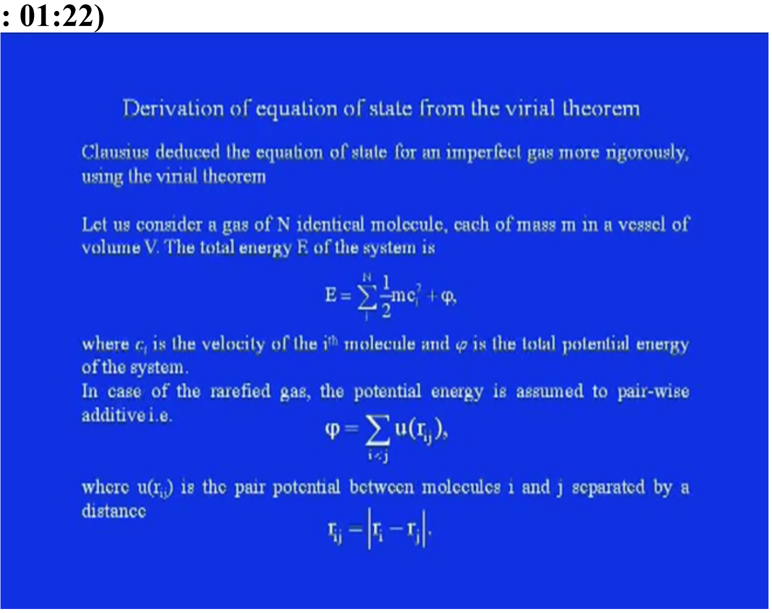
Engineering Physics 1
Dr. M. K. Srivastava
Department of Physics
Indian Institute of Technology-Roorkee

Module-01
Lecture-07
Vanderwaal's equation of states - Part 02

Right now I will start how to derive Vanderwaal's equation of state from more fundamental point view means how to how to start from the basic interaction of the; among the constitution and how to derive it from a more fundamental point of view or from the first principle of stages. So, let me try the how to deduce the equation of state for the real gases using the virial theory. This is not the rigorous virial theorem very often encountered in the statistical mechanics.

So, here we have started just from the simple classical mechanics approach, now let me start it.

(Refer Slide Time: 01:22)



Derivation of equation of state from the virial theorem

Clausius deduced the equation of state for an imperfect gas more rigorously, using the virial theorem

Let us consider a gas of N identical molecule, each of mass m in a vessel of volume V. The total energy E of the system is

$$E = \sum_{i}^{N} \frac{1}{2} m c_i^2 + \varphi,$$

where c_i is the velocity of the i^{th} molecule and φ is the total potential energy of the system.

In case of the rarefied gas, the potential energy is assumed to pair-wise additive i.e.

$$\varphi = \sum_{i<j} u(r_{ij}),$$

where $u(r_{ij})$ is the pair potential between molecules i and j separated by a distance

$$r_{ij} = \left| r_i - r_j \right|.$$

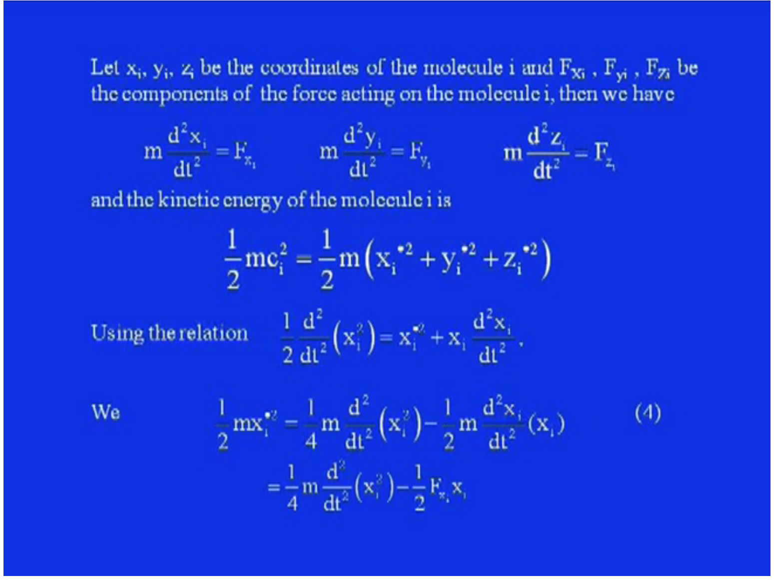
Clausius first did this equation of state for an imperfect or real gas more rigorously using this virial theorem. So, how he had done it let me start it step by step. So, now let us consider a gas of N identical molecules each having mass m in a vessel of volume V. The total the total energy E of the system consists of the total kinetic energy + total potential energy.

Total kinetic energy means summed over kinetic energy of individual molecule plus the interaction energy obviously here we will take simple pair-wise interaction means which depends only on the relative separation between the molecules ok. So, Total energy of the system

E = summed I = 1 to over N half mci square + 5 however ci is the velocity of the ith molecule and Phi is the total potential energy of the system.

Any way we are not going to deal the any real gas, still we have taken from assumptions closer to ideal gas slightly deviated from the ideal gas that in the case of verified the potential energy is assumed to be pear wise additive that means Phi summed I less than j u of ri j where u of r ij, pear potential between the molecules i and j separated by distance which is nothing mode of ri – rj.

(Refer Slide Time: 03:08)



Let x_i, y_i, z_i be the coordinates of the molecule i and F_{x_i}, F_{y_i}, F_{z_i} be the components of the force acting on the molecule i, then we have

$$m\frac{d^2x_i}{dt^2}=F_{x_i} \qquad m\frac{d^2y_i}{dt^2}=F_{y_i} \qquad m\frac{d^2z_i}{dt^2}=F_{z_i}$$

and the kinetic energy of the molecule i is

$$\frac{1}{2}mc_i^2=\frac{1}{2}m\left(x_i^{\bullet 2}+y_i^{\bullet 2}+z_i^{\bullet 2}\right)$$

Using the relation $\frac{1}{2}\frac{d^2}{dt^2}\left(x_i^2\right)=x_i^{\bullet 2}+x_i\frac{d^2x_i}{dt^2}$.

We

$$\frac{1}{2}mx_i^{\bullet 2}=\frac{1}{4}m\frac{d^2}{dt^2}\left(x_i^2\right)-\frac{1}{2}m\frac{d^2x_i}{dt^2}(x_i) \qquad (4)$$

$$=\frac{1}{4}m\frac{d^2}{dt^2}\left(x_i^2\right)-\frac{1}{2}F_{x_i}x_i$$

Let xi, yi, zi be the cartesian coordinates of the molecular xyz component of the position of the molecule ith molecule and similarly F of xi, F of yi, F of zi be the components of the force acting on the molecule i. Then we have three separate Newton's law m d2xi by dt square = F of xi, m d2yi by dt square = F of yi, m d2zi by dt square = F of zi Newton's Law in three co-ordinate, X coordinate, Y coordinate and Z coordinate.

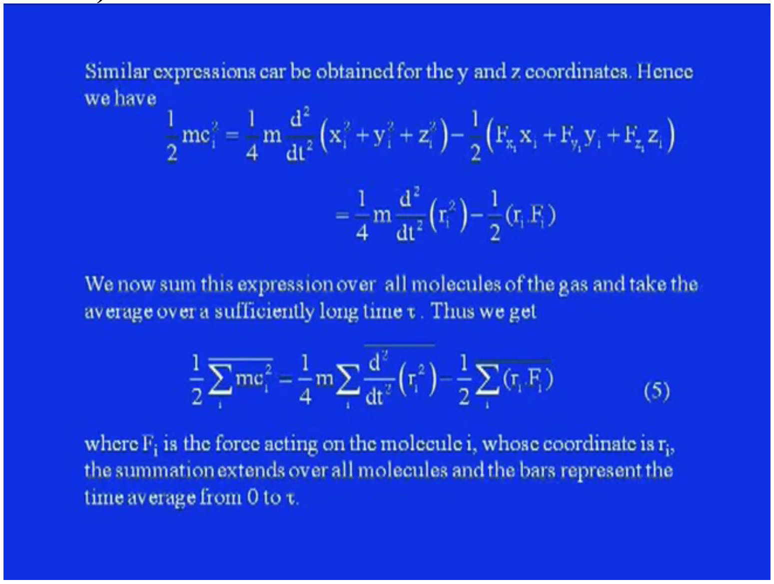
Similarly the kinetic energy of the ith molecule is am half mc square which is nothing but the summed over m because it is the identical molecule same will come out m X i dot square + Yi dot square + Zi dot square where Xi dot, Yi dot, Zi dot t represent the velocity of the molecule in the X, Y, Z direction of the ith molecule ok. Using the relation simple identity differential calculus half d2 by dt2 Xi square = Xi dot square + d2 dXi by dt ok, dtXi dt square ok.

If you will use this relation in the kinetic energy equation so for individually for individual components means X component kinetic energy is half m xi dot square equal to half times half =

4 so one fourth m by d2 by dt Xi square – half m d2 Xi by d2 square Xi ok. So, 1 by 4 m d2 by dt Xi dot Xi square – half md2 Xi by dt2 is nothing but F of Xi in so half F of Xi to Xi. So, this is the kinetic energy of the X component Kinetic energy can be written in this way.

Similarly we can follow the same identity for the Y component and Z component also and get them together.

(Refer Slide Time: 05:58)



Similar expressions car be obtained for the y and z coordinates. Hence we have

$$\frac{1}{2}mc_i^2 = \frac{1}{4}m\frac{d^2}{dt^2}\left(x_i^2 + y_i^2 + z_i^2\right) - \frac{1}{2}\left(F_{x_i}x_i + F_{y_i}y_i + F_{z_i}z_i\right)$$

$$= \frac{1}{4}m\frac{d^2}{dt^2}\left(r_i^2\right) - \frac{1}{2}(r_i.F_i)$$

We now sum this expression over all molecules of the gas and take the average over a sufficiently long time τ. Thus we get

$$\frac{1}{2}\overline{\sum_i mc_i^2} = \frac{1}{4}m\sum_i \overline{\frac{d^2}{dt^2}\left(r_i^2\right)} - \frac{1}{2}\overline{\sum_i (r_i.F_i)} \qquad (5)$$

where F_i is the force acting on the molecule i, whose coordinate is r_i, the summation extends over all molecules and the bars represent the time average from 0 to τ.

What will get it half mci square = 1 by 4 m d2 by dt2 Xi square + Yi square + Zi square – half of F of Xi X component of force into displacement Xi in the X direction + Y component of force multiplied by the displacement in the Y direction + Z component of the force multiplied by the Z component of the displacement. Obviously of this is for the repeated indices tells that summation which is for the ith molecule.

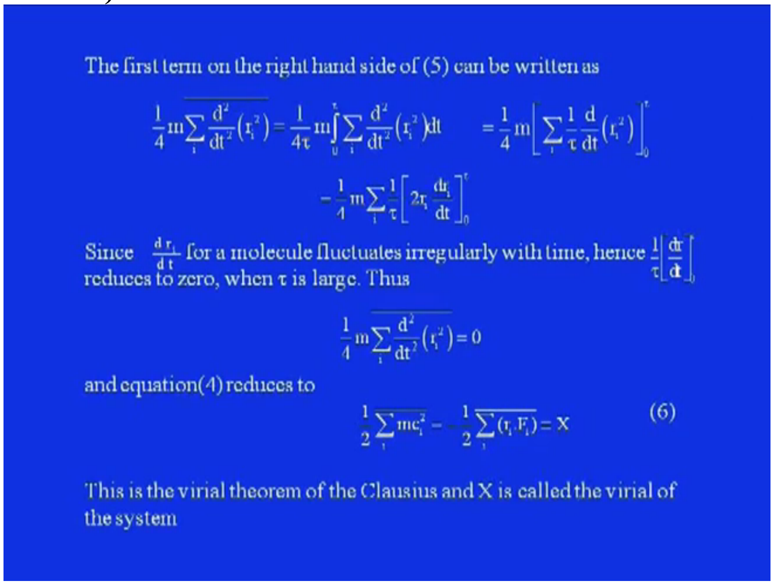
So, if you rewrite this in terms of the r coordinate, spherically what we can get this 1 by 4 m d2 dt2 ri square - half ri dot Fi ok. We now sum the expression of all molecule of the gas and take a average over a sufficiently long time. So, we get half summed over average over mci square that means we are taking the time average = 1 by 4 m summation average of dt by dt2 ri square - half time average of summed over ri Fi Fi dot.

Time average has come from very fundamental fact that the motion of the atoms or molecule in the gas completely random. They are always under the experience of random force. So, we are interested over the time value of those average quantities over a large time scale obviously that time is always much, much greater than the collision all time over and asymptotic time scale, so, this so that is that gives the concept of time average.

Because the force each and every molecule or atom always experiencing by random force. So, we have to take some time average of it okay. so, finally where Fi is the force acting on the molecular which is coordinating with ri, so that is a ri dot Fi dot the summation extent over all molecules and the bars represent the time average which starts from 0 to Tau. Obviously that Tau is larger than the collision time scale ok.

So, if you, all though this is not I do not want to tell this thing in this lecture but this thing if you look for the Lange dynamics or Faulkner plain equation there you will see there are two type of time scale. One time scale which are less than the collision time scale and random force still exist, another time scale where time is much, much greater than the collision time scale that actually we are looking for the time average over a very long infinite time which is known as the steady state system.

(Refer Slide Time: 09:36)



The first term on the right hand side of (5) can be written as

$$\frac{1}{4}m\overline{\sum_i \frac{d^2}{dt^2}(r_i^2)} = \frac{1}{4\tau}m\int_0^\tau \sum_i \frac{d^2}{dt^2}(r_i^2)dt \qquad = \frac{1}{4}m\left[\sum_i \frac{1}{\tau}\frac{d}{dt}(r_i^2)\right]_0^\tau$$

$$-\frac{1}{4}m\sum_i \frac{1}{\tau}\left[2r_i\frac{dr_i}{dt}\right]_0^\tau$$

Since $\frac{dr_i}{dt}$ for a molecule fluctuates irregularly with time, hence $\frac{1}{\tau}\left[\frac{dr}{dt}\right]_0^\tau$ reduces to zero, when τ is large. Thus

$$\frac{1}{4}m\overline{\sum_i \frac{d^2}{dt^2}(r_i^2)} = 0$$

and equation(4) reduces to

$$\frac{1}{2}\overline{\sum_i mc_i^2} - \frac{1}{2}\overline{\sum_i (r_i.F_i)} = X \qquad (6)$$

This is the virial theorem of the Clausius and X is called the virial of the system

So, the first time if you take the time average you will get it what I will get it the first time in the right hand side of equation can be write down that 1 by 4 just use see it 1 by 4 m average of dt2 by dt2 ri dot square bar means time average. If you write down the summation in terms of the integral form of from the definition of obtaining any average quantities 1 by 4 Tau basically 1 by t, t is the time. 0 to t F of t dt that is the general definition of time average.

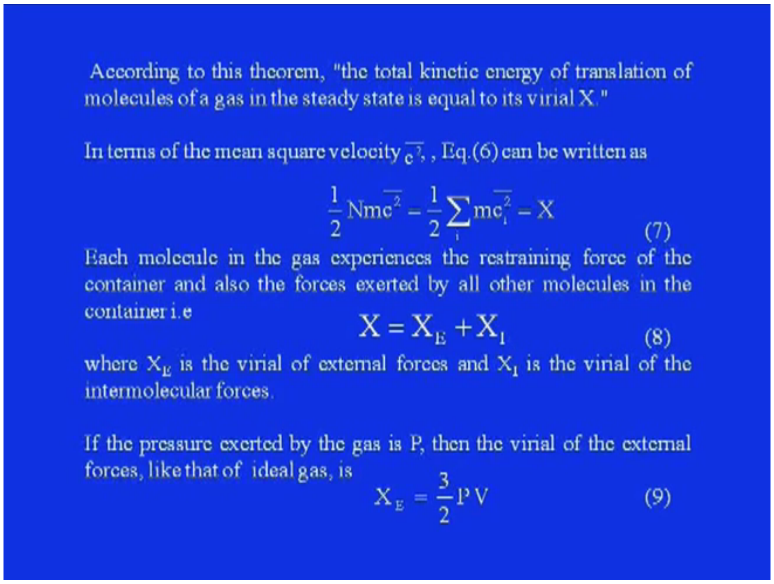
So, same thing applies here also 1 by 4 Tau 1 by 4 is already there so 1 by 4 Tau m 0 to Tau summed over i dt by dt2 ri square dt. So, if you do it then I can always write down this thing as 1 by 4 m summed over ri 1 by Tau d2 ddt of ri square 0 to Tau. So, this thing has come after doing it by part by part. If you do this integration by parts then this thing you can get it. So, then it will put the upper and lower limits of time, so you will get it 1 by 4 m summed over i 1 by Tau 2ri dri by dt because ddt of ri square is 2ri by dt 0 to Tau.

Since dri by dt is nothing but the velocity of the ith molecule since I told you that each molecule are always experiencing very random force. So, the velocity which is nothing but the dri by dt the velocity of the molecules are always fluctuating rapidly because the velocity arises because of the random forces. So, obviously velocity will fluctuate very irregularly. So, if you average it over a long time velocity you will get 0.

So, that is the reason dri by dt for a molecule fluctuating irregularly with time hence 1 by Tau dri dt 0 to Tau obviously reduces to 0 when Tau is very large. So, that finally first term is 1 by 4 m d2 dt2 riy square average will be the 0. This is because of the force motion is completely random this is the basic physics behind this average. So, the equation finally reduced to half average of the total kinetic energy average summed over I mci square bar means average is nothing but -half summed over i ri dot Fi which is let us all say X.

So, this is varial theorem of Clausius and where X is called the virial of this system. so what does it mean by virial theorem the total kinetic energy of all the molecules is nothing but is equal to the X which is nothing but the virial of the system. Once if I will calculate X then I will get what is the total value of the kinetic energy average kinetic energy ok.

(Refer Slide Time: 13:18)



According to this theorem, "the total kinetic energy of translation of molecules of a gas in the steady state is equal to its virial X."

In terms of the mean square velocity $\overline{c^2}$, , Eq.(6) can be written as

$$\frac{1}{2}Nm\overline{c^2} = \frac{1}{2}\sum_i m\overline{c_i^2} = X \qquad (7)$$

Each molecule in the gas experiences the restraining force of the container and also the forces exerted by all other molecules in the container i.e

$$X = X_E + X_I \qquad (8)$$

where X_E is the virial of external forces and X_I is the virial of the intermolecular forces.

If the pressure exerted by the gas is P, then the virial of the external forces, like that of ideal gas, is

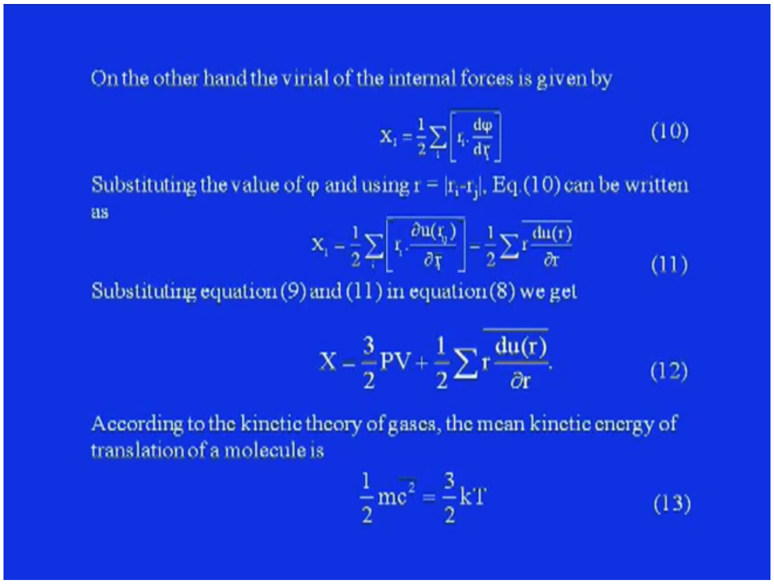
$$X_E = \frac{3}{2}PV \qquad (9)$$

According to this theorem the total kinetic energy of translation of molecules of a gas in the steady state is equal to its virial X, as I have already told where X is nothing but the - half summed over i ri dot Fi and then take its time average. This is nothing but virial of the system So, in terms of means square velocity c square bar equation 6 can be rewritten has half N is the total number of molecules Nmc square.

This is the definition of mean square velocity which is nothing but the half summed I mci square which is nothing but the X. Each molecule in the gas experiences the restraining force of the container and also the force exerted by all other molecules in the container. So, each molecule in the gas are experiencing two kinds of force, one is the restraining forces of the container and other force which is exerted by all the remaining molecules in the container. So, virial obviously since forces to component, so, virial X, virial of the system can be decomposed into two parts.

One part is due to the external force which is another XE, another part is the due to the intermolecular forces. So, X can be written as X = XE + Xi, E stands for the external forces, I stand for the intermolecular forces. So, if the pressure; now calculate XE and XI re separately then I will add together and then I will get this equation of state. So, what is XE if the pressure exerted by the gas is P then the virial of the external forces like that of an ideal gas is nothing but XE is nothing but the 3 by 2 PV that you that is well understood.

(Refer Slide Time: 15:42)



On the other hand the virial of the internal forces is given by

$$X_i = \frac{1}{2}\sum_i \overline{\left[r_i \cdot \frac{d\varphi}{dr_i} \right]} \qquad (10)$$

Substituting the value of φ and using $r = |r_i - r_j|$. Eq.(10) can be written as

$$X_i = \frac{1}{2}\sum_i \overline{\left[r_i \cdot \frac{\partial u(r_{ij})}{\partial r_i} \right]} = \frac{1}{2}\sum r \overline{\frac{du(r)}{\partial r}} \qquad (11)$$

Substituting equation (9) and (11) in equation (8) we get

$$X = \frac{3}{2}PV + \frac{1}{2}\sum r \overline{\frac{du(r)}{\partial r}}. \qquad (12)$$

According to the kinetic theory of gases, the mean kinetic energy of translation of a molecule is

$$\frac{1}{2}m\overline{c^2} = \frac{3}{2}kT \qquad (13)$$

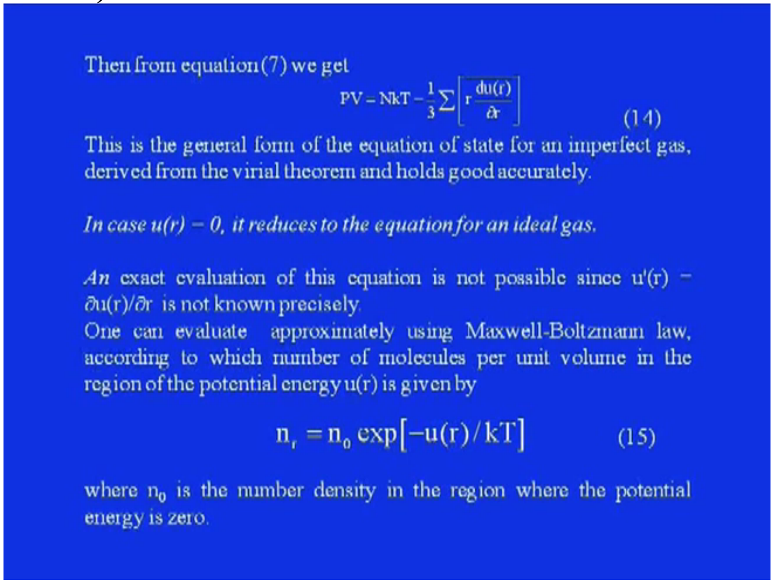
Second part on the other hand virial of the internal forces is given by Xi = half summed over i ri dot del Phi by del ri average ok. What does; how this has come let me explain it. As you know Xi is half summed over i ri Fi dot intermolecular force. And intermolecular forces derived by the potential energy. So, Fi is nothing but derived by the potential energy which is the as you have told you; Phi is the total potential energy.

Phi is the total potential energy of the system and the internal intermolecular force arises because of the potential energy. So, F is derived from the potential energy which is nothing but dPhi by dri ri bar is nothing but the average value of r ok. Substituting these values of i and using ri = mod of ri – rj. So, the virial of the internal forces can be rewritten as half summed over i ri ri dot del U rij by del ri bar take its total time average.

So, what if you skip this notation and notation is well understood because of this repeated indices that half summed over r dU del U r by dr then take its average. So, I skip the indices which is well understood which is the repeated indices. So, substituting these values of Xi and XE so the total X means total viral of the system is which is 3 by 2 PV which is nothing but due to external force which is just like the ideal gas 3 by 2 PV + due to the intermolecular force, intermolecular potential which is half summed over r del U r by dr and take its time average.

According to kinetic theory of gases the mean kinetic energy of translation of a molecule is half mc bar square = 3 by 2 KT that we have already talked about in the in my earlier lectures that kinetic energy is a measure of the temperature is a measure of the reference of kinetic energy half mc bar square = 3 by 2 KT obviously this kinetic energy only to the translational motion ok. So, then PV =NKT- then if you rewrite this equation that means you will bring PV in the left hand side then you will get it.

(Refer Slide Time: 19:06)



Then from equation (7) we get

$$PV = NkT - \frac{1}{3}\sum\left[\overline{r\frac{du(r)}{\partial r}}\right] \qquad (14)$$

This is the general form of the equation of state for an imperfect gas, derived from the virial theorem and holds good accurately.

In case $u(r) = 0$, it reduces to the equation for an ideal gas.

An exact evaluation of this equation is not possible since $u'(r) = \partial u(r)/\partial r$ is not known precisely.

One can evaluate approximately using Maxwell-Boltzmann law, according to which number of molecules per unit volume in the region of the potential energy u(r) is given by

$$n_r = n_0 \exp[-u(r)/kT] \qquad (15)$$

where n_0 is the number density in the region where the potential energy is zero.

PV = NKT- one third summed over r dur by dr then take its time average. This is the general form of the equation of state for an imperfect gas derived from the virial theorem and holds good accurately. So, if you feel it where is the first glance if you see this; if you will put what is the u, is the measure of intermolecular interaction. If in the ideal gas equation of state we know there are no intermolecular interactions.

So, if you put u of r = 0 then it reduces to the ideal equation of state. So, this is the first check up of this equation of state that we are going in the right direction. So, if you want to evaluate exactly then you have to know what is the form of intermolecular interaction. So if you know the form of intermolecular interaction then you will plug in the expression in form of dur by dr then calculate is time average do all sorts of summation and finally you can get the equation of state for the real gases which is which is true in principle it is true.

But as you know that its exact evaluation of the equation is not possible. Since du by dr is not known precisely which is why it is not known precisely because we do not know what is the exact form of intermolecular interaction. Because we know atom is formed by one of the most fundamental interaction which is nothing but the electrostatic coulomb interaction. Because suppose let us take hydrogen molecule hydrogen atom which is bound because of the electrostatic coulomb interaction between electron and proton.

So, this is well understood because you know in quantum mechanics this problem analytically solved. But how molecule is formed by two hydrogen atom is H2 exactly cannot calculate how you cannot calculate how two hydrogen atom from a hydrogen molecule. So, you have to look for some empirical equation of state because here exactly in principle the formation of molecule should be obtained through the electrostatic are electromagnetic interaction between all point like electric charges.

But since here two atoms are not electrically charged object, so in principle they are not interacting electromagnetically directly. But they are interacting electromagnetic through in the shielded form, which people is to call Leonard Jones potential, Vandervaal's forces etc. They are electromagnetic forces they are which is in the shielded form. In the dipole approximation, quadruple approximation you can expand atom in terms of dipole quadruple.

Then two atoms can interact with dipole interaction or quadruple interaction which is nothing but the select form of electromagnetic interaction. So, in principal this equation of state, this is the equation of state for an imperfect gas but provided if you know u of r exactly u of r tells you the intermolecular interactions. So, but in general u of r is not known to us, reason is that you u of r is the intermolecular interaction.

So, if I know u of r exactly there the, I will substituted there and take its time average then I can get the equation of state for an imperfect gas. For the readymade for the readymade check you see if you put u of r = 0 it immediately deduces to the ideal equation of state. That we are going in the right direction because in the ideal equation of state interactions among the constituent is 0 there are no interaction.

So, it gives rise to the ideal gas equation of state, but if you want to evaluate exactly this expression which is given equation 24, this is not possible because we do not know you are exactly. The reason is that the reason why you do not know u of r exactly it has many reasons. Because you do not know how the two atoms or two molecules interacting among themselves because we know at least, let us take a simple example to clarify this statement.

Suppose take single hydrogen atom was taking how a hydrogen atom forms how the bounce rate of hydrogen atom forms we know exactly, reason we know exactly because hydrogen atom form the due to a one of the most fundamental interaction which is known as the electromagnetic interaction between electron and proton. And it seems there this interaction is known fully. So, it is as you know although I do not want to tell you the things in details.

Schrodinger equation which tells the again the energy of this hydrogen atom which exactly soluble analytically for this attractive coulomb interaction between electron and proton but how the true hydrogen atom forms hydrogen molecule that you know exactly analytical we do not know exactly, reason is that two hydrogen atoms cannot interact fundamentally electrostatic coulomb attraction.

Reason is that atom is not an electric charged particle atom is not an electric charge particle but about you know that two hydrogen atom interact each other to form a hydrogen molecule. These interaction nowadays it can be explained in terms of the dipole or quadruple interactions among the two hydrogen atom and these interaction these problem is not solve analytically. People is to take that the two atoms are interacting through the dipole or quadruple interactions.

Sometimes people use to call this is a shielded electromagnetic interactions. So, people us to call Vanderwaals is nothing but a shielded electromagnetic force. So, these things are not easily even for a simplest case which is the hydrogen atom which consists of only one electron. If you want to look for the intermolecular interaction having that many multi electron system, so this is very complicated thing however nowadays people are able to improve not using the density functional approach.

Anyway I am not going to digress; I am not going to tell it because it will be too much digression for this stock. Nowadays people have developed a new method which is the remarkable in the theoretical physics which is known as the density functional approach. Through which people are able to extract intermolecular, almost the exact, exact form of the intermolecular interaction. If you can extract intermolecular interaction they in principle you can get a exact form of the equation of state for the real gas.

But for the sake of simplicity for the real gas for the analytical point of view It is very hard to get an analytical equation of state for any real gas. So, let me start it, let me get some of this; let me extract some of this form of this equation of state for the real gas. So, here I would like to tell you something about the Maxwell Boltzmann distribution. As you remember, as you quite remember in my earlier lecture Maxwell Boltzmann distribution of speed.

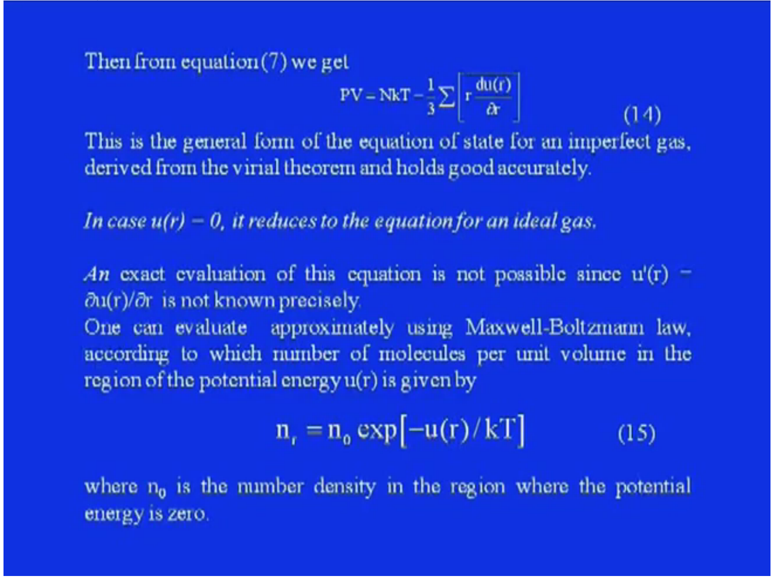
Maxwell Boltzmann distribution has two kinds of thing, one it tells how many atoms or molecules having the velocity in between v and v + dv or he tells the velocity distribution of molecular or energy distribution of molecules, how atoms or molecules are distributed among the energy in terms of E and E + dE and this is one Maxwell Boltzmann distribution law. Another Maxwell Boltzmann distribution that I have also told you at the end of the lecture of Boltzmann distribution.

There I told you how this molecules are, atoms or molecule are in general how the particle are distributed according to their potential energy distribution which obviously potential energy tells you in the coordinates space means how the particle are distributed in the coordinate space. So, you see there are two kinds of beautiful distribution of the same Maxwell Boltzmann one tells the distribution of molecular in the momentum space.

In its Fourier space which is nothing but the coordinates it can also tell how the particles are distributed in the code in space between r and r + dr. So, let me explain that Maxwell Boltzmann distribution ok. So, let me tell few things more Maxwell Boltzmann distribution in the velocity space tells how quickly system will be equilibrated or how system will achieve thermal equilibrium quickly. This is the; these will be dealt with the Maxwell distribution law of speeds.

The Maxwell Boltzmann distribution in the coordinate space is tells how the particles will be, how they diffuse the property of the particle which is in the coordinates space ok.

(Refer Slide Time: 30:02)



Then from equation (7) we get

$$PV = NkT - \frac{1}{3}\sum\left[r\frac{du(r)}{\partial r}\right] \qquad (14)$$

This is the general form of the equation of state for an imperfect gas, derived from the virial theorem and holds good accurately.

In case $u(r) = 0$, it reduces to the equation for an ideal gas.

An exact evaluation of this equation is not possible since $u'(r) = \partial u(r)/\partial r$ is not known precisely.

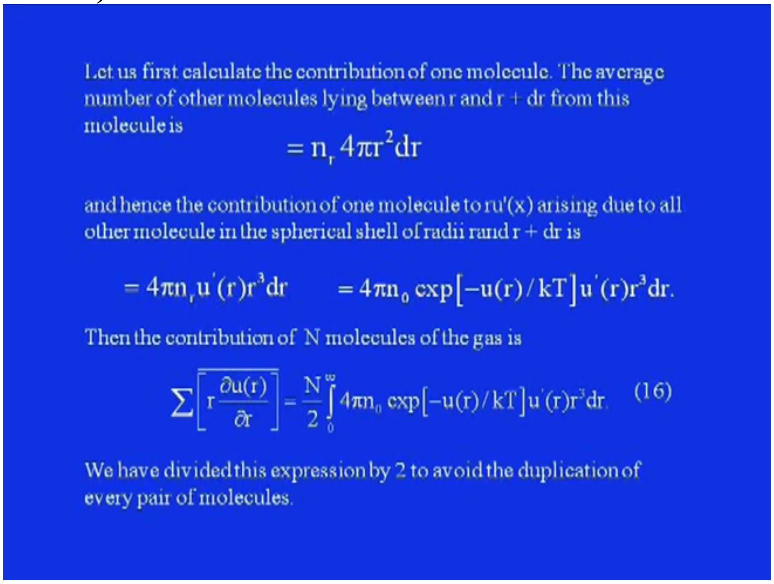
One can evaluate approximately using Maxwell-Boltzmann law, according to which number of molecules per unit volume in the region of the potential energy $u(r)$ is given by

$$n_r = n_0 \exp\left[-u(r)/kT\right] \qquad (15)$$

where n_0 is the number density in the region where the potential energy is zero.

So, now let me start, one can evaluate approximately; this del u by del r times del u by del r and its average this thing somebody can evaluate approximately using the Maxwell Boltzmann law. According to its number of molecules per unit volume in the region of the potential energy ur is given n of r subscript r means it is a function of r n of r = n of where r = 0 e to the power of –ur by KT that we have already derived by in my last lecture in the Maxwell Boltzmann distribution of speeds. Where n naught is the number density in the reason for potential energy is 0 where u of r is 0 ok.

(Refer Slide Time: 30:55)



Let us first calculate the contribution of one molecule. The average number of other molecules lying between r and r + dr from this molecule is

$$= n_r 4\pi r^2 dr$$

and hence the contribution of one molecule to ru'(x) arising due to all other molecule in the spherical shell of radii rand r + dr is

$$= 4\pi n_r u'(r) r^3 dr \qquad = 4\pi n_0 \exp\left[-u(r)/kT\right] u'(r) r^3 dr.$$

Then the contribution of N molecules of the gas is

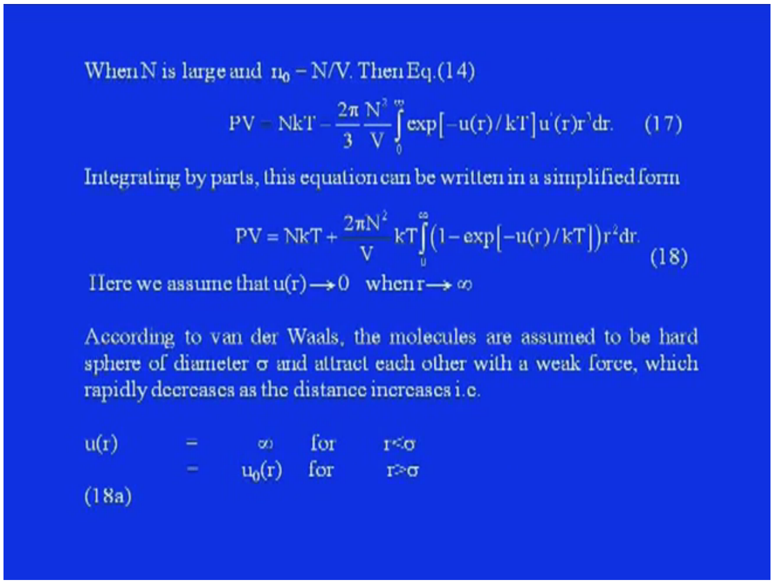
$$\sum \overline{\left[r \frac{\partial u(r)}{\partial r} \right]} = \frac{N}{2} \int_0^\infty 4\pi n_0 \exp\left[-u(r)/kT\right] u'(r) r^3 dr \qquad (16)$$

We have divided this expression by 2 to avoid the duplication of every pair of molecules.

Let us first calculate the contribution of one molecule. The average number of other molecules lying between r and r + dr from this molecule is nr 4Pi r squared dr and hence the contribution of 1 molecule to r u prime r, u prime means del u by del r arising due to all other molecule in the spherical shell of radii r and r + dr is 4 Pi nr u prime r rq dr which is if 4 Pi n naught just you substitute n of r, so 4 Pi nr exponential - ur by KT, u prime r qdr.

So, then the contribution of and molecules of the gas is, if you will take summed over r del u by del r and its average = n by 2, 0 to infinity 4 Pi n naught exponential - ur by KT at u prime r rq dr. To testing the account over counting ok, so we have divided this expression by 2, to avoid the duplication of every pair of molecules.

(Refer Slide Time: 32:19)



When N is large and $n_0 - N/V$. Then Eq.(14)

$$PV = NkT - \frac{2\pi}{3}\frac{N^2}{V}\int_0^\infty \exp[-u(r)/kT]\,u'(r)r^3dr. \qquad (17)$$

Integrating by parts, this equation can be written in a simplified form

$$PV = NkT + \frac{2\pi N^2}{V}kT\int_0^\infty (1-\exp[-u(r)/kT])r^2dr. \qquad (18)$$

Here we assume that $u(r) \longrightarrow 0$ when $r \longrightarrow \infty$

According to van der Waals, the molecules are assumed to be hard sphere of diameter σ and attract each other with a weak force, which rapidly decreases as the distance increases i.e.

$$\begin{aligned} u(r) &= \infty \quad \text{for} \quad r<\sigma \\ &= u_0(r) \quad \text{for} \quad r>\sigma \end{aligned}$$

(18a)

When N is large and putting n naught = N by V which is nothing but the density than equation 14 gives that means that equation of state is PV = NKT – 2 PI by 3 N square by V substitute n naught it which is nothing but N by V, there is another N outside of the situation that gives you the N square, so Pv = NKT - 2 Pi by 3 N square by V 0 to infinity e to the power of -ur by KT prime r rq dr.

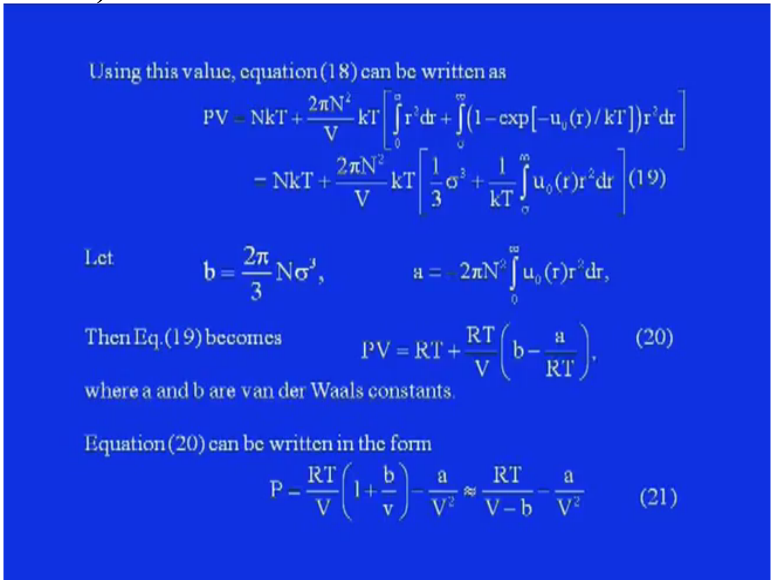
So, if you integrated by parts this equation can be written in a simplified form PV =NKT + 2 PI N square by V KT 0 to infinity 1 – e to the power – ur by KT r square dr. If you assume ur tends 0 when r tends to infinity obviously I should assume this because we know whenever in the ideal gas approximation people use to take why there are no interaction potential between the molecule.

Reason is that idea behind that assumption is the; since the separation between the molecule is far, far large. Then the range of interaction so that is the reason there is no interaction potential. So, obviously if you take r tends to infinity ur tends to 0, so putting to Vanderwaals the molecules are assume to be hard sphere of diameter Sigma and attract each other with weak force who is rapidly decreases as the distance increases.

That means he has taken some potential energy form, so whenever two atoms or molecules close together they will stick to; whenever they touch each other they experiencing huge potential. Whenever the separation distance is very large they are not feeling any interaction due to other. So, he has taken some kind of form of this potential which is below which is given as ur = infinite when r tends to Sigma he takes some finite interaction u0 of r when r greater than Sigma.

If r is much, much greater than Sigma then it will be 0. So, if you plug in this kind of potential energy form in the above expression it so what you will get it.

(Refer Slide Time: 35:06)



Using this value, equation (18) can be written as

$$PV = NkT + \frac{2\pi N^2}{V} kT \left[\int_0^{\sigma} r^2 dr + \int_{\sigma}^{\infty} (1 - \exp[-u_0(r)/kT]) r^2 dr \right]$$

$$= NkT + \frac{2\pi N^2}{V} kT \left[\frac{1}{3}\sigma^3 + \frac{1}{kT} \int_{\sigma}^{\infty} u_0(r) r^2 dr \right] \quad (19)$$

Let $b = \frac{2\pi}{3} N\sigma^3$, $a = -2\pi N^2 \int_0^{\infty} u_0(r) r^2 dr$,

Then Eq.(19) becomes $PV = RT + \frac{RT}{V}\left(b - \frac{a}{RT}\right)$, (20)

where a and b are van der Waals constants.

Equation (20) can be written in the form

$$P = \frac{RT}{V}\left(1 + \frac{b}{v}\right) - \frac{a}{V^2} \approx \frac{RT}{V - b} - \frac{a}{V^2} \quad (21)$$

You will get PV = NKT + 2 Pi N square by V KT then you split this integration into two form, 0 to infinity you can make it, you can make it into two form, 0 to Sigma and Sigma to infinity. So, 0 to Sigma you know u fo r = infinity e ot the power - infinity is zero so only one will survive so r square dr. So, that is the reason first term of this integration reduces to 0 to Sigma r square dr.

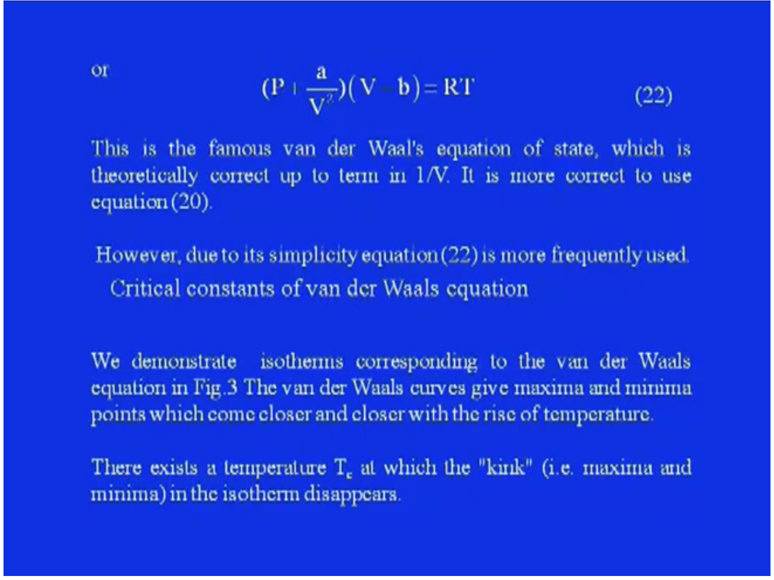
Second part is Sigma to infinity where it will take the form u0 of r this form just you see this from u0 r. Then Sigma to infinity 1- e to the power of –u0 r by KT r square dr. So, you do this integration, so NKT + 2 Pi N square by V KT one third Sigma cube + I by KT Sigma to infinity u0 of r r square dr. So, let us take, let us say b = 4 Pi 2Pi by 3 N Sigma cube and let us take assume let us take a = 2 PI N square 0 to infinity u0 r r square dr.

Then the above equation will be deduced in terms of a and b PV = RT + RT by V into b – a by RT where a and b are Vanderwaals constants. So, equation 20 can be written in the form P= RT by V 1 + b by V – a by V square, so which is RT if you we will 1 + b by V – A by V square which is RT which you will 1- b by V when you bring it to the denominator when b is much, much smaller than capital V.

So, RT by V - b - a by V square if you will bring a by V square on the left hand side so you will get P + a by V square into b - V = RT which is nothing but the famous Vanderwaal's equation of state. So finally we have derived Vanderwaal's equation of state from the more fundamental description of the atoms and molecules which constitute a system. So, that is the beauty through which is one kind of first principal calculation in physics which tells, which bring the Vanderwaals equation of state.

Although it was derived it very heuristically by incorporating the salient feature of the real gases. But anyway we are able to derive a form of Vanderwaal's equation of state from the virial theorem

(Refer Slide Time: 38:15)



or

$$(P + \frac{a}{V^2})(V - b) = RT \qquad (22)$$

This is the famous van der Waal's equation of state, which is theoretically correct up to term in 1/V. It is more correct to use equation (20).

However, due to its simplicity equation (22) is more frequently used.

Critical constants of van der Waals equation

We demonstrate isotherms corresponding to the van der Waals equation in Fig.3 The van der Waals curves give maxima and minima points which come closer and closer with the rise of temperature.

There exists a temperature T_c at which the "kink" (i.e. maxima and minima) in the isotherm disappears.

Which is theoretically correct of two terms one maybe because if you will see it, we have terminate the series 1 by V at etcetera term, so so that is the reason who is this equation is theoretically correct up to term i by V more correct to use equation 20 instead of 22 but due to its form of simplicity this form of equation is more frequently use, so, just for the sake of completeness if you want to write down the Vanderwaals equation of state for N moles of gas.

Then you substitute small v to Capital V by N so we will get P + N square a by V square into V – b = NRT.