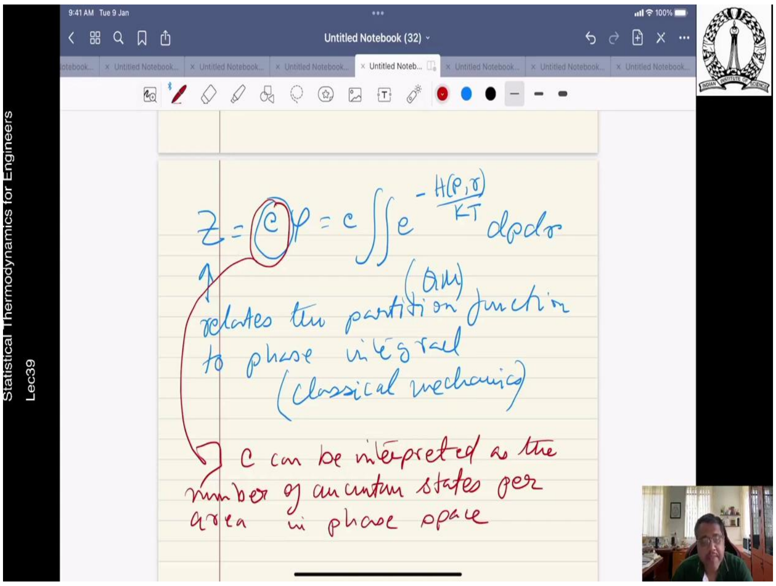
Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bengaluru
Lecture 50

Connecting Quantum Mechanics to Classical Mechanics

(Refer Slide Time: 0:10)



$$Z = \boxed{C}\varphi = C\iint e^{-\frac{H(p,r)}{KT}}\,dp\,dr$$

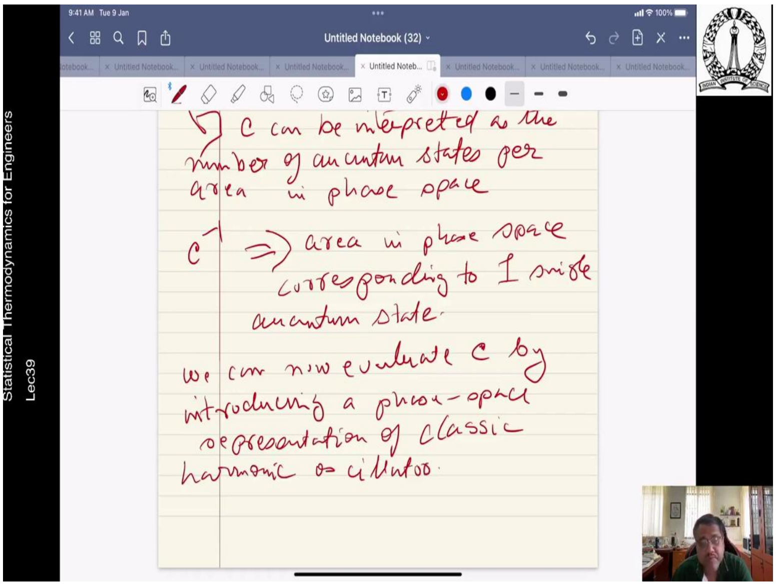
relates the partition function (QM) to phase integral (classical mechanics)

C can be interpreted as the number of quantum states per area in phase space

Welcome to lecture number 39 of the Statistical Thermodynamics for Engineers Course. So, we just now saw that we write it once again that is Z is equal to C9 is also equal to C double integral exponential minus H p,r by KT dpdr. So, in this particular case as we saw. So, it is highly this equation is highly significant because it relates, relates partition function, partition function to the phase integral, phase integral. So, partition function is basically quantum mechanics base integral is classical mechanics this is classical mechanics partition function is quantum mechanics.

So, so definitely it is more importantly definite point by the definite point in the phase space is permitted by classical mechanics the same is not true for quantum mechanism due to uncertainty principle on this basis the value of C establishes a statistical mechanical you know (())(1:34) of the correspondence principle. So, C this constant C over here this guy this can be interpreted as the number C can be interpreted as the number of quantum states, number of quantum states per area per area in phase space, per area in phase space.

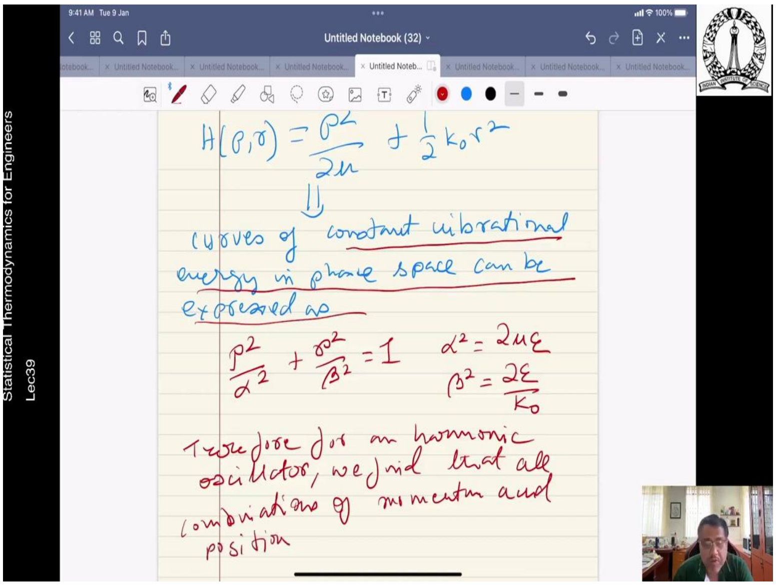
(Refer Slide Time: 2:18)



↳ C can be interpreted as the number of quantum states per area in phase space

$C^{-1} \Rightarrow$ area in phase space corresponding to 1 single quantum state.

We can now evaluate C by introducing a phase-space representation of classic harmonic oscillator.



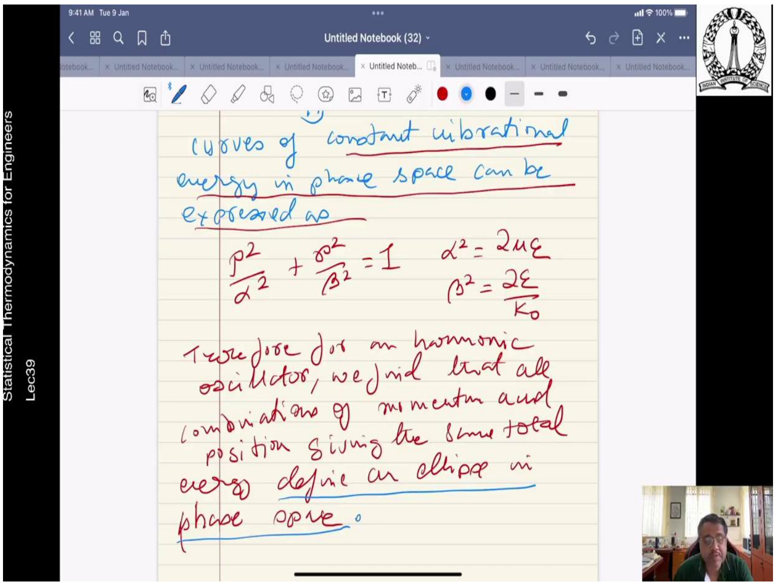
$$H(p,r) = \frac{p^2}{2\mu} + \frac{1}{2}k_0 r^2$$

$$\Downarrow$$

curves of constant vibrational energy in phase space can be expressed as

$$\frac{p^2}{\alpha^2} + \frac{r^2}{\beta^2} = 1 \qquad \alpha^2 = 2\mu\varepsilon \qquad \beta^2 = \frac{2\varepsilon}{k_0}$$

Therefore for an harmonic oscillator, we find that all combinations of momentum and position



curves of constant vibrational energy in phase space can be expressed as

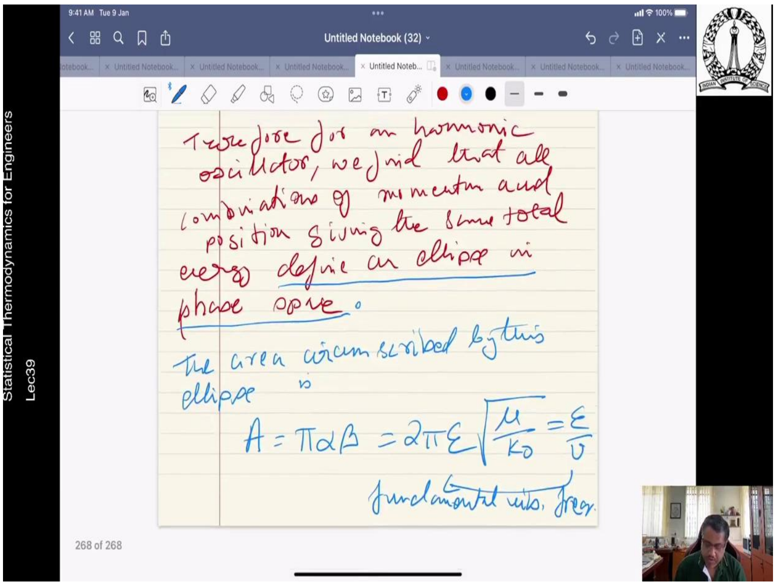
$$\frac{p^2}{\alpha^2} + \frac{r^2}{\beta^2} = 1 \qquad \alpha^2 = 2\mu\varepsilon \qquad \beta^2 = \frac{2\varepsilon}{k_0}$$

Therefore for an harmonic oscillator, we find that all combinations of momentum and position giving the same total energy define an ellipse in phase space.

So, this is the interpretation of C as a result inverse of C, C inverse, C inverse you must be the area in phase space corresponding to one single quantum state, one single quantum state. So, we can now evaluate C can now evaluate evaluate C by introducing, introducing a phase space representation, representation of classic harmonic classic harmonic oscillator. So, if you look at this, you look at this, if you look at this expression once again which is a Hamiltonian k naught r square, if we look at this one, if we write this. So, from here curves of constant vibrational energy in phase space can be expressed as.

So, the curves of constant vibrational energy in the phase space can be expressed as square square r beta square is equal to 1, alpha square is equal to 2 mu beta square is equal to k naught, these are curves these are curves of constant vibrational energy in the phase space it is expressed like this, constant vibration energy. So, for an harmonic oscillator therefore for an harmonic oscillator we find we find that all are combinations of momentum, momentum and position, combinations once you are giving the top same, giving the same total energy, total energy we define an ellipse an ellipse in phase space, in phase space.

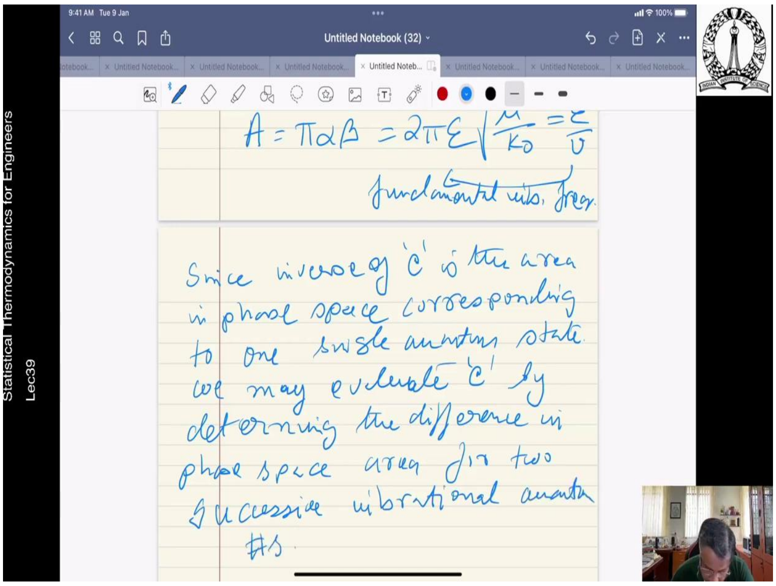
(Refer Slide Time: 6:29)



Therefore for an harmonic oscillator, we find that all combinations of momentum and position giving the same total energy define an ellipse in phase space.

The area circumscribed by this ellipse is

$$A = \pi \alpha \beta = 2\pi \varepsilon \underbrace{\sqrt{\frac{\mu}{k_0}} = \frac{\varepsilon}{\nu}}_{\text{fundamental vib. freq.}}$$



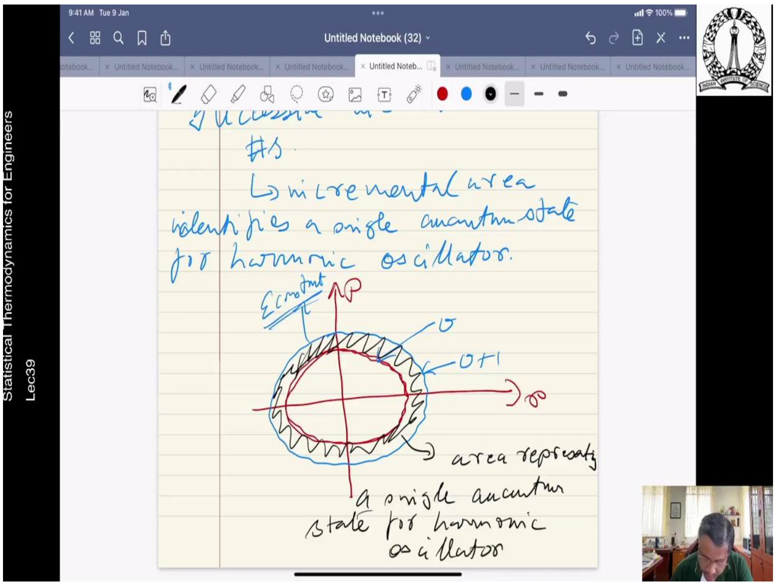
$$A = \pi\alpha\beta = 2\pi\epsilon\sqrt{\frac{\mu}{k_0}} = \frac{\epsilon}{\nu}$$

fundamental vib. freq.

Since inverse of 'C' is the area in phase space corresponding to one single quantum state we may evaluate 'C' by determining the difference in phase space area for two successive vibrational quanta #s.

So, the area circumscribed by this ellipse, the circumscribed by this ellipse, ellipse is A alpha beta equal to 2 pi epsilon energy by k naught equal to this. So, so this is expressed in terms of the fundamental this is the fundamental vibrational frequency because the inverse of C is the is the area in the phase space corresponding to one quantum state we may evaluate C by determining the differences in phase space area for two successive vibrational quantum numbers. So, since inverse of C is the area the area in phase space corresponding to one single quantum state we may evaluate C by determining, determining the difference in phase space area for two successive for two successive vibrational quantum numbers, two successive vibrational quantum numbers.

(Refer Slide Time: 9:09)

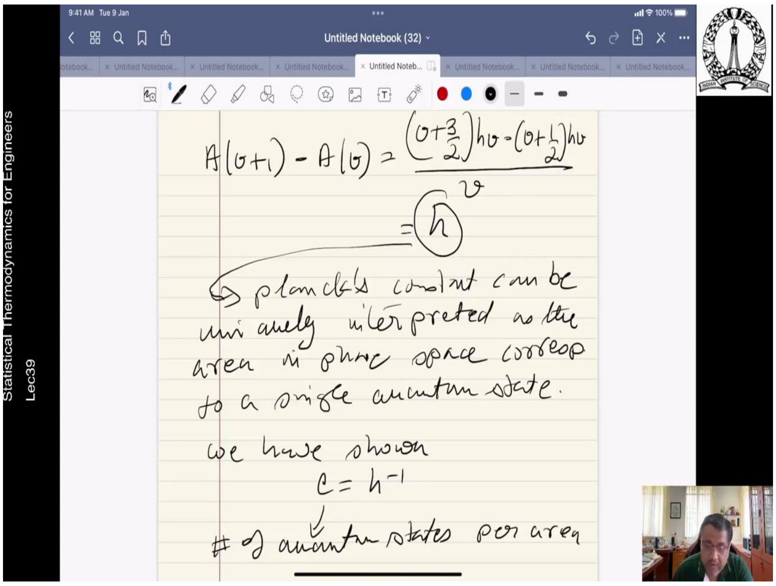


#s.

↳ incremental area identifies a single quantum state for harmonic oscillator.

This incremental area identifies a single quantum state, this incremental area identifies, identifies a single, single quantum state harmonic oscillator. So, if you look at this now let us draw this thing. So, e constant(())(10:02). So, this is v, this is v plus 1 and this area representing in a single quantum state, state for harmonic oscillator for harmonic oscillator. So, this equation is highly significant as we already saw over there.

(Refer Slide Time: 11:19)



$$A(v+1) - A(v) = \frac{(v+\frac{3}{2})h\nu - (v+\frac{1}{2})h\nu}{\nu}$$

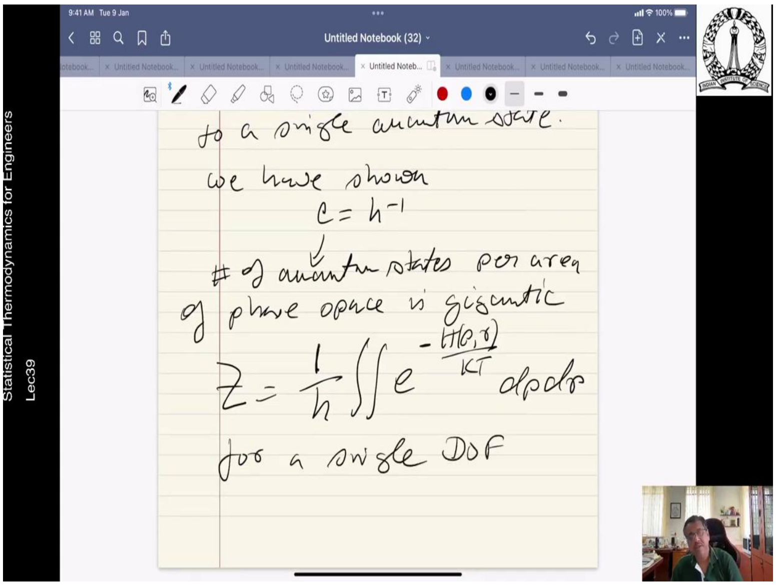
$$= \boxed{h}$$

→ planck's constant can be uniquely interpreted as the area in phase space corresp to a single quantum state.

we have shown

$c = h^{-1}$

# of quantum states per area



to a single quantum state.

we have shown

$c = h^{-1}$

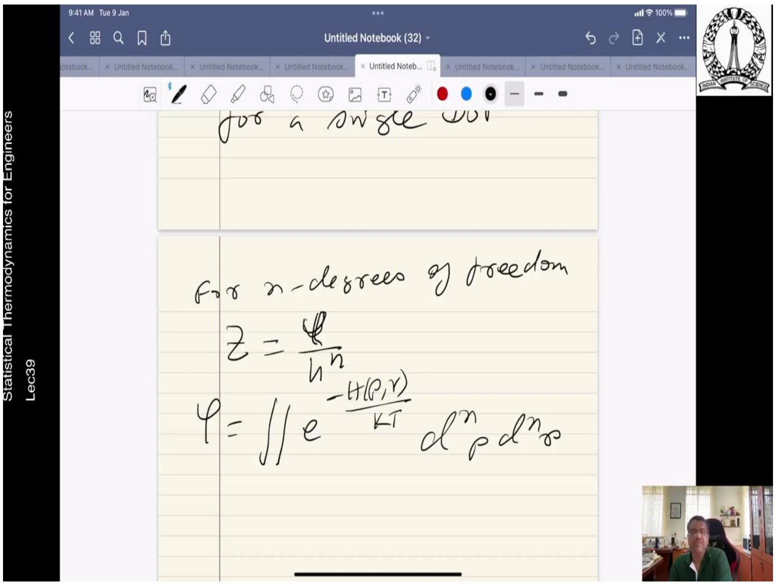
# of quantum states per area of phase space is gigantic

$$Z = \frac{1}{h}\iint e^{-\frac{H(p,x)}{kT}}\,dp\,dx$$

for a single DoF

So, now using this figure now what we can do we can find out the two areas area v plus 1 minus area A v which is basically equal to now v which is equal to h. So, we find that this is the Planck's constant the Planck’s constant, constant can be uniquely interpreted as the area in phase space if corresponding to a single quantum state the single quantum state. So, by utilizing the phase space representation, phase space representation as portrait in the figure we have shown, we have shown C is equal to therefore h inverse given the magnitude of the Plank’s constant. So, the number of quantum states. So, therefore this implies number of quantum states per area, per area, per area of phase space phase space is gigantic, it is enormous. So, therefore the partition function remember we wrote it as C. So, now this becomes 1 over h integral e minus hbr by KT dpdr for a single DoF.

(Refer Slide Time: 13:43)

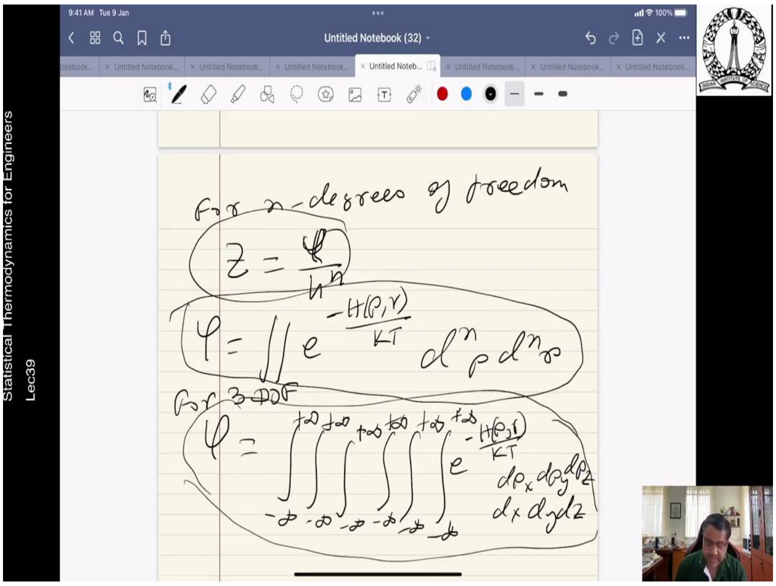


for a single DoF

For n-degrees of freedom

$$Z = \frac{\varphi}{h^n}$$

$$\varphi = \iint e^{-\frac{H(p,r)}{KT}} d^n p \, d^n r$$



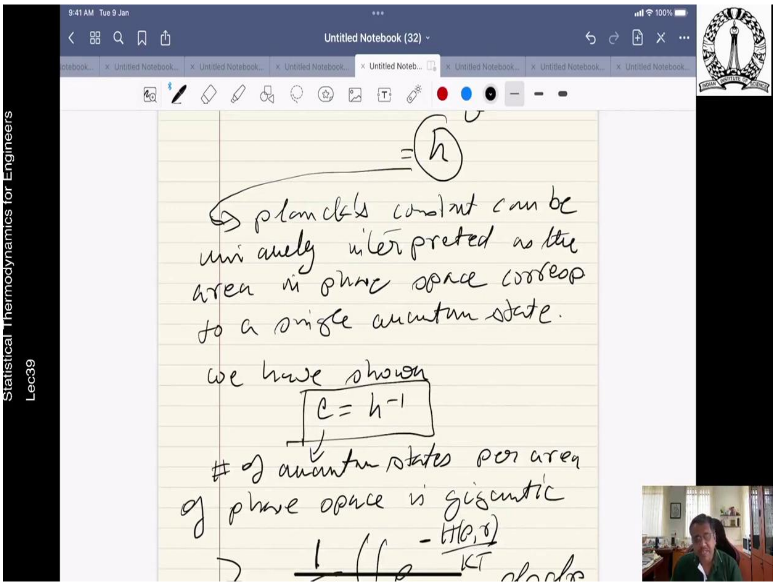
For n-degrees of freedom

$$Z = \frac{\varphi}{h^n}$$

$$\varphi = \iint e^{-\frac{H(p,r)}{KT}} d^n p \, d^n r$$

For 3 DoF

$$\varphi = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-\frac{H(p,r)}{KT}} dp_x \, dp_y \, dp_z \, dx \, dy \, dz$$



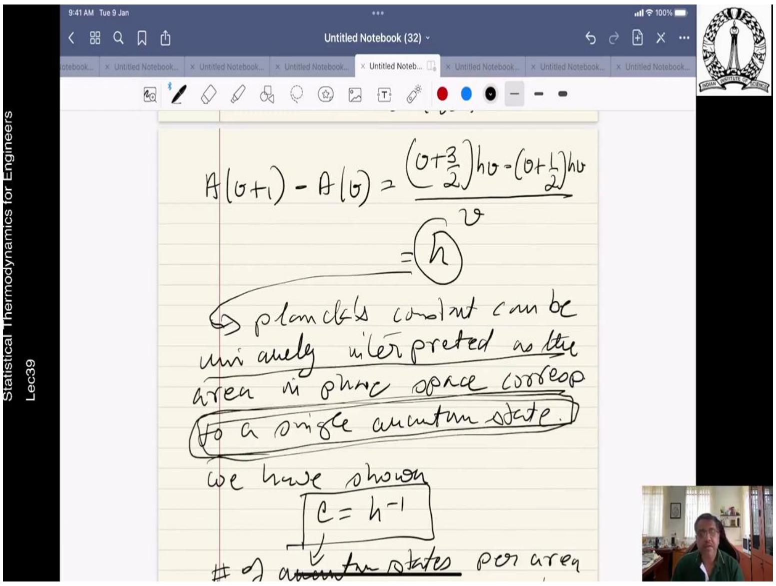
$= h$

→ planck's constant can be uniquely interpreted as the area in phase space corresp to a single quantum state.

We have shown $\boxed{C = h^{-1}}$

# of quantum states per area of phase space is gigantic

$\frac{1}{\ }\iint e^{-\frac{H(p,r)}{kT}}$ dpdr



$A(v+1) - A(v) = \frac{(v+\frac{3}{2})h\nu - (v+\frac{1}{2})h\nu}{\nu}$

$= h$

→ planck's constant can be uniquely interpreted as the area in phase space corresp to a single quantum state.

We have shown $\boxed{C = h^{-1}}$

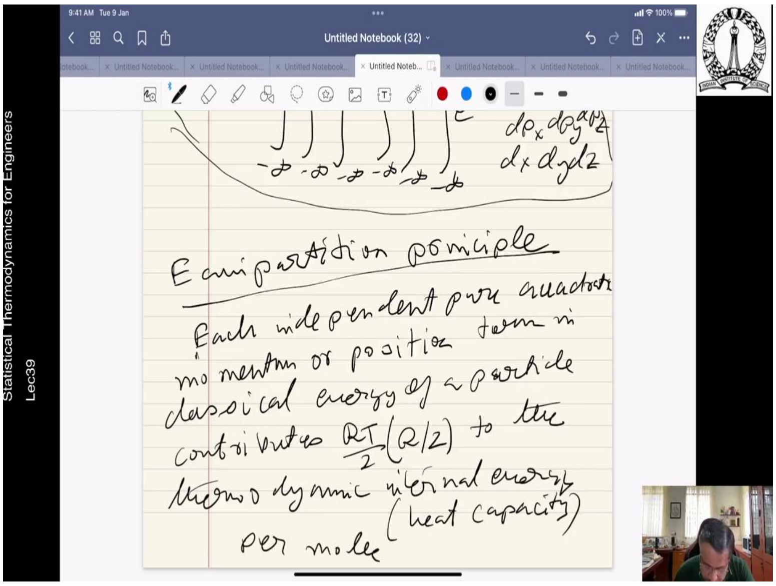
# of quantum states per area

So, for n degrees of freedom for n degrees freedom, freedom the partition function can be related to the phase integral as h n, phase integral itself is written, or a cartesian coordinate having say 3 degrees of freedom, 3 degrees of freedom. So, this becomes for 3 DoF, so H P, r has been cast in terms of generalized momentum and position vectors r thus indicating a potential dependence on all three momentum and position coordinates.

So, you can see that for n degrees of freedom this is what is valid and this is a sample phase integral of three degrees of freedom is a little bit more complicated than that and we also saw the association very clear association between C and the number of quantum states and basically h the Planck's constant and the Planck's constant was uniquely interpreted as the area in the phase space corresponding to a single quantum state.

So, this sets the stage now that we know all these things now well done we have defined the phase integral we are now prepared to evaluate the contributions of U and CV from translational, rotational and vibrational energy levels. So, u n c v the electronic mode cannot be considered as an input always requires application of quantum mechanics in general the contribution from each of the classical energy mode is prescribed by the equipartition principle.

(Refer Slide Time: 16:33)



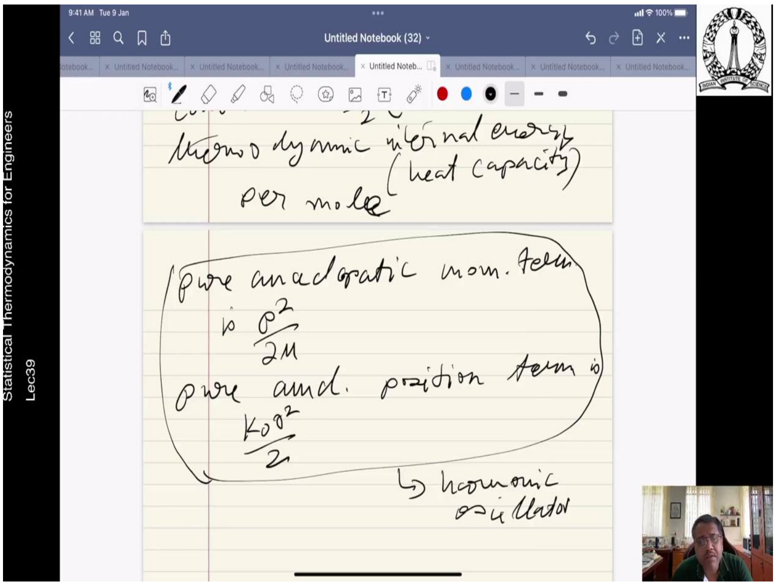
$\int_{-\infty}\int_{-\infty}\int_{-\infty}\int_{-\infty}\int_{-\infty}\int_{-\infty} e \; dp_x\, dp_y\, dp_z\, dx\, dy\, dz$

Equipartition principle

Each independent pure quadratic momentum or position term in classical energy of a particle contributes $\frac{RT}{2}$ $(R/2)$ to the thermodynamic internal energy (heat capacity) per mole

So, let us write what is the equipartition principle. So, equipartition partition principle each independent pure quadratic momentum or position term in the classical energy of a particle contributes as R T by 2 to the thermodynamic internal energy heat capacity (())(17:00). So, each independent, independent pure quadratic momentum or position term in classical energy of a particle contributes RT by 2 R by 2 to the thermodynamic internal energy or heat capacity. So, that is R by 2 for heat capacity per mole.

(Refer Slide Time: 18:27)



thermodynamic internal energy (heat capacity) per mole

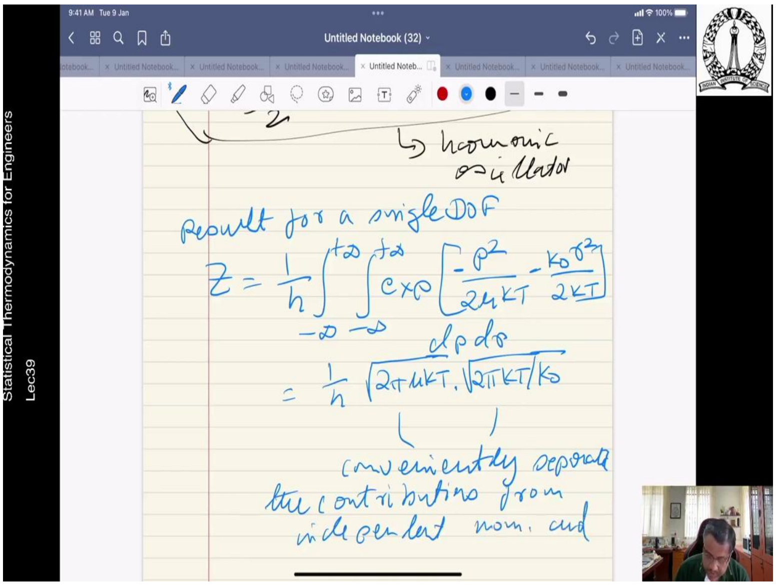
pure quadratic mom. term is $\frac{p^2}{2\mu}$

pure quad. position term is $\frac{k_0 r^2}{2}$

↳ harmonic oscillator

To prove this principle we again make use of the harmonic oscillator for this case show that the pure quadratic momentum term is P square by 2 mu where the pure quadratic positioned term is k naught r square by 2. So, pure quadratic momentum or term p square by 2 mu where the pure quadratic position term is k naught r square by 2. So, if we use, make use of the this is all making use of the harmonic oscillator to prove this principle that is what we have done.

(Refer Slide Time: 19:25)



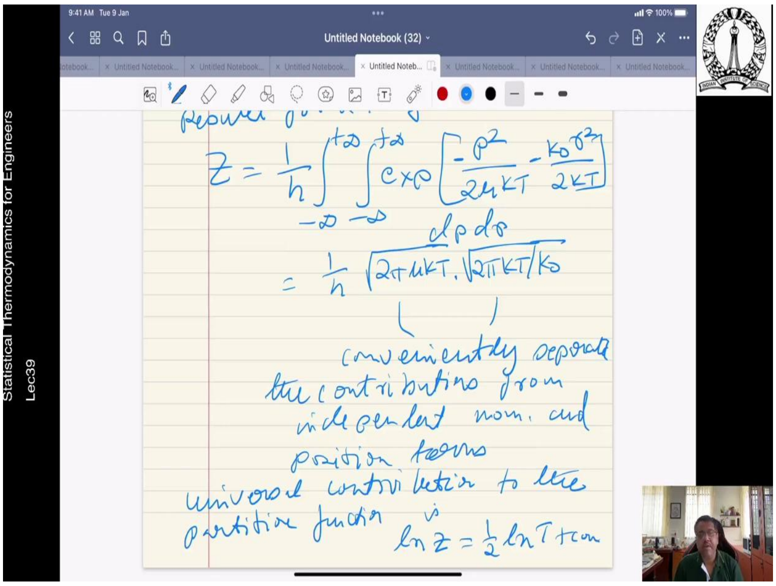
↳ harmonic oscillator

Result for a single DOF

$$Z = \frac{1}{h}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \exp\left[-\frac{p^2}{2\mu kT} - \frac{k_0 r^2}{2kT}\right] dp\,dr$$

$$= \frac{1}{h}\sqrt{2\pi\mu kT}\,.\,\sqrt{2\pi kT/k_0}$$

conveniently separate the contributions from independent mom. and

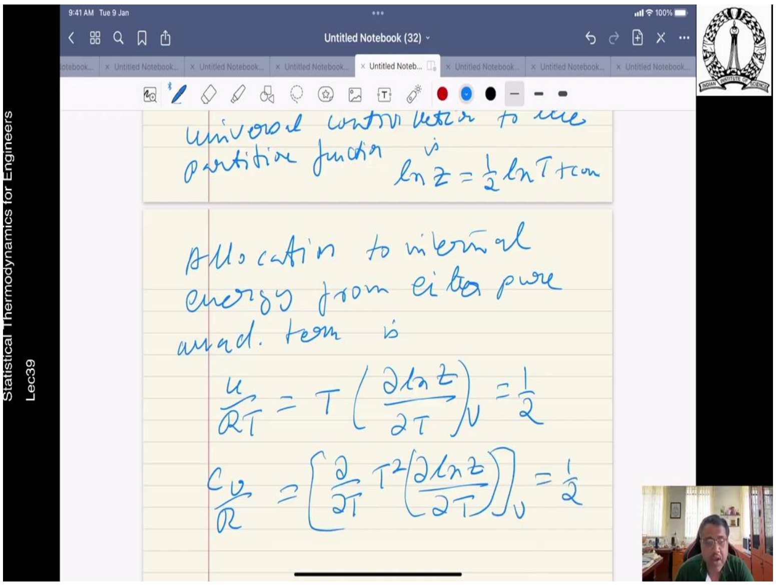


$$Z = \frac{1}{h}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \exp\left[-\frac{p^2}{2\mu kT} - \frac{k_0 r^2}{2kT}\right] dp\,dr$$

$$= \frac{1}{h}\sqrt{2\pi\mu kT}\cdot\sqrt{2\pi kT/k_0}$$

conveniently separate the contributions from independent mom. and position terms

universal contribution to the partition function is $\ln Z = \frac{1}{2}\ln T + \text{con}$

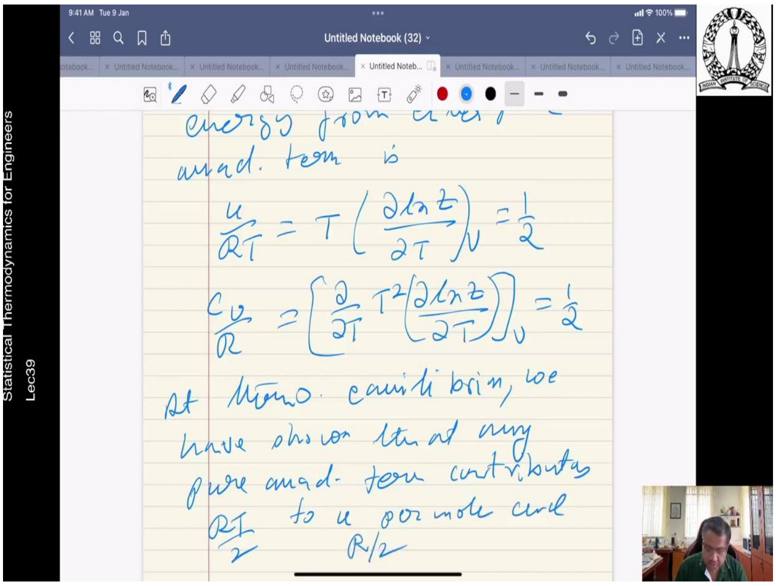


universal contribution to the partition function is $\ln Z = \frac{1}{2}\ln T + \text{con}$

Allocation to internal energy from either pure quad. term is

$$\frac{u}{RT} = T\left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{1}{2}$$

$$\frac{c_v}{R} = \left[\frac{\partial}{\partial T}T^2\left(\frac{\partial \ln Z}{\partial T}\right)\right]_V = \frac{1}{2}$$



energy from either pure quad. term is

$$\frac{u}{RT} = T\left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{1}{2}$$

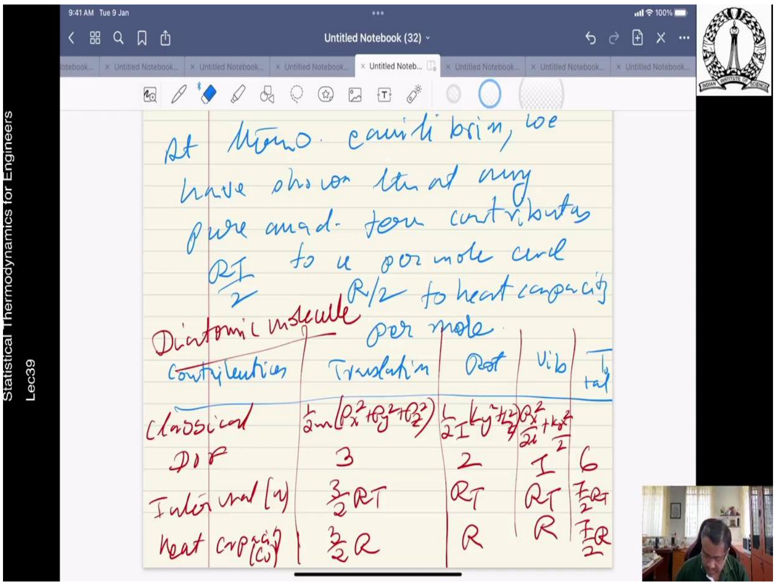
$$\frac{c_v}{R} = \left[\frac{\partial}{\partial T}T^2\left(\frac{\partial \ln Z}{\partial T}\right)\right]_V = \frac{1}{2}$$

At thermo. equilibrium, we have shown that any pure quad. term contributes $\frac{RT}{2}$ to u per mole and $R/2$

Now, for a result for a single degree you can see the math is a little bit of math involved. So, you can check that out I am just going to write the result for a single DoF is Z equal to 1 over h minus infinity plus infinity minus infinity to plus infinity exponential minus p square by 2 mu KT minus K naught square 2 KT dpdr also equal to 1 over h root over 2 pi mu KT multiplied by 2 pi KT by K naught. So, we have conveniently done what we have separated the contributions to the partition function from the independent momentum and positions terms, we have successfully conveniently separated, separated the contributions, contributions from independent momentum and position terms, position terms.

So, we have separated their contributions to the partition function. On this basis, on this basis the universal contribution to the partition function in either case is given by universal contribution to the partition function, to the partition function is ln Z… So, the allocation. So, the allocation to internal energy, to internal energy from either pure quadratic term is for example U by RT is T Z v is equal to half similarly Cv by R equal to, Cv by r equal to, also equal to half. Therefore, at thermodynamic equilibrium at thermodynamic equilibrium we have shown that any pure, pure quadratic term contributes RT by 2 into u and per mole and R by 2.

(Refer Slide Time: 23:24)



At thermo. equilibrium, we have shown that any pure quad. term contributes $\frac{RT}{2}$ to u per mole and $R/2$ to heat capacity per mole.

Diatomic molecule

Contribution	Translation	Rot	Vib	Total
Classical	$\frac{1}{2m}(p_x^2+p_y^2+p_z^2)$	$\frac{1}{2I}(L_y^2+L_z^2)$	$\frac{p_x^2}{2\mu}+\frac{kx^2}{2}$	
DOF	3	2	1	6
Internal (u)	$\frac{3}{2}RT$	RT	RT	$\frac{7}{2}RT$
Heat capacity (Cv)	$\frac{3}{2}R$	R	R	$\frac{7}{2}R$

R by 2 the heat capacity per mole this conclusion is clearly unaffected whether the pure quadratic term is based on momentum or position. So, this validates what we call the equipartition, classical equipartition principle. So, if we just write this thing with the contribution translation rotation vibration total. So, the classical, the contribution classical, then you have 1 over 2 m px square plus p y square plus p z square, degrees of freedom is 3.

Internal energy mu is 3 by 2 RT and heat capacity, capacity is CV equal to 3 by 2 R the rotation of contribution is 1 over 2 I y square plus z square is 2.

So, you already know RT and the vibrational contribution is px square by 2 mu plus k naught x square by 2 . So, 1 RT R the total contribution would be this is 6 7 by 2 RT, this is 7 by 2 R this (())(25:24) for a diatomic molecule. So, now of course you can calculate once you know all these things in details now you can calculate invoke the equipartition principle and we can determine internal energy and heat capacity for a diatomic molecule which is what we summarize just now the translational mode is purely 3D or quadratic momentum terms one for each translational mode of freedom rotation has two degrees of freedom.

Corresponding to two pure quadratic momentum terms in comparison the vibration process a single degree of freedom but single degree but two independent quadratic terms one based on momentum and the other base of position. The additional quadratic term for vibration arises (())(26:16) from its potential energy which is missing from its, from its translational and rotational modes.

We will cover more of this in the next class when we look at these principles that I mean we use this to calculate the effect of temperature on say the specific heat of a particular molecule and then once it is done then we can of course calculate all the other properties that are there h and CV and enthalpy and all these other things in the subsequent class. Thank you, thank you for this.