Thermal Physics
Prof. Debamalya Banerjee
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture –1
Foundation of Kinetic Theory of Gasses

Hello and very warm welcome to this new course in NPTEL platform the thermal physics. Now during this course we will be learning thermodynamics the classical thermodynamics and also some parts related to kinetic theory of gas and the transport related phenomena. So, our journey will begin from the kinetic theory of gas and we will slowly go into the domain of classical thermodynamics.

Now it is a 30 hours course and you already have the books with the text books which are marked which are suggested by me for this particular course and at the same time all any of these text books will work and of course I will give you regular problem sets, assignments classroom problems everything will be given. More than that on top of that we will also have a live discussion forum at least two or three during this entire duration of the course where you can ask question directly to me during the video conferencing session and of course you have the regular discussion forum where you can post your questions post your queries.

So, either me or the TA's who are associated with this course will be answering all those questions ok. So, let us start without any further delay. Before we begin our lecture the or before we begin our discussion on the kinetic theory that is why we will start. We will I would like to revisit some of the very basics or very preliminaries of the thermal physics ok.

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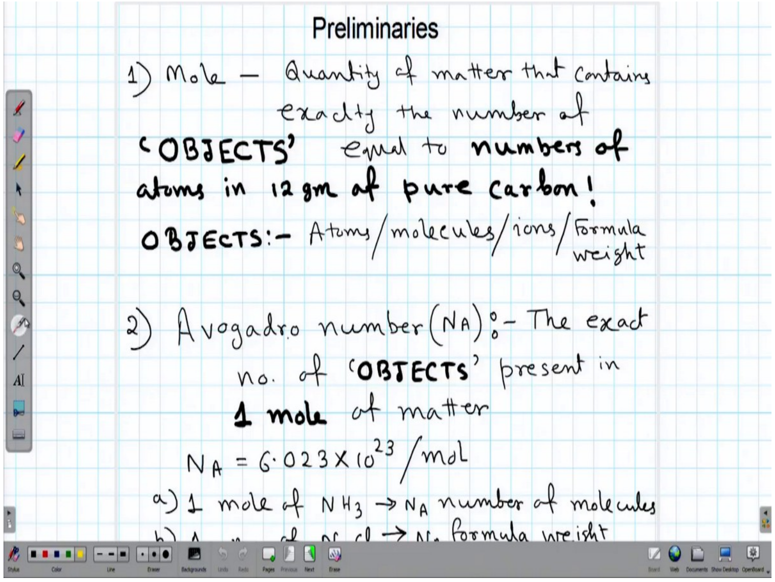

Preliminaries

1) Mole – Quantity of matter that contains exactly the number of **'OBJECTS'** equal to **numbers of atoms in 12 gm of pure carbon!**

OBJECTS:- Atoms/molecules/ions/Formula weight

2) Avogadro number (NA):- The exact no. of **'OBJECTS'** present in **1 mole** of matter

$N_A = 6.023 \times 10^{23} / \text{mol}$

a) 1 mole of $NH_3 \rightarrow N_A$ number of molecules

b) → formula weight

So, let me start with the definition of a mole. Now what is a mole? Now in chemistry and physics when we are talking about a mole this is actually the quantity of matter that contains exactly the number of objects equal to the number of atoms in 12 grams of pure carbon that is the definition of a mole. Now what is an object? Object could be anything object could be atom object could be molecule object would be ions or object could be formula weight depending on which system we are talking about.

Next comes the definition of Avogadro number. The exact number of objects present in one mole of matter. In the first definition we say that the number of object that is equal the number of atoms in 12 grams of pure carbon is one mole but what is that number that number is NA the Avogadro number which is given by 6.023 into 10 to the power 23 per mole or we can also write it as mole inverse instead of writing it like this we can write up sorry yeah we can write this as mole inverse, right.

Now Avogadro number is not a pure number as we might see this is the number of atoms or molecules or ions per mole. So, there is a unit associated with it. So, let us take an example one mole of ammonia is NA numbers of mole has NA numbers of molecules and if we talk about one moles of NaCl it has NA formula weight of NaCl present in that. Similarly if we talk about one mole of helium gas it will be exactly NA number of atoms in that gas assembly because we know that helium is a monoatomic gas right.

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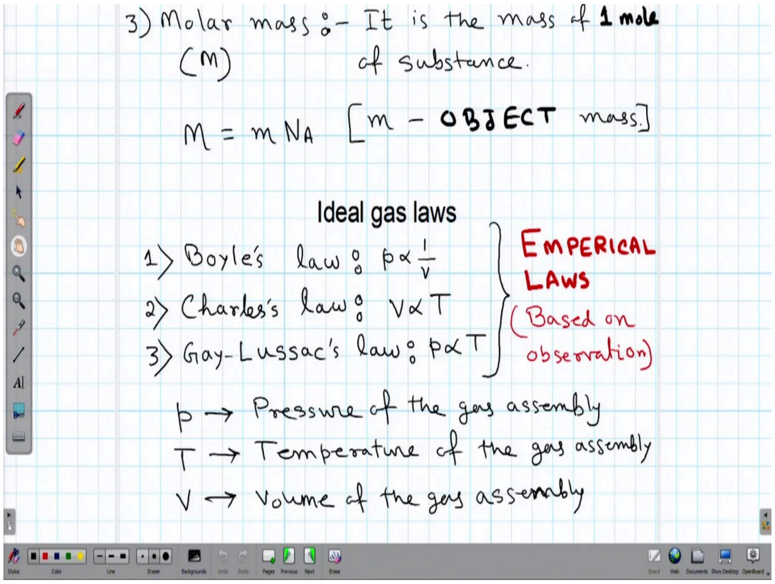

3) Molar mass :- It is the mass of 1 mole
(M) of substance.

$M = m N_A$ [m - OBJECT mass]

Ideal gas laws

1> Boyle's law : $p \propto \frac{1}{V}$

2> Charles's law : $V \propto T$

3> Gay-Lussac's law : $p \propto T$

EMPERICAL LAWS
(Based on observation)

p → Pressure of the gas assembly

T → Temperature of the gas assembly

V → Volume of the gas assembly

Next the third definition is the definition of molar mass what is that. So, we are talking about the number of moles we are talking about the Avogadro number which is the number that is present in one mole and then the molar mass that is the mass of one mole of substance. Now mass of one mole of substance means for example if we have one mole of hydrogen this is one gram of hydrogen one mole of carbon is one mole of one 12 grams of carbon because 12 grams of carbon 12 gram makes one mole for carbon right.

Now that is written as capital M and if the small m remain of small m is the object mass if that is the case then capital M is equal to small m times NA where NA is the Avogadro number, ok. Now I am pretty sure that you are all familiar with this definition but I thought I would anyway recap this because sometimes it is you know sometimes we mix up the definitions and we while solving problems we find it difficult next is the ideal gas laws ok.

So, what do you mean by ideal gas laws? We have the Boyle's law which says for constant temperature the pressure of a gas is inversely proportional to its volume. Similarly there is Charles's law that says for constant pressure system the volume is proportional to its temperature and then there is Gay-Lussac's law which says the pressure is proportional to temperature where the volume is fixed. So, pressure p remains p is the notification I mean p denotes the pressure T denotes the temperature and V denotes the volume of the gas assembly. Now interesting point to note is that all these three laws are actually empirical laws what do you mean by empirical laws.

So, these are based on observation. So, we have a system or we have we have or not we would say the scientists have measured perform different measurements on gas assembly the pressure and volume relation volume and temperature relation pressure and temperature relation on certain gas assembly and found that these laws are mostly valid ok. So, that is why these are called empirical laws.

And why these are called ideal gas laws? Because it has been found that it is these laws are valid for most of the for. So, for gases with very low I mean under certain circumstances. So, we will come back to that what are these those circumstances slowly and slowly we will go into that but typically let me tell you when the pressure is low the volume is large and the temperature is moderate only when these laws are strictly valid.

If we go to very low or very high temperature or the pressure goes up or the volume becomes very small then this empirical gas laws are not valid anymore. So, that is to say there is a certain range of pressure and temperature in which these laws are valid for in general for a gas assembly ok. So, then what was done that these three laws are there. Now let us assume a situation in which pressure temperature volume these three parameters in a gas assembly are all changing together.

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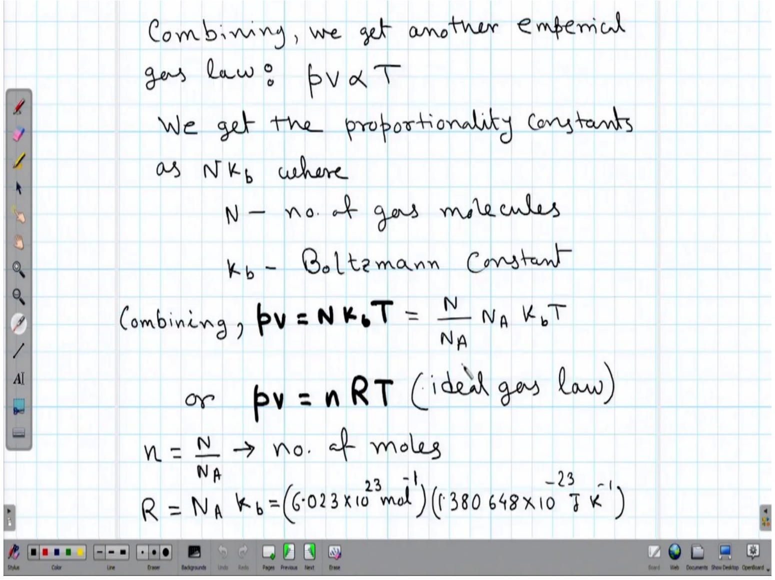

Combining, we get another emperical gas law: $pV \propto T$

We get the proportionality constants as Nk_b where

N – no. of gas molecules

k_b – Boltzmann Constant

Combining, $pV = Nk_bT = \frac{N}{N_A} N_A k_b T$

or $pV = nRT$ (ideal gas law)

$n = \frac{N}{N_A}$ → no. of moles

$R = N_A k_b = (6.023 \times 10^{23}\ mol^{-1})(1.380648 \times 10^{-23}\ J\ K^{-1})$

Then combining these three laws we get that something called the ideal gas law. Now what is ideal gas law? Ideal gas law is p that p V the product p V is proportional to T when all p, V and T are varying together. Now the proportionality constant once again measured experimentally is N k b T where n is the number of gas molecules it was found out that n is the number of gas molecules and k b is the Boltzmann constant.

Now combining we have p V proportional to T with this proportionality constant of N k b T. So, we can write p V equal to N k b T. Now instead of n we can write N by NA times NA into k b T. Now this N by NA this one this quantity N by NA is nothing but the number of moles of the system and NA times k b is nothing but another constant because NA is a constant k b is a constant that is also a constant R the product.

So, we get the celebrated ideal gas law which is p V equal to n R T or p V equal to capital N k T. Once again there are scopes of confusion I also sometime get confused between these two forms which one is what please remember when its k b then it is the number of molecules. So, it become a molecular level law and when it is R then we have number of moles. So, for one mole of gas it will be simply p V equal to RT ok.

So, the values of n once again the value of this gas constant R is given by NA times k b which is 6.023 into 10 to the power 23 multiplied by 1.380648 into to the power -23 which is the value of

Boltzmann constant.

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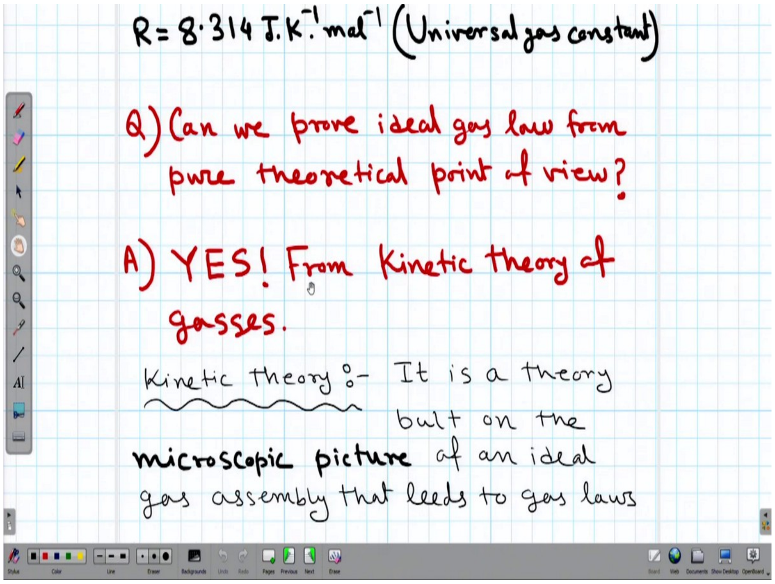

$R = 8{\cdot}314\ J.K^{-1}.mol^{-1}$ (Universal gas constant)

Q) Can we prove ideal gas law from pure theoretical point of view?

A) YES! From Kinetic theory of gasses.

Kinetic theory :- It is a theory bult on the microscopic picture of an ideal gas assembly that leeds to gas laws

And all together we get a value of R is equal to 8.314 joules per kilo calorie inverse per mole inverse which is the universal gas constant ok, fantastic. Now that we have this ideal gas law which is p V equal to n R T small n R T this is as we all know from our text books school level text books this is the ideal gas law. Once again let me point it out that at this point the ideal gas law remains completely phenomenological in nature or the empirical in nature ok not phenomenological sorry empirical in nature.

That means these are based on observation, ok. Now is there any way by which we can prove the ideal gas law from the from pure theoretical point of view that is the question that we have in mind? The answer is yes when we have when we use the kinetic theory of gases we can actually prove this set of laws from or yeah not only the ideal gas law but all three Charles's law Boyle's law and Guy Lussac's law from very fundamental consideration fundamental physics of the problem physics of the system ok.

So, that is how, so what is kinetic theory kinetic theory is the is a theory built on the microscopic picture of an ideal gas assembly that leads to gas loss not only gas laws we will see that it will lead to pressure expression and mean free path and many other important parameter. But most importantly that this is a microscopic picture it is not a macroscopic picture pressure volume temperature all this quantity their macroscopically measured quantity.

So, pressure volume temperature and n small n which is number of mole these are all macroscopically measured quantity. But in kinetic theory we will have microscopic picture which will be I will be discussing very soon and we will see that this microscopic picture is good enough to explain all this empirical laws ok. So, without further delay let us start with the basic postulates of kinetic theory.

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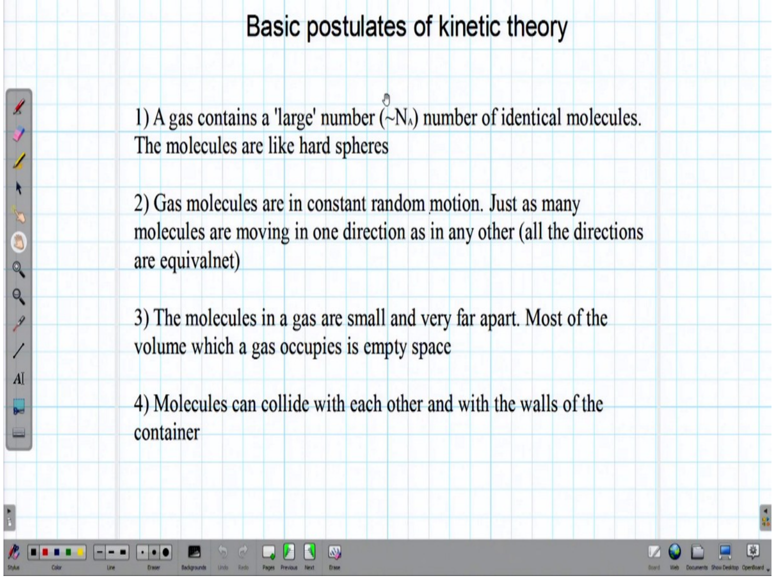

Basic postulates of kinetic theory

1) A gas contains a 'large' number $(\sim N_A)$ number of identical molecules. The molecules are like hard spheres

2) Gas molecules are in constant random motion. Just as many molecules are moving in one direction as in any other (all the directions are equivalnet)

3) The molecules in a gas are small and very far apart. Most of the volume which a gas occupies is empty space

4) Molecules can collide with each other and with the walls of the container

Now in certain books you will find there are 5 points in certain book you will find that there are 8 I mean there are eight points or on basic postulate some books they use 7 points it is more or less the same thing actually but I mean I am not very strict about the number of points that we must have but what is important is we need to have the few basic things which I am going to discuss now embedded in this set of postulates.

First of all that the gas assembly should contain a large number of identical molecules what do you mean by large, large means the number should be of the order of NA the Avogadro number and the basic assumption that we have that this molecules are like hard spheres. So, we do not consider the shape of individual molecules like we might have a tetrahedron shape we can have a bi radical sorry diatomic molecule triatomic molecule.

No, we just consider that these are hard sphere then these gas molecules they are executing constant random motion just. So, that means all the molecules are moving in all random directions such that there is no preferred orientation or preferred direction in the system. So, all the directions are equally probable. So, they are executing random motion in all possible directions during this random motion they are colliding with each other they are colliding with the container wall and all these collisions are elastic in nature ok.

Now also what do you mean by elastic? Elastic means they do not lose any energy because of this collisions ok.

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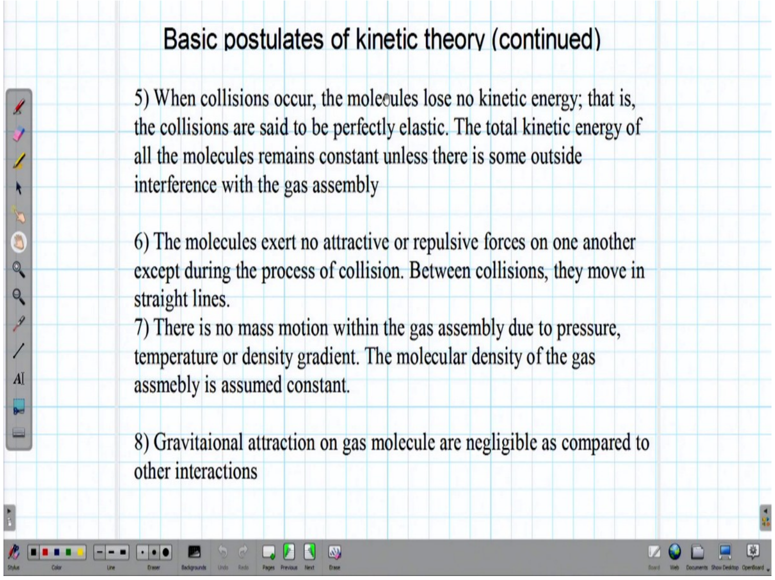

Basic postulates of kinetic theory (continued)

5) When collisions occur, the molecules lose no kinetic energy; that is, the collisions are said to be perfectly elastic. The total kinetic energy of all the molecules remains constant unless there is some outside interference with the gas assembly

6) The molecules exert no attractive or repulsive forces on one another except during the process of collision. Between collisions, they move in straight lines.

7) There is no mass motion within the gas assembly due to pressure, temperature or density gradient. The molecular density of the gas assmebly is assumed constant.

8) Gravitaional attraction on gas molecule are negligible as compared to other interactions

Now the total kinetic energy of the molecules because they are elastic, the collisions are elastic in nature. They remain constant unless there is some outside interference with the gas assembly. Also the molecules do not have any other attractive or repulsive forces between each other and another important point is if you consider the total volume of the molecule for example each molecule has a tiny volume whatever it is the atomic volume. If we combine all these volume together then also the volume of the I mean this volume is very small compared to the total volume of the gas assembly that means we have a container inside which the gas molecules reside with a volume V and let us assume this all the atomic volumes combined together gives you small v.

So, small v is much much less than capital V or rather capital small v by capital V is much much less than one. Also the last but not the least gravitational attraction has no role to play here gravitational attraction or gravitational forces on these molecules are. So, tiny as compared to other effects that we can altogether neglect it ok. So, you can always find this postulate in many different as I said you can find it in many different forms in many different books you can find it also in the internet.

We have chemistry liver text site we have wikipedia site everywhere it is stated in a slightly different manner but these are more or less the basic points which the postulates must cover in order to have a completeness in the system right.

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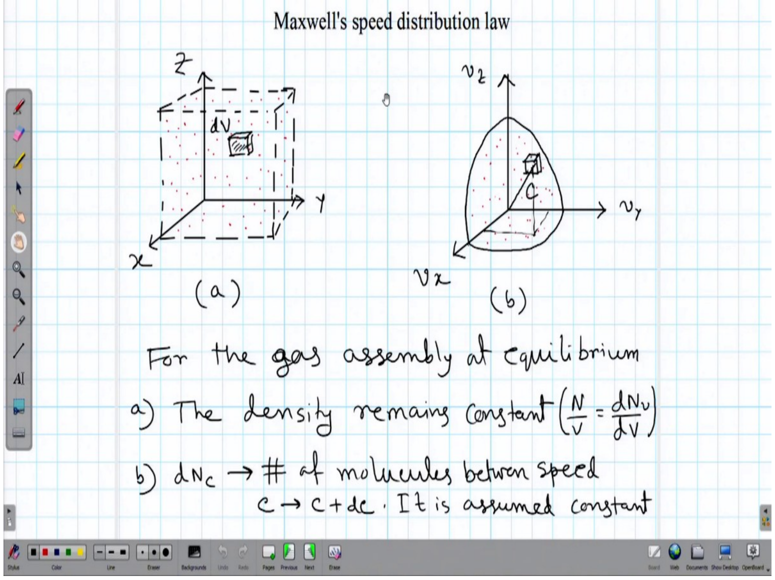

Maxwell's speed distribution law

For the gas assembly at equilibrium

a) The density remains constant $\left(\frac{N}{V} = \frac{dN_v}{dV}\right)$

b) dN_c → # of molecules between speed $c \rightarrow c + dc$. It is assumed constant

Now let us look into it in a slightly more you know pictorial way. So, let us first assume the this picture in the left we have a x y z coordinate which is a standard Cartesian coordinate and we have assumed a volume V ok I should write v here we have assumed a volume V and we have total number of capital N gas molecule present in this for this volume. Now let us assume that there is a tiny volume d dv present here which is at some location we do not know but later in in some location in this container and let me tell you one thing the shape of this container is not important.

What is important is the total volume ok. And let us assume that there is a small volume dv that contains a small number dN v ok of this molecule. Now the outcome of this or from the postulate we can conclude that the density of this gas assembly remains constant ok because all the directions are equally probable and there is no velocity or temperature or you know pressure gradient inside the system these are all written in this postulate.

So, basically the system is in total chemical thermal sorry yeah mechanical thermal and chemical equilibrium with the surrounding. What are these terms? I will explain once again when we will be discussing classical thermodynamics. But let me tell you once this happens the density remains constant that means N by v is equal to dN v by dv and let us assume that dN c is the total number of molecules in this entire gas assembly between speed c to c + dc it is also assumed constant.

And our as ok of course depending on the value of c itself but once we fix c if we are looking to find out the number of molecules present between I mean in the vicinity of a fixed speed value c then this is also a constant, ok. So, now we that this is our picture a on the left hand side, now we represent the same thing in a slightly different manner we now switch to the velocity coordinate. What do you mean by velocity coordinate?

Velocity coordinate means we have instead of x y and z Cartesian axis we map velocity of each of this particles in the three dimensional velocity space when we have v x v y and v z axis. So, I have just drawn one eighth of the total space basically or so and please remember that velocity could be in any direction. So, we can have velocity components in all this eight quadrant of this coordinate system or I do not know what should I call it no not quadrant four five yeah. So, I hope you understand.

So, the each half of this coordinate system will con contain some of these molecules because it is a velocity space velocity is a vector. We have just drawn the positive part v x v y and v z. So, each molecule from here will have a direct representation in this I mean in this entire space but we are just looking at the positive part of it where v x v y v is at all positive ok. So, of a molecule with all three positive quant I mean with a velocity or rather with a speed c for which all three of v x v y and v z are positive will be represented by a point here.

If for example v y is negative then it will be in the neighboring quadrant of the coordinate system neighboring compartment of the coordinate system ok. So, in this representation if we once again you know point out that there is a element this is given by dv x, dv x dv y dv z. So, this is the volume element in this velocity space.

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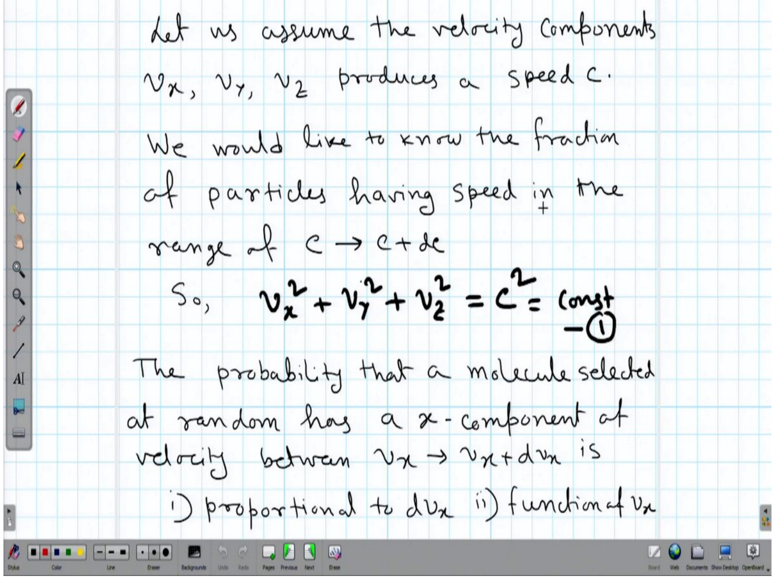

Let us assume the velocity Components v_x, v_y, v_z produces a speed c.

We would like to know the fraction of particles having speed in the range of $c \to c+dc$

So, $v_x^2 + v_y^2 + v_z^2 = c^2 = \text{const}$ — ①

The probability that a molecule selected at random has a x-component of velocity between $v_x \to v_x + dv_x$ is

i) proportional to dv_x ii) function of v_x

Now let us assume that we are talking about a fixed speed c. So, that means we first make c constant but of course you have to understand that many combination of the velocity comp the many combination of the x y z velocity components can produce the same value of c. So, it is not only I mean this equation actually does not identify v x v y visit uniquely but it actually acts as a constraint equation ok in this three dimensional space.

So, we have one constraint equation and the probability that a molecule selected at random has an x component of velocity between v x and v x plus dv x is proportional to dv x and function of v x y proportional to d v x because if we increase enhance the range of the velocity distribution I mean velocity distribution with of course we will have more number of molecules and of course this the probability we are talking about that a molecule has a x component of velocity between v x and v x plus dv x will be a function of v x itself depending on whether the value of v x is very small or very large the probability might vary ok.

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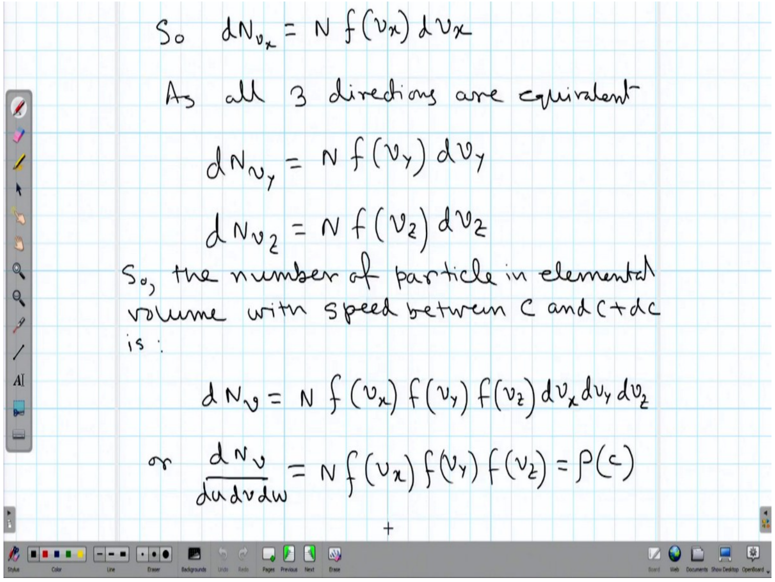

So $dN_{v_x} = N f(v_x)\, dv_x$

As all 3 directions are equivalent

$$dN_{v_y} = N f(v_y)\, dv_y$$

$$dN_{v_z} = N f(v_z)\, dv_z$$

So, the number of particle in elemental volume with speed between C and C+dC is :

$$dN_v = N f(v_x) f(v_y) f(v_z)\, dv_x\, dv_y\, dv_z$$

or $\dfrac{dN_v}{du\,dv\,dw} = N f(v_x) f(v_y) f(v_z) = \rho(c)$

So, we can write this in a mathematical form as yeah where is it right dN v x dN v x is the probability of finding a molecule with a velocity component between v x and dv x that is N times N being the total number of molecules some function f v x times dv x, dv x is the interval in which this is the allowed interval in which the velocity might x component of velocity might lie.

Now let us go back to the postulates we say that all three directions are equally probable. So, that is to say there is no preferred direction in this gas assembly. So, if this is the rule for x direction the same rule should apply for y and z directions as well right. So, we can write two equations once again we have two other relations that identical relation for dN v y and dN v z as well. So, combining this we can say that the total number of particles in the elemental volume with speed between c plus c and c plus dc.

That is to say in that elemental volume to have elemental volume in the velocity space of course this space to have velocity components between x v x and v x plus dv x v y and v y and dv y v z and v z plus dv z is n times f of v x f of v y f of v z times dv x dv y dv z, right? And if I now just bring this volume elemental volume in the denominator what do we get we get the density of molecules with speed lying between c to c plus dc and as we have already said when once we fix the value of c rho c is a constant.

So, next we so immediately we get a second equation that says rho is equal to n times f v x f v y f v z which is equal to a constant. So, we have two equations one equation is this constraint equation which tells us that two of this v x v y and v z can be chosen independently because they are related by one constraint equation. So, please remember I mean plus try to recall your classical mechanics text or your mathematical methods wherever you have encountered this.

You have constraint equation you have n number of independent coordinates and k number of constraint equations. So, the total number of independent coordinate is N minus k simply.

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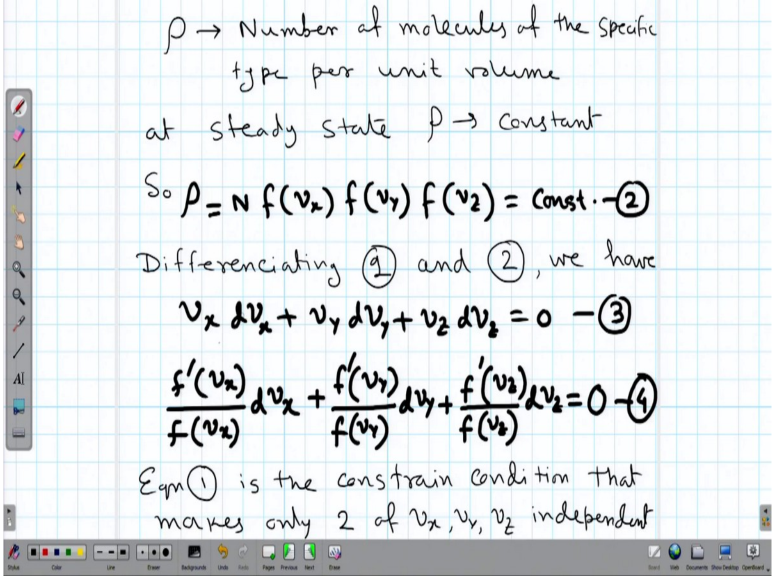

$\rho \rightarrow$ Number of molecules of the specific type per unit volume

at steady state $\rho \rightarrow$ Constant

So $\rho = N f(v_x) f(v_y) f(v_z) = \text{Const.}$ – ②

Differenciating ① and ②, we have

$$v_x\, dv_x + v_y\, dv_y + v_z\, dv_z = 0 \quad -③$$

$$\frac{f'(v_x)}{f(v_x)} dv_x + \frac{f'(v_y)}{f(v_y)} dv_y + \frac{f'(v_z)}{f(v_z)} dv_z = 0 \quad -④$$

Eqn ① is the constrain condition that makes only 2 of v_x, v_y, v_z independent

So, here we have three numbers of independent you know three numbers of independent variables and one constraint equation. So, we have essentially two independent variables which of which are this two which of these two are independent? We do not know. So, in order to you know find out or we or rather we in order to you know overcome this problem what do we do? We first take the derivative of the first relation take the derivative of the second relation and rearrange slightly and we get this two differential forms one is this one v x dx v y dy or sorry I should write v x ok.

So, there is a mistake in this relation let me correct it for you first of all this is not dx dy dz but these are v x ok sorry v x v y v z and in here there should be dv x dv y dv z. I will have to remove this relation all together right. So, let us do it quickly yeah if prime v x f v x dv x plus f prime v y f v y dv y plus f prime oops sorry f prime v set f v z dv z sorry this is not complete yet just have to write equal to zero. So, this is my fourth relation. Now we have a relation three and four and what we can do is we can eliminate this.

So, as we have already said there is a one of this v a sorry two of this v x v y and v z they are independent and we have these two relations. Now how to make this relation independent of each other I mean these three coefficients independent of each other in coefficient of dv x dv y dv z and equate them equal to zero individually we will see in the next lecture, thank you.