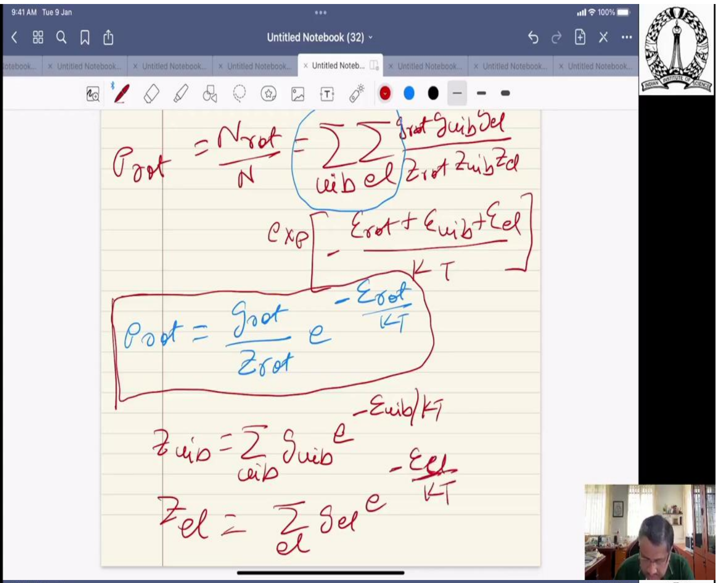
$$Z_{int} = Z_{rot}\, Z_{vib}\, Z_{el}$$



$$Z_{int} = Z_{rot}\, Z_{vib}\, Z_{el}$$

$$g_{int} = g_{rot}\, g_{vib}\, g_{el}$$

Probability of being in a specific rotational energy level regardless of vibrational and electronic

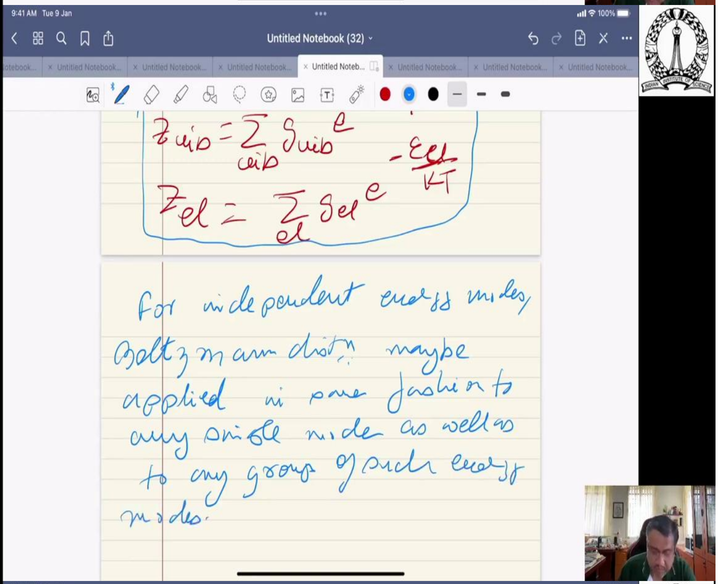


$$P_{rot} = \frac{N_{rot}}{N} = \sum_{vib}\sum_{el} \frac{g_{rot}\, g_{vib}\, g_{el}}{Z_{rot}\, Z_{vib}\, Z_{el}} \exp\left[-\frac{\varepsilon_{rot}+\varepsilon_{vib}+\varepsilon_{el}}{kT}\right]$$

$$\boxed{P_{rot} = \frac{g_{rot}}{Z_{rot}}\, e^{-\frac{\varepsilon_{rot}}{kT}}}$$

$$Z_{vib} = \sum_{vib} g_{vib}\, e^{-\varepsilon_{vib}/kT}$$

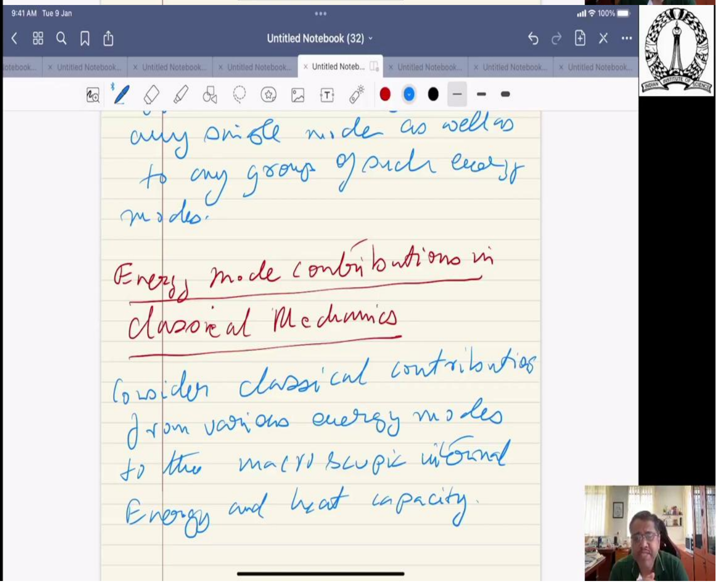
$$Z_{el} = \sum_{el} g_{el}\, e^{-\frac{\varepsilon_{el}}{kT}}$$



$$Z_{vib} = \sum_{vib} g_{vib}\, e$$

$$Z_{el} = \sum_{el} g_{el}\, e^{-\frac{\varepsilon_{el}}{kT}}$$

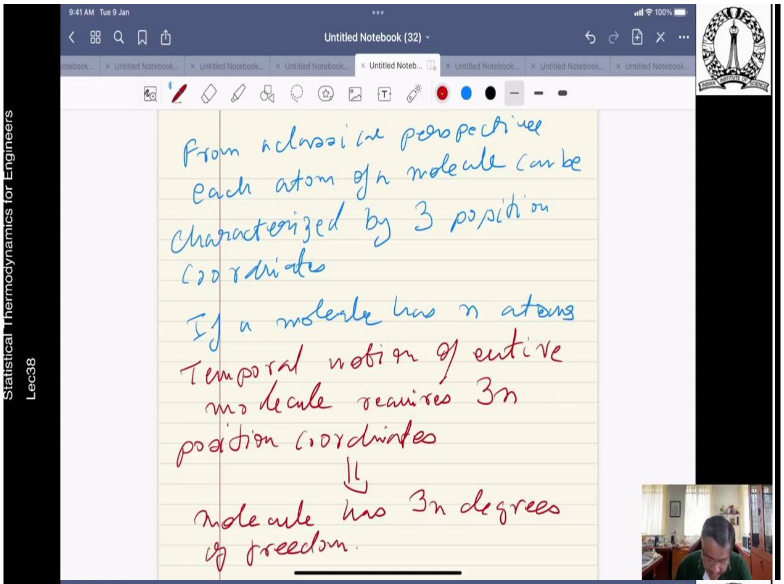
For independent energy modes, Boltzmann distn maybe applied in same fashion to any single mode as well as to any group of such energy modes.



any single mode as well as to any group of such energy modes.

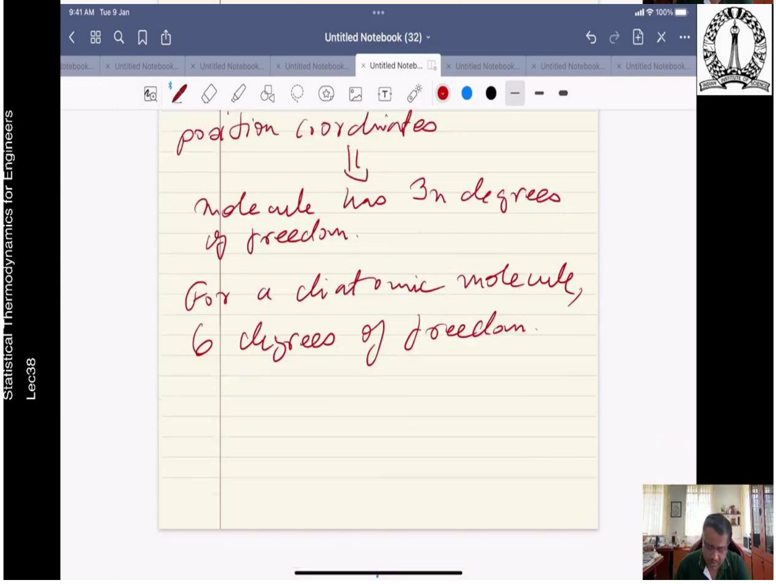
Energy mode contributions in classical Mechanics

Consider classical contributions from various energy modes to the macroscopic internal Energy and heat capacity.



From a classical perspective
each atom of a molecule can be
characterized by 3 position
coordinates

If a molecule has n atoms
Temporal motion of entire
molecule requires 3n
position coordinates
$\Downarrow$
molecule has 3n degrees
of freedom.



position coordinates
$\Downarrow$
molecule has 3n degrees
of freedom.

For a diatomic molecule,
6 degrees of freedom.

Welcome to lecture number 38 of the statistical thermodynamics course. So, in the last lecture, what we did was that we found out that for example, internal energy is written as u by RT is equal to T d ln Z tr plus T d ln Z rotation by dt this is a V plus T d ln Z vibrational by dt V plus T ln Z electronic by dt.

The entropy on the other end specific entropy s by R equal is s by R translational plus s by R rotational plus s by R vibrational plus s by R electronic. So, this is the specific entropy now, for the translational mode so, in this case, translational mode sR tr is written as d ln Z tr dt V plus ln Z tr by N plus 1 and then of course, you have the internal rate which is given as ln Z internal divide by dt plus ln Z internal for each of the internal modes.

So, separation of energy modes also facilitate probability calculations associated with stat thermo, for example, if you want to find out P, let us write it as P rotation, vibration, electronics which means that the probability of being in a specific rotational, vibrational and electronic energy level which would mean the number of particles in that rotation, vibration and electronic configuration divided by the total number of particles which essentially translates.

Now g rotation, g vibration, g electronics divided by the corresponding partition functions rotation and vibration electronic then of course there is an exponential term which is minus E rotation plus E vibration plus E electronic divide by kT, where we know that the partition functions are like this Zee internal is equal to Zee rotation Zee vibration Zee electronic and then g internal which is the degeneracy is g rotation g vibration and g electronic.

So, this is this represents what this represents the probability of a particular probability of being in a particular or a specific rotational vibrational and electronic energy level. Now if we want to evaluate like this the probability say of being in specific rotational energy level regardless of vibrational a and electronic energy levels we can say that P rot rotational equal to N rot by N which is double summation the sum over all the vibrational levels is a sum together of all the rotational levels.

Now, so g rot g vibration into electronic divided by Z rot Z vib Z el then of course, everything is still within the summations. So, and this is minus E rot plus Evib plus electronic divided by kT. So, you can see that we have summed over all the rotation and over all the electronic energy levels because we are interested in a particular rotational energy level and we disregard we are not really concerned about what are the corresponding vibrational and electronic energy levels.

So, this is g rot divided by Z rot exponential energy rot by kT. So, of course, Z vib with summation over all vibrational energy levels kT and Z electronic Z electronic is summation over all electronic energy levels all electronic energy levels exponential minus El kt. So, these are the mainly the two for independent energy levels a Boltzmann distribution may be applied in the same fashion to any single mode as well as to any group of such energy modes.

So, as well as to any groups of such energy modes for independent energy modes, Boltzmann distribution may be applied be applied in same fashion in any single mode as well as to any group of such energy modes. So, now, so, this stages are separate we know now, how to calculate the probabilities, how to calculate the properties because properties is also depend on your partition function actually more specifically on the logarithm natural logarithm of the partition function. So, now, we come to the chapter where we say energy mode contributions in classical mechanics so, now the stage is set that we consider, we consider the classical contributions from various energy modes to the macroscopic internal energy and heat capacity.

So, our eventual goal is to compare the classic and appointed allocations from each of the translational rotational and vibrational modes. So, let us consider classical contributions from various energy modes to the macroscopic internal energy and the heat capacity. So, our goal as we said is to calculate the allocations from each of the translational, rotational and vibrational modes.

So, if we look at a very classical definition look at very classical definition of a system each atom of a system say from a classical perspective, from classical perspective each atom, each atom of a molecule can be recognized can be characterized by 3 position coordinates just like XYZ. Now, if a molecule has n atoms the temporal notion of the entire molecule of a requires 3n position coordinate mostly these are independent of each other.

So, the position of one add is not dependent directly on the other. So, 3n position coordinates. So, we therefore, say that the molecule as a molecule has 3n degrees of freedom, the molecules has 3n degrees of freedom. Now, for a diatomic molecule, for a diatomic molecule, diatomic molecule where there are 2, the number of atoms is 2 so, there would be like 6 degrees of freedom, 6 degrees of freedom.

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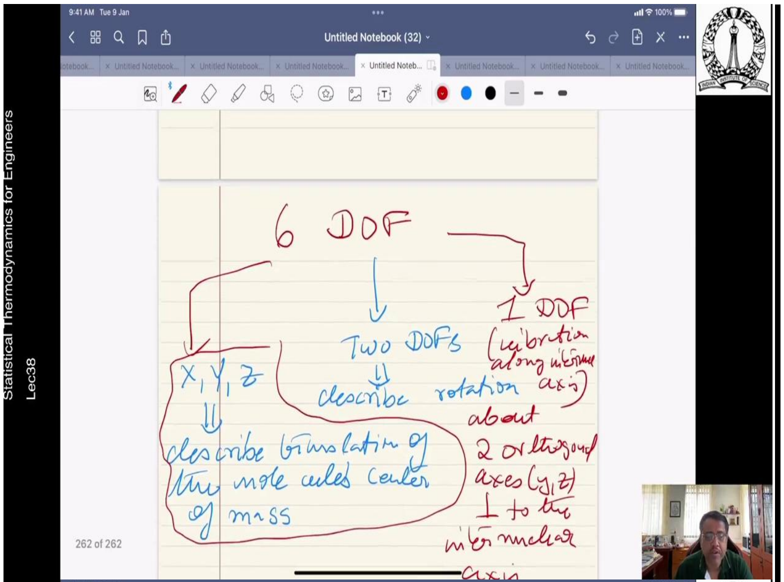
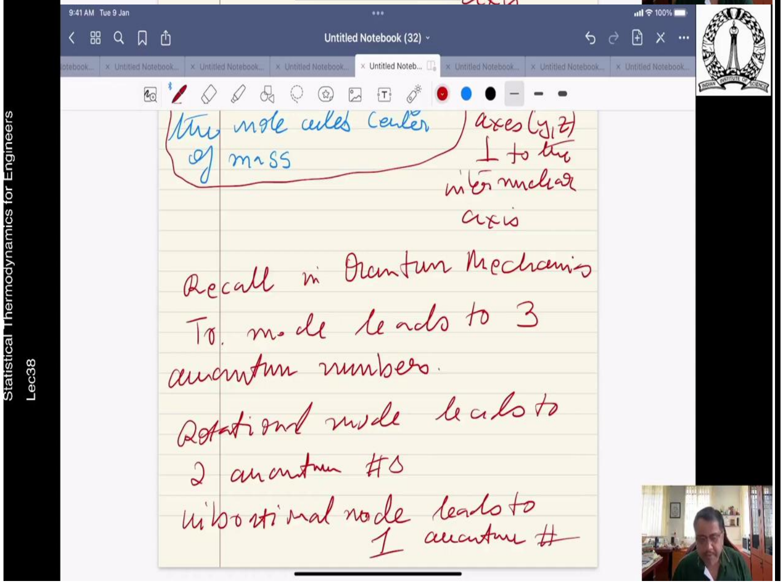


6 DOF

X, Y, Z $\Downarrow$ describe translation of the molecules center of mass

Two DOFs $\Downarrow$ describe rotation about 2 orthogonal axes (y, z) ⊥ to the internuclear axis

1 DOF (vibration along internuclear axis)



the molecules center of mass

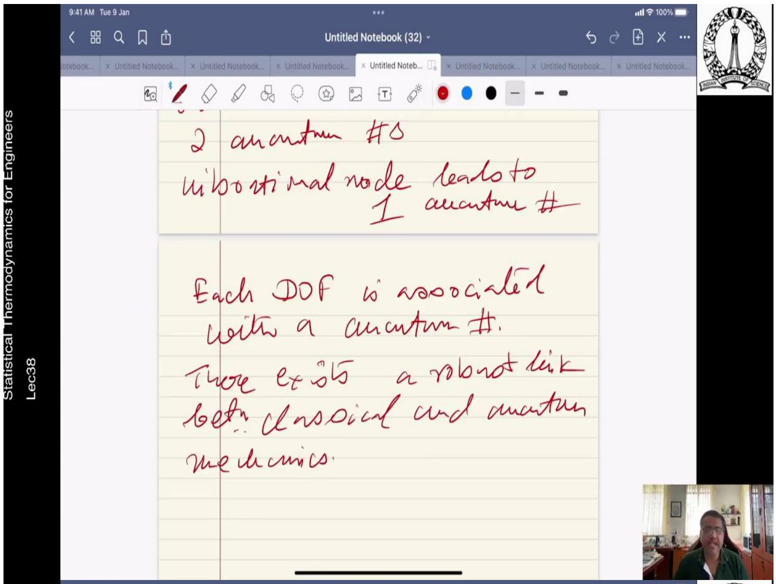
axes (y, z) ⊥ to the internuclear axis

Recall in Quantum Mechanics

Tr. mode leads to 3 quantum numbers.

Rotational mode leads to 2 quantum #s

Vibrational mode leads to 1 quantum #

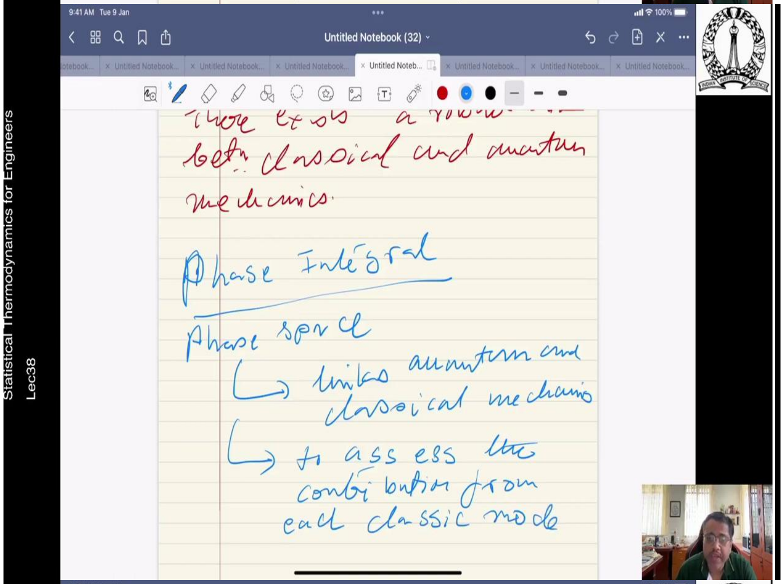


2 quantum #s

vibrational mode leads to 1 quantum #

Each DOF is associated with a quantum #.

There exists a robust link between classical and quantum mechanics.



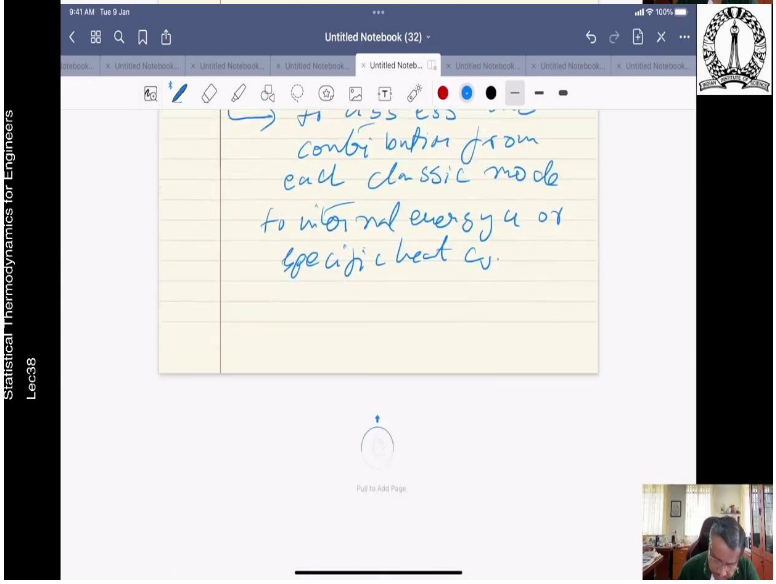
There exists a robust link between classical and quantum mechanics.

Phase Integral

Phase space

→ links quantum and classical mechanics

→ to assess the contribution from each classic mode



→ to assess the contribution from each classic mode

to internal energy u or specific heat c_v.

So, how are the 6 degrees of freedom so, altogether 6 degrees of freedom we can first do this out of the 6, 6 degrees of freedom 3 degrees of freedom x y z is concerned with the first 3 degrees of freedom are used to describe translation of the molecules center of mass. Two degrees of freedom have two DOFs are needed to describe its rotation about 2 orthogonal in all axes the y comma z perpendicular to the inter nuclear axis.

And then there is a 1 degree of freedom still remaining which is used to describe vibration along the inter nuclear axis. So, this is the this can be the fixed degrees of freedom first 3 x y z describes a translation of the center of mass, 2 degrees of freedom or require these 2 degrees of freedom considers rotation about the 2 orthogonal directions from the inter nuclear.

This is the inter nuclear axis, the 2 orthogonal directions represents the 2 degrees of freedom for the rotation and then lastly vibration can happen along this inter nuclear axis therefore, it has got 1 degree of freedom. So, this has got a very robust link now, consistent with this description, we recall that in quantum mechanics the translational mode leads to 3 quantum numbers.

The rotational mode leads to 2 quantum numbers and vibrational mode leads to 1 quantum number. Leads to 1 quantum number so we can see each degree of freedom so, we can almost say each degree of freedom is represented or can be associated is associated with a quantum number, with a quantum number.

So, there is a very robust link between classical and quantum mechanics. So, there exists a robust link between classical and quantum mechanics. So, there exists this very nice association I should say between the two. Next let us look at something called the phase integral, now, to assess the contribution from each classical energy mode to the internal energy U or specifically cv we must develop classical representation of a partition function.

So, in pursuit of the goal we introduced this concept of phase space which provides the necessary link between quantum and classical mechanics. So, this end we will so, first let us write down the obvious phase space does two things it links, quantum and classical mechanics and use to assess the contribution from each classic mode to internal energy u or specific heat cv.

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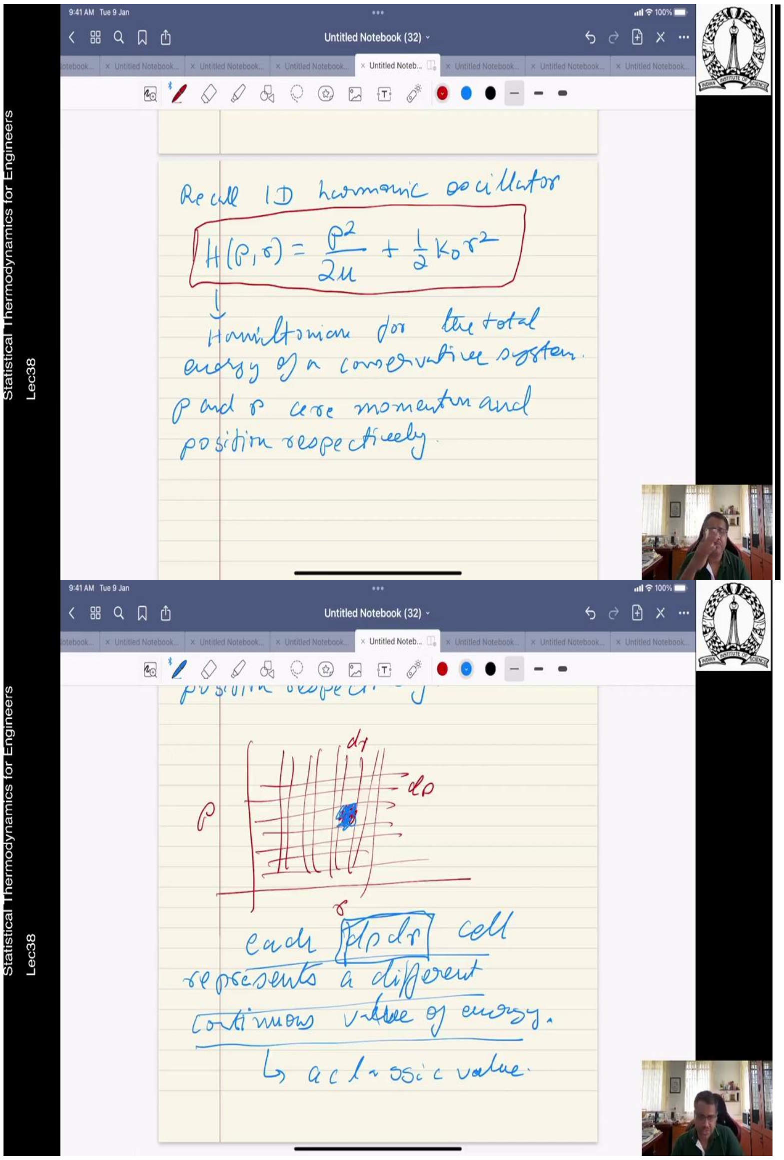

Recall 1D harmonic oscillator

$$\boxed{H(p,r) = \frac{p^2}{2\mu} + \frac{1}{2}k_0 r^2}$$

↓ Hamiltonian for the total energy of a conservative system.

p and r are momentum and position respectively.

each $\boxed{dp\,dr}$ cell represents a different continuous value of energy.

↳ a classic value.

So, let us recall the 1 dimensional harmonic oscillator 1D harmonic oscillator harmonic oscillators. Hamiltonian defining the total energy of a conservative system the Hamiltonian with describes the total energy of a conservative system so, if we write that p comma r p square by 2 mu plus half k naught r square this is the Hamiltonian for the total energy of a conservative system P and R are momentum and position respectively.

So, this equation that you see over here is an important result from classical mechanics mandates that each degree of freedom each degree of freedom mandates a position and momentum coordinate.

In fact the central importance of momentum and position in classical mechanics is manifested by the phase space diagram. So, phase space diagram will be something like this. So, you have the momentum and the position and you could represent a different value of the energy. If you look at it like this this is P this is R and then you have it so, each is a like dr and there is a dp. See if you look at this so (())(22:30).

So, each dp dr cell represents a different continuous value of energy. So, each cell can be represented in a single classic value of the continuous energy. Therefore, we must assert the number of quantum states within a cell in a number of quantum states within a single cell in the phase space must be the classical analog to degeneracy.

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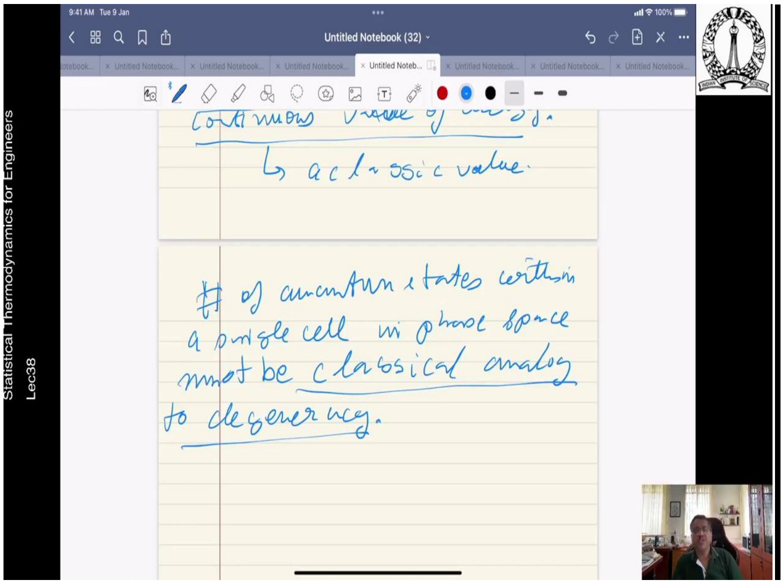
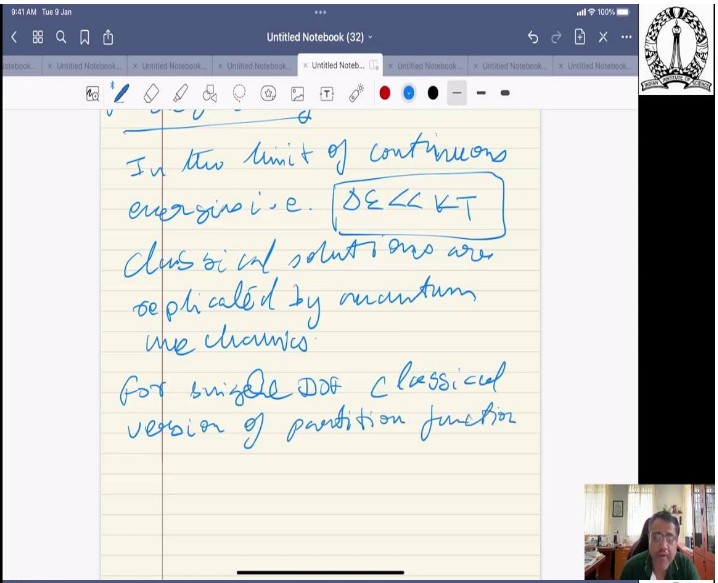


continuous value of energy.

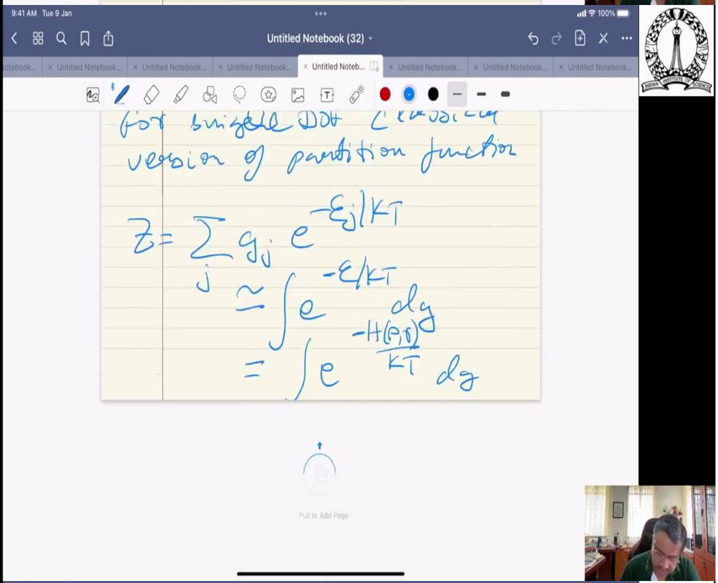
↳ a classic value.

# of quantum states within a single cell in phase space must be classical analog to degeneracy.



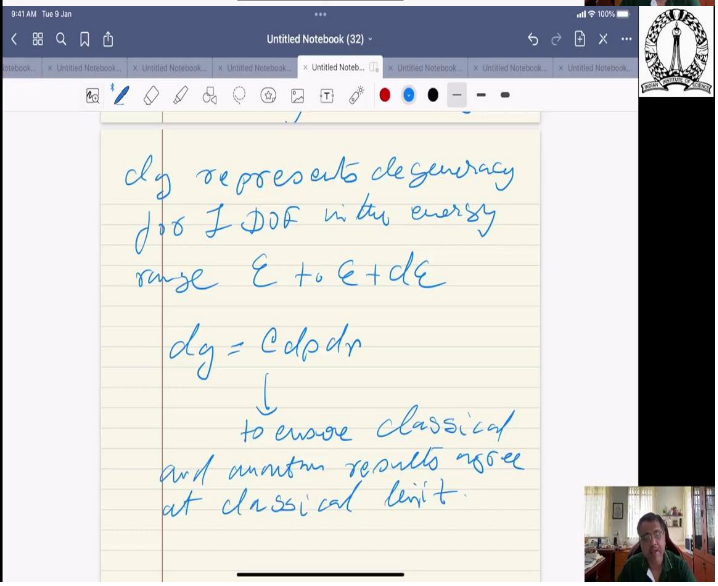
In the limit of continuous energies i.e. $\boxed{\Delta E << KT}$ classical solutions are replicated by quantum mechanics

For single DOF classical version of partition function



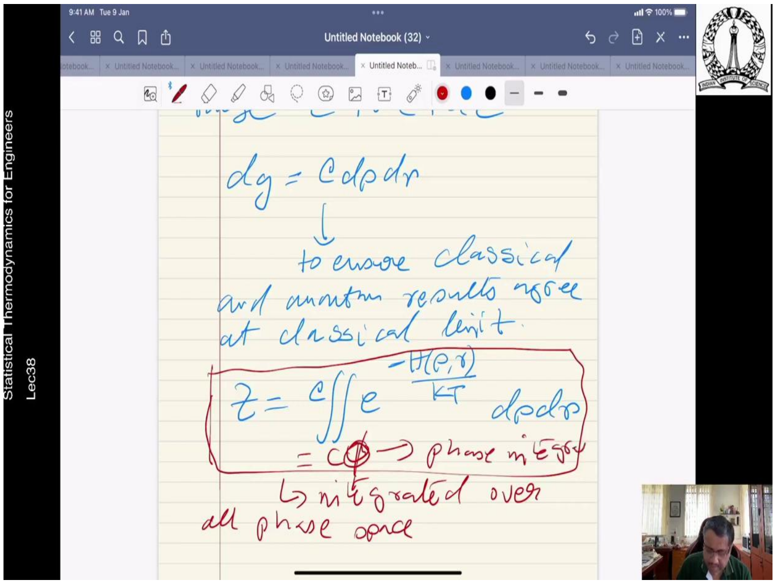
version of partition function

$$Z = \sum_j g_j e^{-\mathcal{E}_j/KT}$$
$$\simeq \int e^{-\mathcal{E}/KT} dg$$
$$= \int e^{\frac{-H(p,r)}{KT}} dg$$



dg represents degeneracy for 1 DOF in the energy range $\mathcal{E}$ to $\mathcal{E}+d\mathcal{E}$

$$\underset{\substack{\downarrow \\ \text{to ensure classical and quantum results agree at classical limit.}}}{dg = C\,dp\,dr}$$



$$dg = C\,dp\,dr$$

to ensure classical and quantum results agree at classical limit.

$$\boxed{Z = C\iint e^{-\frac{H(p,r)}{kT}}\,dp\,dr = C\phi \rightarrow \text{phase integral}}$$

↳ integrated over all phase space

So, number of quantum states within a single cell within a cell in phase space must be classical analog to degeneracy. So, the correspondence principle indicates that the classical solutions must be replicated by quantum mechanics in the limit of continuous energies. So, the in the limit of continuous energies that is delta E less than kT.

A classical solutions must be replicated by quantum mechanics, classical solutions are replicated by quantum mechanics, replicated by quantum mechanics. For single DOF degree of freedom a classical version of continuous the classical version of partition function comes. So, one is Z summation j gj exponential minus Ej by kT this is almost equal to integral e by kT dg, in other words is equal to exponential minus H p comma r by kT dg.

So, dg represents the degeneracy for 1 DOF in the energy range. So, E plus dE because the classical energy can be always portrayed with the phase space, we assumed that the quantum counterpart to the differential degeneracy of one momentum coordinate to the other can be explained now can be expressed in our Cdpdr where c is a constant to ensure classical quantum results agree at classical limit.

So, substituting this we can have Z equal to C there are two integrals e H p comma r by kT dpdr. If so, this will be the (())(28:02) this will be the partition function in that limit the classical counterpart with the differential degeneracy. So, this is what it is where the integration is carried out over all phase space and this can be also written as c phi(())(28:32), this is called the phase integral.

In the next class we will see that is how this, how this result can be subsequently used. How this can be used to establish contributions from the different modes. So, we will see in the next class. We will stop here, we will continue next lecture.