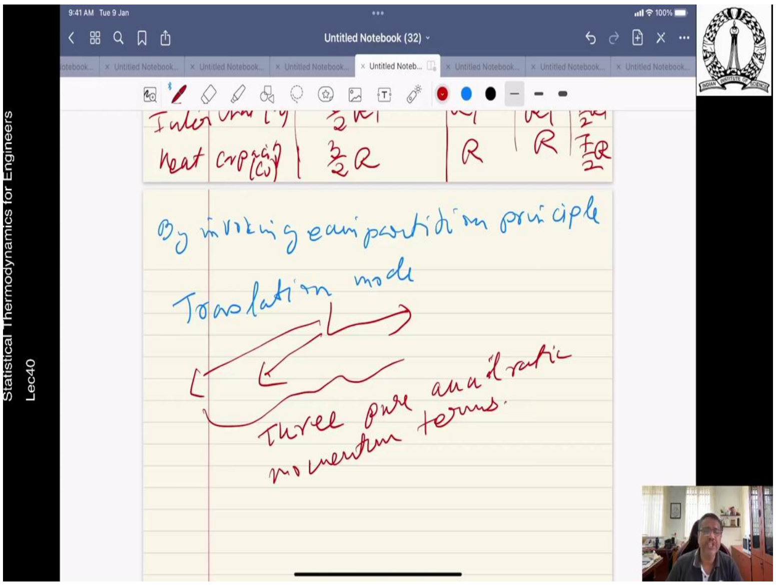
Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bengaluru
Lecture 51

The Equipartition principle and ideal gas

Welcome to lecture number 40 of this Statistical Thermodynamic Course for Engineers. So, if you look at it here we already saw that for a diatomic molecule what are the different contributions, what are the different contributions that you are going to have for a diatomic molecule. So, so we already saw that for a diatomic molecule the, the contributions part that what are the classical contributions of the translational, rotational, vibrational modes. So, we are going to continue in this line and we are going to write that.

(Refer Slide Time: 0:45)

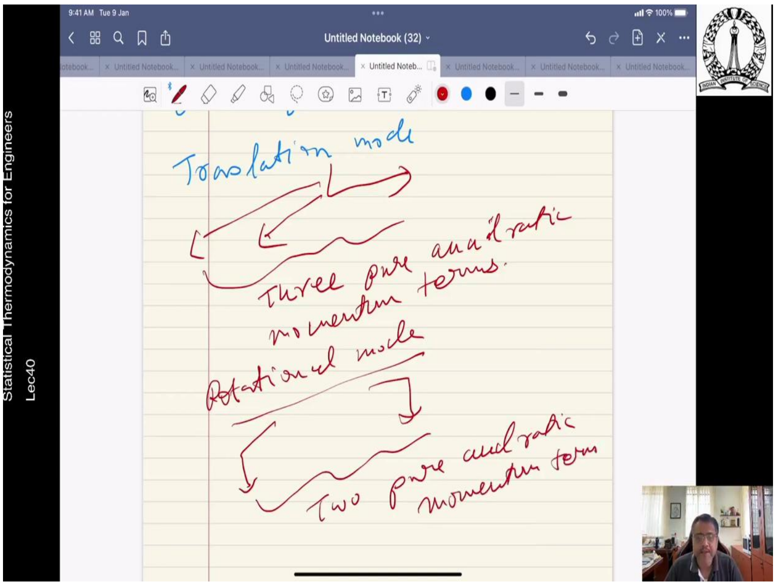


Heat capacity (C_v) | $\frac{3}{2}R$ | R | R | $\frac{7}{2}R$

By invoking equipartition principle

Translation mode

Three pure quadratic momentum terms.

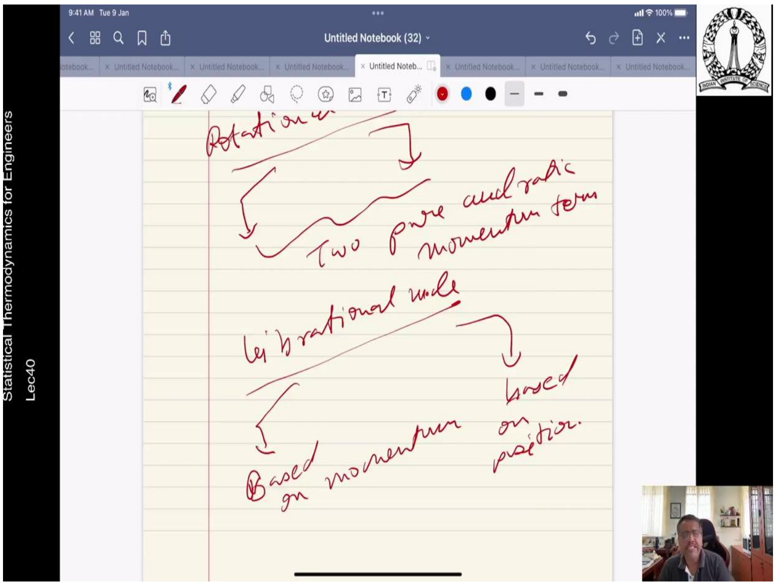


Translation mode

Three pure quadratic momentum terms.

Rotational mode

Two pure quadratic momentum term



Rotation

Two pure quadratic momentum term

Vibrational mode

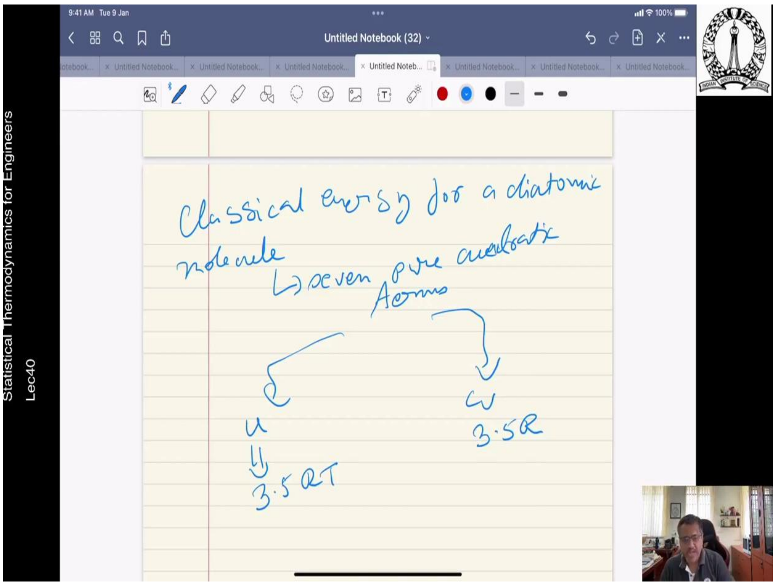
Based on momentum

based on position.

By invoking equipartition principle, equipartition principle, principle we can determine the internal energy and the heat capacity as it is summarized in the table just above. So, the translational mode, if you look at it translational mode that is characterized by, that is characterized by three altogether three pure quadratic momentum terms, pure quadratic momentum terms, quadratic momentum terms one for each translational degree of freedom.

Similarly, the rotational mode, the rotational mode, the rotational mode actually has two degrees of freedom which basically corresponds to two pure quadratic, two pure quadratic moment of terms. Now the vibrational mode on the other hand, vibrational mode, mode this has got only one degree of freedom but it has got two independent quadratic terms one based on momentum, momentum and the other is based on position, on position, the additional quadratic term arises from it is potential energy which was missing in the translation and the rotational modes. So, the summary of the classical energy for a diatomic molecule displays.

(Refer Slide Time: 2:58)

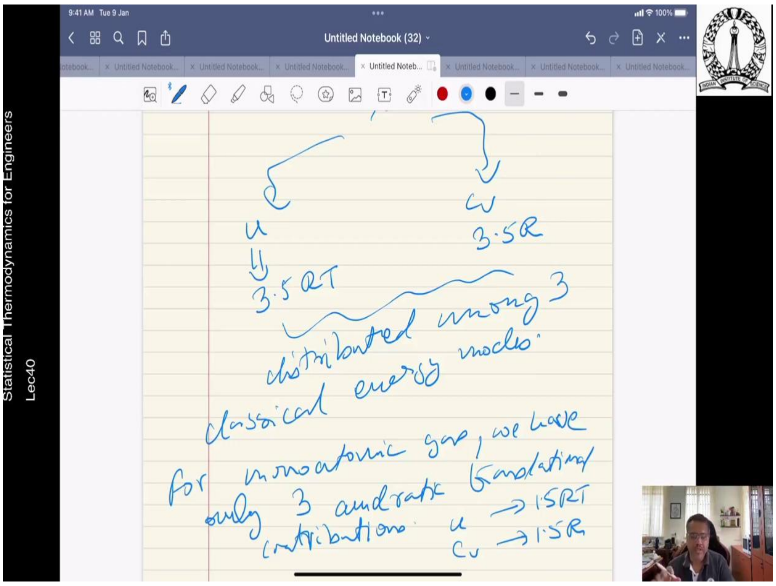


Classical energy for a diatomic molecule

↳ seven pure quadratic terms

u ⇓ 3.5 RT

c_v 3.5R



u ⇓ 3.5 RT

c_v 3.5R

distributed among 3 classical energy modes.

For monoatomic gas, we have only 3 quadratic translational contributions.

u → 1.5RT

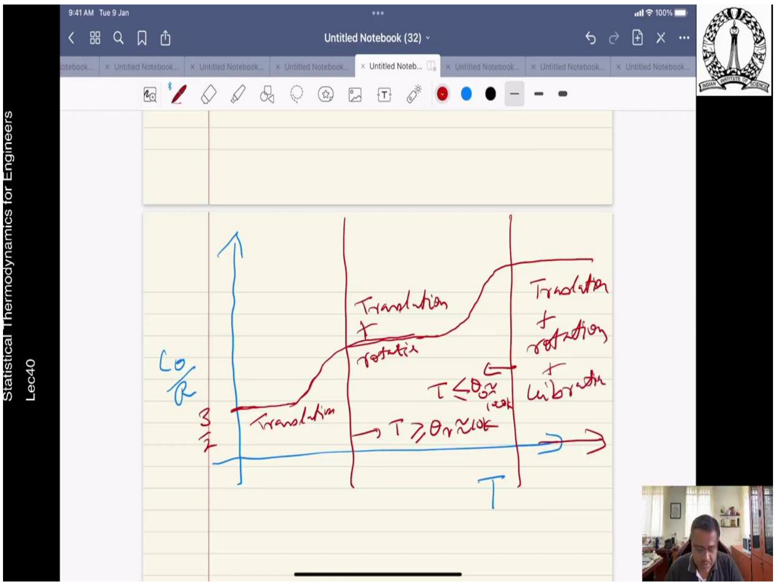
c_v → 1.5R

So, if we write it properly the classical energy for a diatomic molecule, diatomic molecule it is composed of seven pure quadratic, quadratic terms, terms the implication is an internal energy and heat capacity per mole is therefore. So, this implies that internal energy u will have something like 3.5 RT and this c v will have something like 3.5 R per mole as distributed among the three classical energy modes, as distributed among the three classical energy modes, these are distributed, distributed among three classical energy modes, classical energy modes.

So, for monoatomic gas, monoatomic gas, however, we have only three, we have only three quadratic, quadratic, quadratic translational contributions, contributions and therefore the u will be like 1.5 RT, c v will be 1.5 R which is 3 by 2 R. So, the classical predictions for internal energy and specific heat agree very well with the quantum predictions for monotonic gases, however the agreement is 0.4 for diatomic gases because acceptor temperatures approaching thousand and two thousand Kelvin this behavior can be understood if you take into consideration the characteristics mode temperatures. If you recall the translational and rotational modes have characteristic temperatures much less than 300 Kelvin whereas the characteristic temperature of the vibrational mode is much greater than 300 Kelvin.

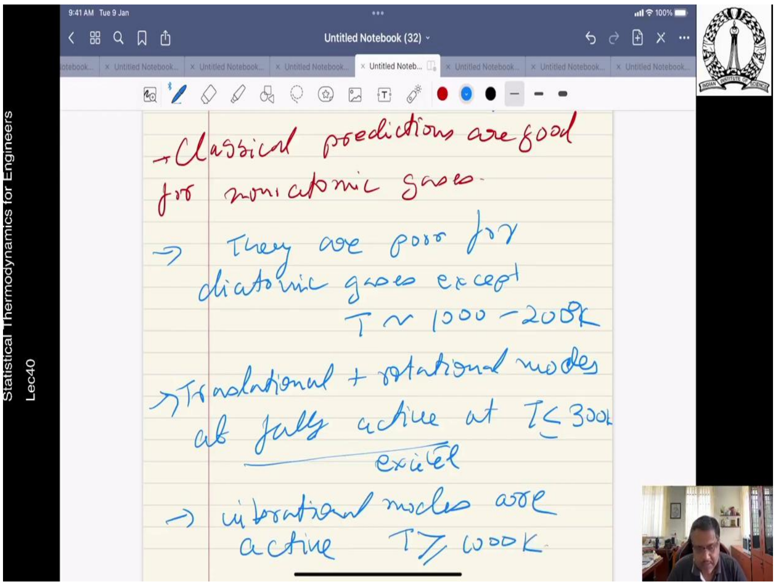
Therefore, the translational and the rotational modes are fully excited thus matching their classical contributions at room temperature, vibrational mode approaches for the excitation only at much higher temperatures on this basis we would expect the diatomic energy, internal energy and heat capacity per mole to be like 2.5 RT and 2.5 R respectively near room temperature. So, the influence of temperature on the specific heat for a diatomic molecule can be shown like this let us draw this figure so that it is easily understandable.

(Refer Slide Time: 6:08)



So, this is the temperature, this is c v by R so that is what we write is basically and let us put three demarcations now and this is already known, let us extend it little bit. So, let us mark it at 3 by 2. So, this is translation view and then starts to pick up and it goes like this. So, this is pure translation, this is translation and here the temperature is greater than equal to theta R which is approximately 10 Kelvin. So, this is translation plus, plus rotation and then it starts to pick up once again (())(7:11) over there. So, this is, this is valid when temperature is less than equal to theta vibration which is roughly of the order of 1000 Kelvin.

(Refer Slide Time: 7:42)

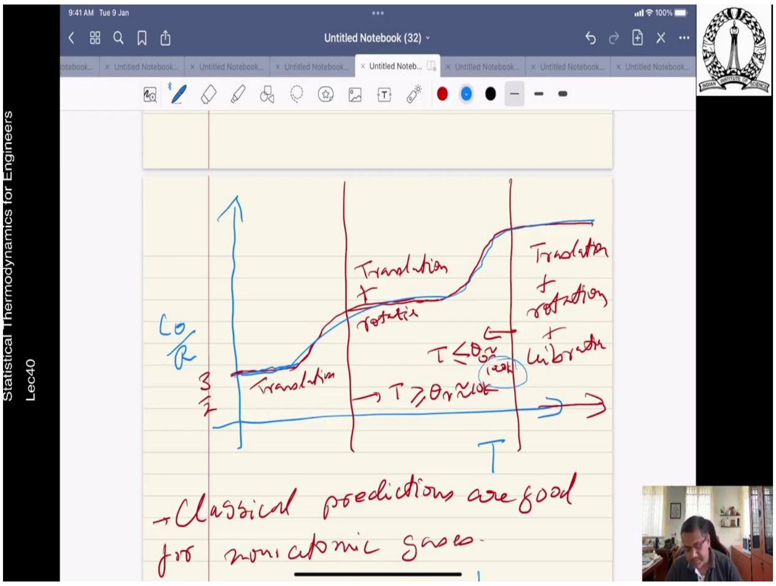


- Classical predictions are good for monatomic gases.

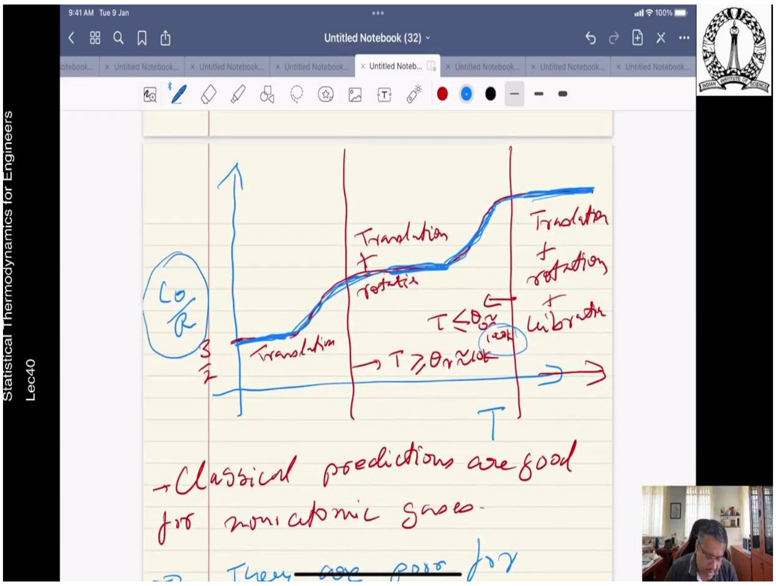
→ They are poor for diatomic gases except $T \sim 1000 - 2000K$

→ Translational + rotational modes are fully active at $T \leq 300K$
excited

→ vibrational modes are active $T \geq 1000K$.



- Classical predictions are good for monatomic gases.



- Classical predictions are good for monatomic gases.

They are poor for

So, this part is now translation plus rotation plus vibration something like that. So, what did we learn if you look at this particular table we would see that the classical that is what we said that the classical predictions, predictions are good for monoatomic gases, gases it is the first point. Second point is that they are poor for diatomic gases, diatomic gases except when the temperatures approaching is about 1000 to 2000 Kelvin 2000 Kelvin.

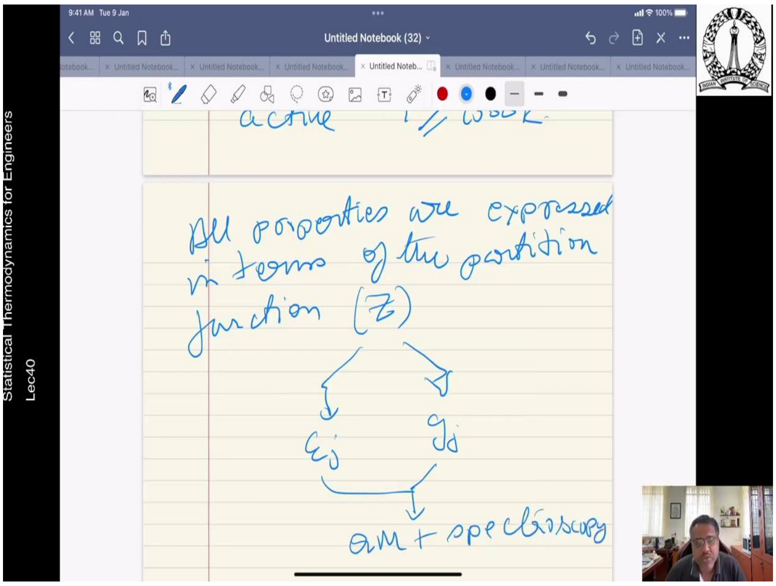
So, this behavior as we already said that translational plus rotational modes are fully active fully active at T less than equal to 300 Kelvin vibrational mode where they are fully active or fully excited whatever you call it but however the vibrational mode, vibrational modes, modes are active, are active at T exceeding about 1000 Kelvin. So, that is a full excitation level.

So, the and this is what is shown in this particular figure the initially it is all translational then as soon as about we reached 10 kelvin the rotation starts to kick in. So, there is a jump and then it starts to increase once again when we have this marker of about 1000 Kelvin. So, that is the basis. So, the temperature, influence on temperature of the specific heat follows this kind of a behavior, the plateaus that we see signals full excitation of an energy mode. So, here when it plateaus that means all the translational and the rotational modes are fully activated.

Here it means all the translational modes are activated this growth period shows that the rotational modes are getting activated not all of them are activated this is the same transition which shows that vibrational modes have started to get activated and this is the full activation or the full excitation of all the vibrational modes as well. So, this fascinating behavior actually reflects that using quantum mechanics and statistical thermodynamics when applied to gaseous systems we can generate we will see how the, the specific heat of, of a gas actually undergoes this very nice transitions.

So, we have provided. So, far a methodology for determining let us see what we did by statistical thermodynamics we have provided a methodology for determining the most probable macro state considering an isolated system the most probable macro state in fact showed that internal energy and entropy in the dilute limit expressions and we have successful analytical expressions for all intensive thermodynamic properties of an ideal gas now these properties are expressed in terms of a partition function.

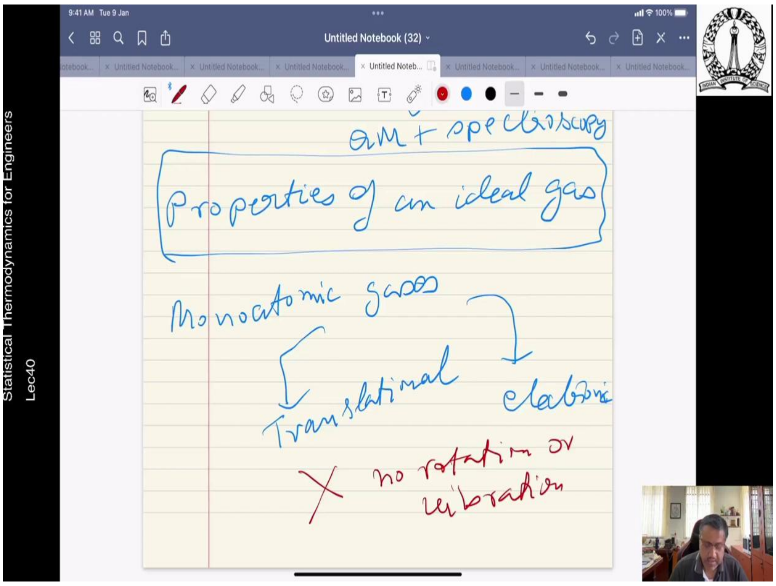
(Refer Slide Time: 11:22)



All properties are expressed in terms of the partition function (Z)

ϵ_j g_j

QM + spectroscopy



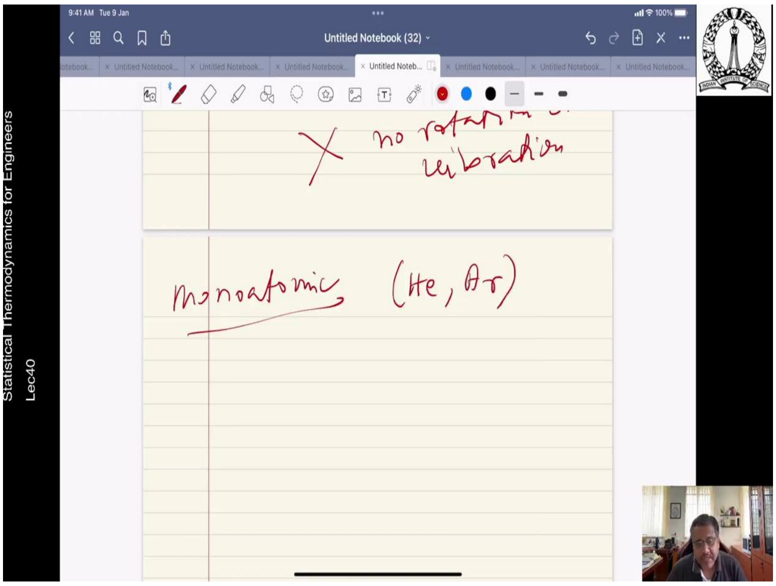
QM + spectroscopy

Properties of an ideal gas

Monoatomic gases

Translational electronic

✗ no rotation or vibration



✗ no rotation or vibration

Monoatomic (He, Ar)

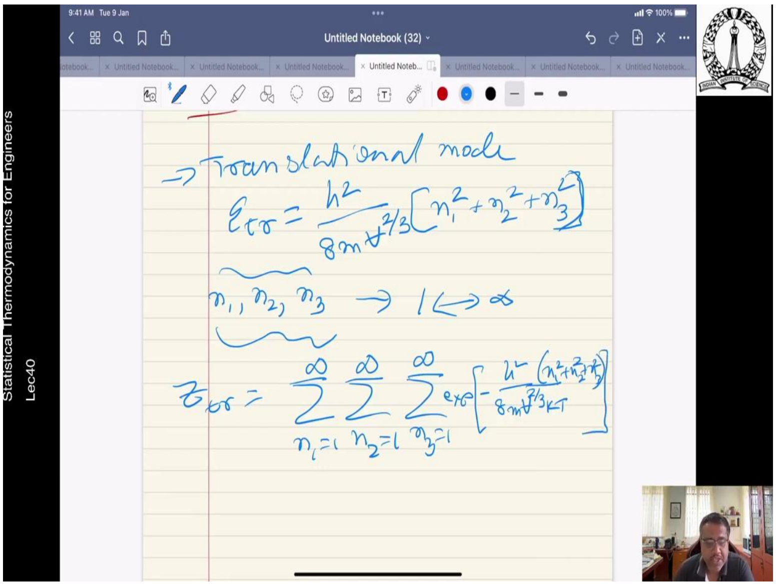
So, all properties we know all properties are expressed, are expressed in terms of the partition function, in terms of the partition function, in terms of the partition function so that is what we what we saw and which requires which is Z which requires two information's e j and g j. So, obtaining such data how do you get this these two information comes from quantum mechanics plus spectroscopy this also we saw now we have access to the spectroscopic information we can now finally calculate the properties of an ideal gas.

So, our motto is to calculate the properties of an ideal gas this is our motto and this is what we are going to do in this particular lecture and the next one probably. However, we should do it we can start with a monoatomic gas which requires only the translational and the electronic modes there is no rotation and no vibration then we can go to diatomic gas which requires information on the rotational and the vibrational energy management and then of course one can consider all the atomic gas which is basically multiple atoms.

So, monoatomic gas has got the advantage monoatomic gases this has got two modes one is translational, translational and the other one is electronic. So, no rotation or vibration not possible because it is a single atom. Similarly, of course you have for the other types for the diatomic gases of course you have a lot of other things. So, monoatomic gas useful there are quite a few useful examples like helium, argon, elemental radicals like atomic hydrogen, atomic nitrogen and atomic oxygen for such gases rotation and vibrations are irrelevant.

So, we consider only translational and electronic energy modes. So, based on the extremely low characteristic temperature the translational mode will produce thermodynamic properties that are closely associated with classical mechanics. Contributions from the electronic mode will come at a much higher temperature. So, this is, this is the situation. So, the classical mode is very well represented by the translational mode or the translational mode very well follows the classical mode so to say.

(Refer Slide Time: 14:23)

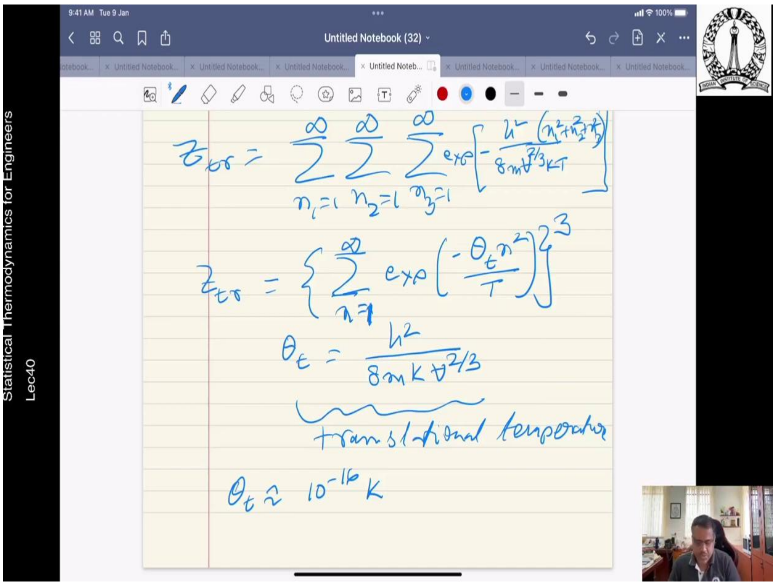


→ Translational mode

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

$$n_1, n_2, n_3 \rightarrow 1 \longleftrightarrow \infty$$

$$Z_{tr} = \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty} \exp\left[-\frac{h^2\left(n_1^2+n_2^2+n_3^2\right)}{8mV^{2/3}kT}\right]$$



$$Z_{tr} = \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty} \exp\left[-\frac{h^2\left(n_1^2+n_2^2+n_3^2\right)}{8mV^{2/3}kT}\right]$$

$$Z_{tr} = \left\{\sum_{n=1}^{\infty} \exp\left(-\frac{\theta_t n^2}{T}\right)\right\}^3$$

$$\theta_t = \frac{h^2}{\underbrace{8mkV^{2/3}}_{\text{translational temperature}}}$$

$$\theta_t \approx 10^{-16}\,K$$

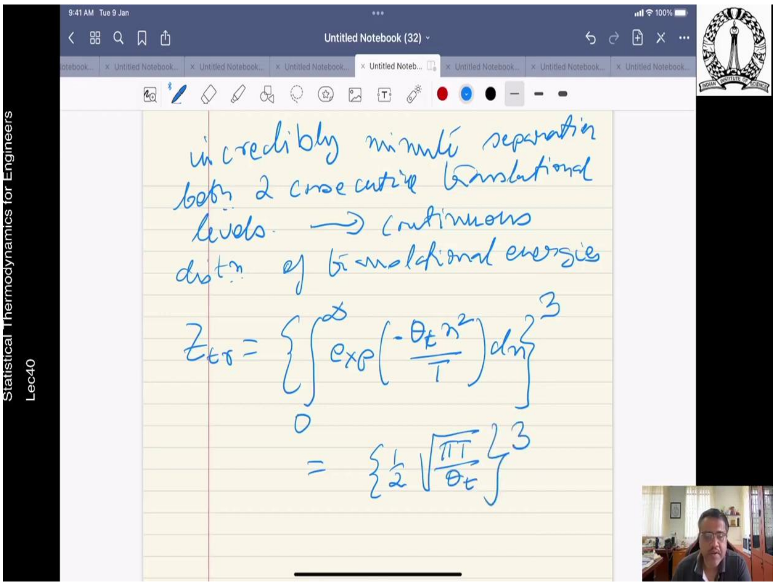
So, for a single gaseous atom. So, this first let us look at the translational mode, mode. So, here energy translation is h square divided by 8 m v two third n 1 square plus n 2 square plus n 3 square, three spatial quantum numbers n 1, n 2, n 3 that can take up n value this can have any values from unity to infinity. So, the contribution to the thermodynamic properties from any independent energy mode can be ascertained(())(15:16) by determining it is first determining it is contribution to the partition function. So, partition functions can be evaluated most directly by basically summing all these up over the states rather than the levels.

So, therefore Z translational is given as first we sum n 1 equal to 1 to infinity, n 2 equal to 1 to infinity, n 3 equal to 1 to infinity, got it and then we write its exponential minus sign h square 8 m v two third KT. Then you have n 1 square plus n 2 square plus n 3 square. So, the partition function the generalized expression for the partition function for the translational mode that will give it as summing over n 1 equal to 1 or n rather, n equal to 1, 1 to infinity exponential theta t n square by t where theta t translational is written as h square divided by 8 m k v two third, v is the volume, so therefore I just cut it cross.

So, we have introduced what we call the translational temperature, translational temperature. So, so summing over all possible values of unity to infinity we are indeed accounting for each quantum state as identified by its unique set of quantum numbers because it is a cube involved over here.

So, we recall that theta t was basically 10 to the power of minus 16 Kelvin. So, any realistic assembly temperature is can be converted to an equivalent integration now because incredibly minute separation between consecutive energy translational energy levels we have a continuous distribution of translational energies, continuous distribution like in classical mechanics. So, the discretization is rather poor.

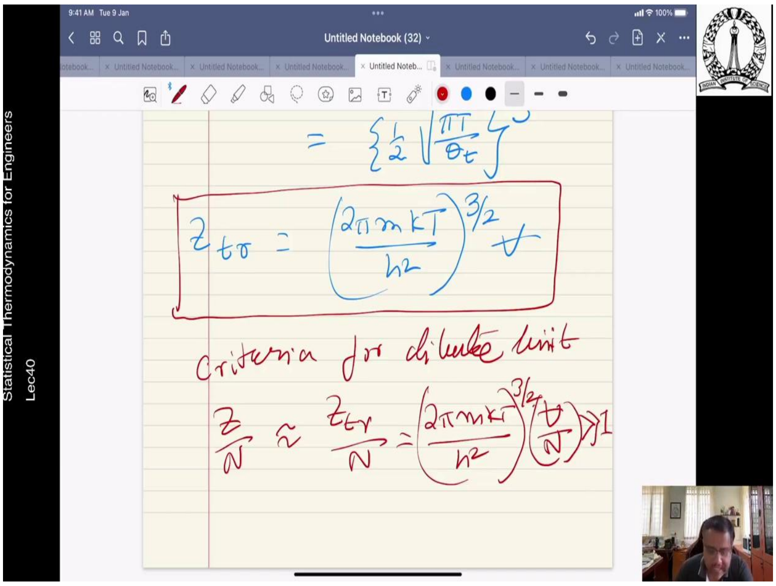
(Refer Slide Time: 18:05)



incredibly minute separation betn 2 consecutive translational levels. → continuous distn of translational energies

$$Z_{tr} = \left\{ \int_0^\infty \exp\left(-\frac{\theta_t n^2}{T} \right) dn \right\}^3$$

$$= \left\{ \frac{1}{2} \sqrt{\frac{\pi T}{\theta_t}} \right\}^3$$



$$= \left\{ \frac{1}{2} \sqrt{\frac{\pi T}{\theta_t}} \right\}^3$$

$$\boxed{Z_{tr} = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V}$$

Criteria for dilute limit

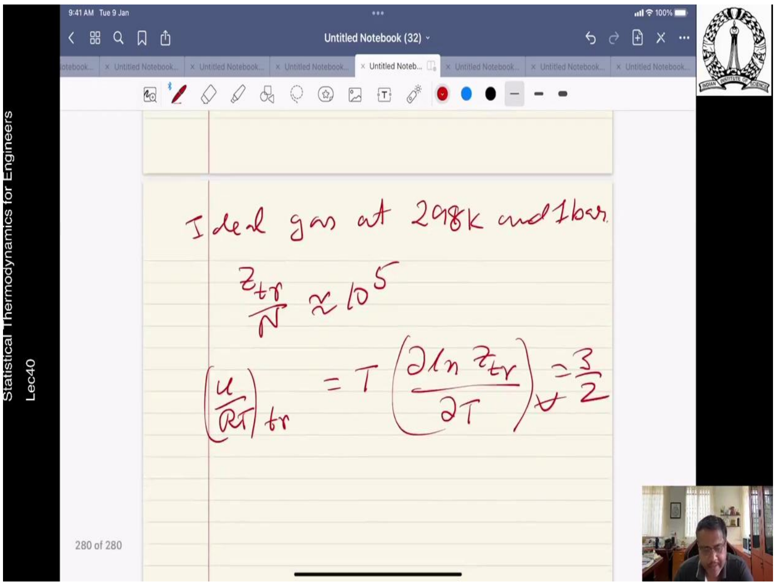
$$\frac{Z}{N} \approx \frac{Z_{tr}}{N} = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \left(\frac{V}{N} \right) \gg 1$$

So, incredibly minute separation situation between two consecutive, consecutive translational levels. So, it leads to an almost continuous distribution, distribution of translational energies. So, the Z translational is equal to 0 to infinity exponential minus theta t n square by T dn cube this integration if you perform it will lead to half pi T by theta t cube.

If we substitute this the Z translational energy therefore becomes 2 pi m K T by h square whole to the power of 3 by 2 into v. So, this is the translational partition function can be also done over energy levels if we do the summation of energy levels using the density of states or evaluating the phase integral but this is what it will get is there a varieties of ways to calculating this is the most important classical analog.

So, quantum mechanics is largely unnecessary for this because the equipartition principle is perfectly suitable for calculating the translational contributions to the thermodynamic properties this is almost a classical equivalent. So, the characteristic temperature of the translational mode is so small that the total number of quantum states is essentially equivalent to that of the translational mode. So, therefore using our criteria for, using criteria for dilute limit, for dilute limit Z by N is almost equal to the Z translational by N which is equal to 2 pi m K T by h square 3 by 2 v over N should be much much greater than 1.

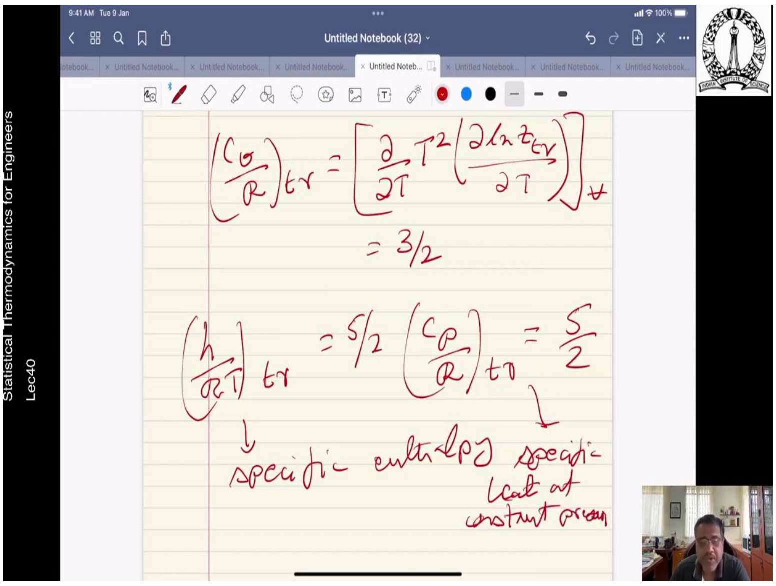
(Refer Slide Time: 21:07)



Ideal gas at 298K and 1bar

$$\frac{Z_{tr}}{N} \approx 10^5$$

$$\left(\frac{u}{RT}\right)_{tr} = T\left(\frac{\partial \ln Z_{tr}}{\partial T}\right)_v = \frac{3}{2}$$



$$\left(\frac{c_v}{R}\right)_{tr} = \left[\frac{\partial}{\partial T} T^2\left(\frac{\partial \ln Z_{tr}}{\partial T}\right)\right]_v$$

$$= 3/2$$

$$\left(\frac{h}{RT}\right)_{tr} = 5/2 \qquad \left(\frac{c_p}{R}\right)_{tr} = \frac{5}{2}$$

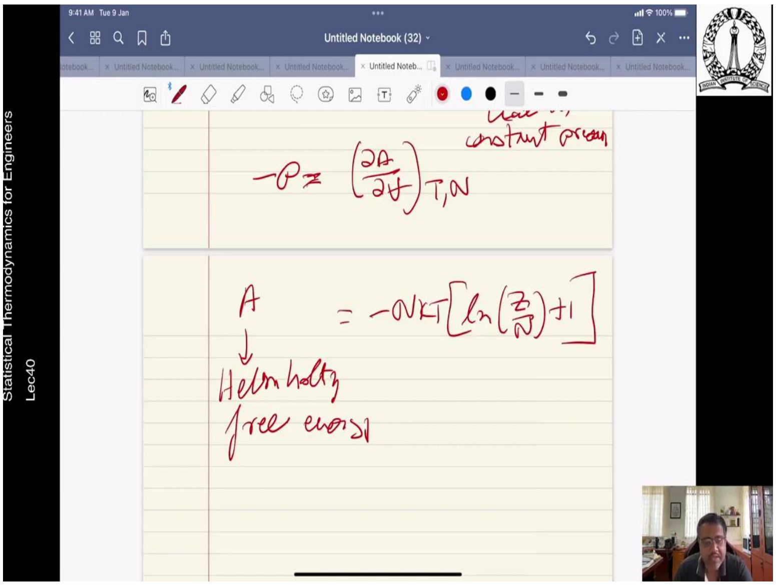
specific enthalpy

specific heat at constant pressu

For any ideal gas say we take an ideal gas, ideal gas at say 298 Kelvin which is a room temperature and 1 bar is STP basically this gives Z translational by N to be a number of equivalent to 10 to the power of 5. So, it means that the total number translational mode number of quantum states is almost the same as that of the translation. So, employing the translational partition function now we may evaluate the contributions of a translational mode to the thermodynamic properties of an ideal gas. So, u R T the translational component is T d l n Z translational divided by d T at constant volume this becomes equal to 3 by 2.

Similarly, for specific heat it is c v by R translational it is equal to d by d T T square d l n Z translational by d T v is also equal to 3 by 2. Therefore, the translational contribution to the internal energy is 1.5 RT and to the specific heat capacity is 1.5 R which is as you expect from the equipartition principle. So, for specific enthalpy also. So, if we look at specific enthalpy that is h by R T translational this will be equal to 5 by 2 and CP by R specific heat at constant pressure that will be 5 by 2 specific enthalpy and specific. So, this is specific enthalpy and this is specific heat, heat constant pressure. So, at this point the pressure can be determined also by combining aspects of classical and thermodynamic properties.

(Refer Slide Time: 23:32)

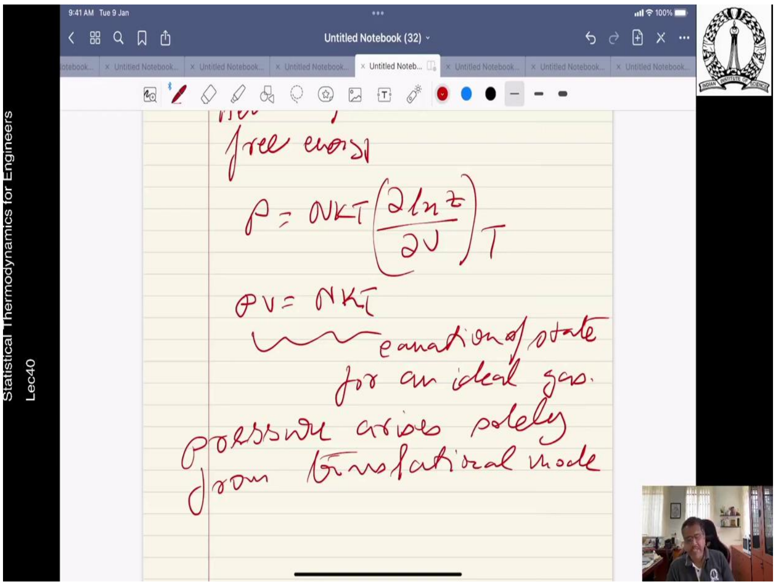


constant pressu

$$-P = \left(\frac{\partial A}{\partial V}\right)_{T,N}$$

$$A = -NKT\left[\ln\left(\frac{Z}{N}\right)+1\right]$$

Helmholtz free energy



free energy

$$P = NKT\left(\frac{\partial \ln Z}{\partial V}\right)_T$$

$$PV = NKT$$

equation of state for an ideal gas.

pressure arises solely from translational mode

So that, so pressure is given as minus p is equal to, equal to d a by d v T comma N. So, where, where your A is basically the Helmholtz free energy, as you all know Helmholtz free energy which is given as minus N K T l n Z by N plus 1 we did all these things earlier also therefore P will equal to N K T d l n Z by d v constant temperature. So, p v will be equal to N K T which of course is the equation of state for ideal gas, equation state for ideal gas. So, the obvious implication is that pressure arises, pressure arises, arises solely from translational mode.

So, as it is expected because it is the momentum exchange at all walls at the independent gaseous particles. So, on the basis of this we can then write all the other partition function for each internal energy mode must depend solely on temperature so then. Similarly, we can write it for entropy, we can write it for the other, other types of properties as well. So, now you can see from this particular, particular work the most important statement was the how the pressure is actually very the translational modes are so dense and so, so gigantic in numbers is super simple(())(25:41) to all the other modes that are available.

So, in the next lecture we are going to see that how we can write entropy for example, we will do a sample problem which will be on Helmholtz free energy and then we will look at the contribution from the electronic energy modes which is a little bit more involved than the, than the other modes so that will that will enable us to calculate the properties the monoatomic gas because as we say that the monoatomic gas essentially depends on the translational and the electronic mode which does not depend on the vibration of the rotation because they do not exist anyways. So, we end the lecture here we will convene with, with a few more a, few, a little bit more detailed understanding of the electronic mode.