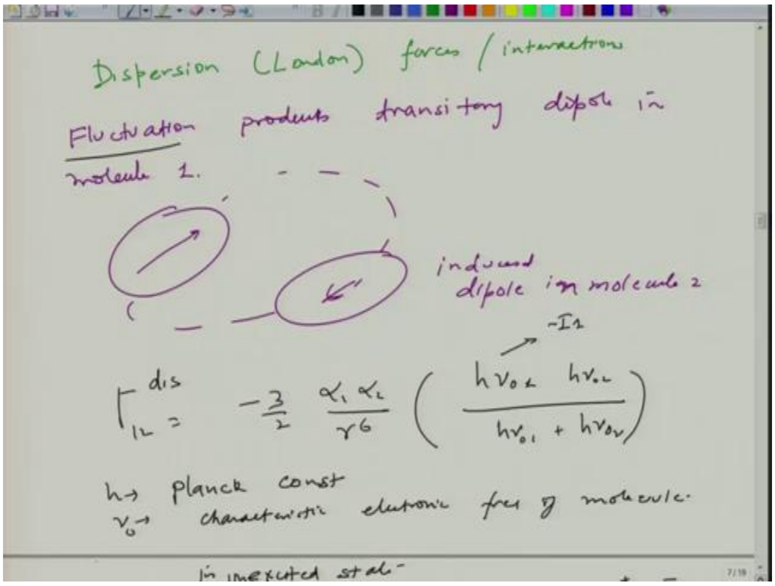
Chemical Engineering Thermodynamics
Professor Jayant K. Singh
Department of Chemical Engineering
Indian Institute of Technology Kanpur
Lecture 32
Repulsive Interaction

Okay, welcome back. In the last class we were talking about the interactions due to various different contributions. So, we looked at point charge interactions, we looked at dipole-dipole moment the intermolecular interactions then permanent dipole and induced dipole and subsequently we looked at London dispersion or something we called it dispersion forces, ok.

(Refer Slide Time: 0:43)



Dispersion (London) forces / interactions

Fluctuation produces transitory dipole in molecule 1.

induced dipole in molecule 2

$\sim I_1$

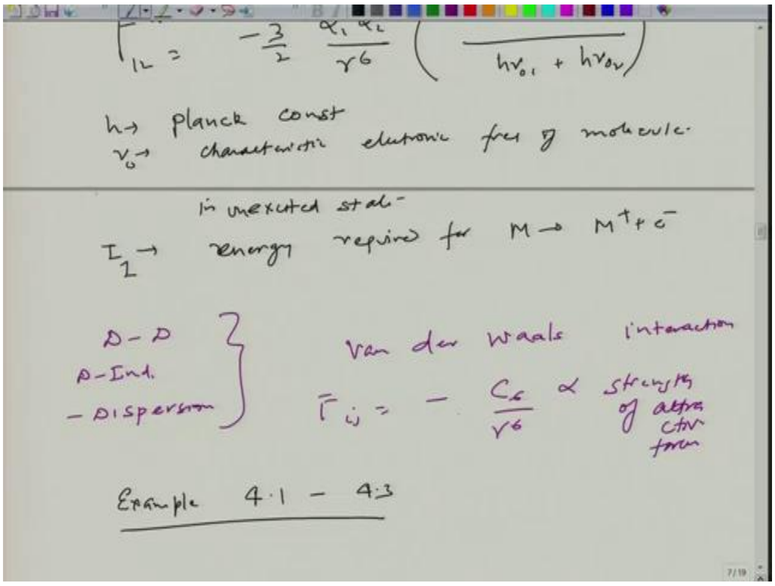
$\Gamma^{dis}_{12} = -\frac{3}{2}\frac{\alpha_1\alpha_2}{r^6}\left(\frac{h\nu_{01}\, h\nu_{02}}{h\nu_{01} + h\nu_{02}}\right)$

$h \rightarrow$ planck const

$\nu_0 \rightarrow$ characteristic electronic freq of molecule

in unexcited state

$$\Gamma^{dis}_{12} = -\frac{3}{2}\frac{\alpha_1\alpha_2}{r^6}\left(\frac{h\nu_{01}h\nu_{02}}{h\nu_{01} + h\nu_{02}}\right)$$



$\Gamma_{12} = -\frac{3}{2}\frac{\alpha_1\alpha_2}{r^6}\left(\frac{\quad}{h\nu_{01} + h\nu_{02}}\right)$

$h \rightarrow$ planck const

$\nu_0 \rightarrow$ characteristic electronic freq of molecule

in unexcited state

$I_1 \rightarrow$ energy required for $M \rightarrow M^+ + e^-$

$\left.\begin{array}{l} D-D \\ D-Ind. \\ -Dispersion \end{array}\right\}$ van der waals interaction

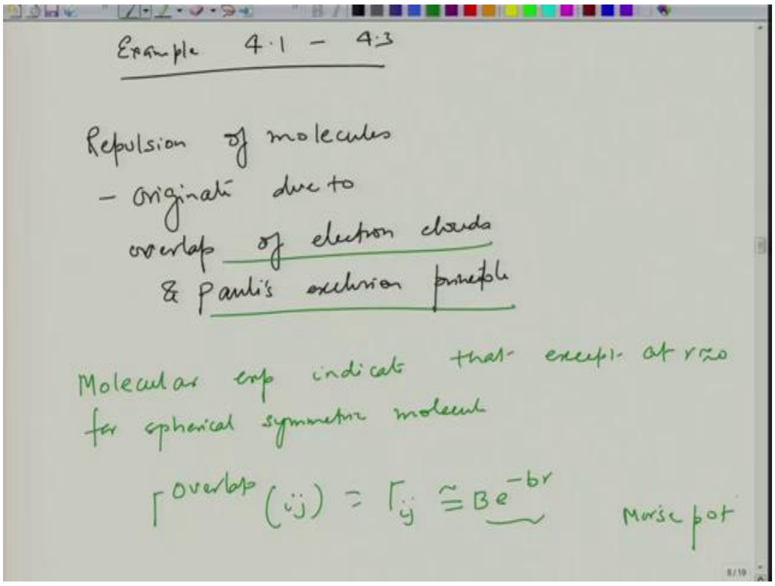
$\Gamma_{ij} = -\frac{C_6}{r^6}$ $C_6 \propto$ strength of attractive forces

Example 4.1 - 4.3

$$\overline{\Gamma_{ij}} = -\frac{C_6}{r_6} \propto \textit{strength of attractive forces}$$

So, this is what we last we talk about that non polar molecules may have momentarily a dipole moment which can induced a dipole moment in a molecular tube and leading to something called London forces interactions and effectively all these interactions which we talked about where in the point charge once they follow this dependency that interactions are proportional to minus 1 by R6. So, this includes the dipole-dipole, dipole induced and dispersion, ok.

(Refer Slide Time: 1:20)



Example 4.1 – 4.3

Repulsion of molecules
– originate due to
overlap of electron clouds
& Pauli's exclusion principle

Molecular exp indicate that except at $r \approx 0$
for spherical symmetric molecule

$\Gamma^{overlap}(ij) = \Gamma_{ij} \cong Be^{-br}$ Morse pot

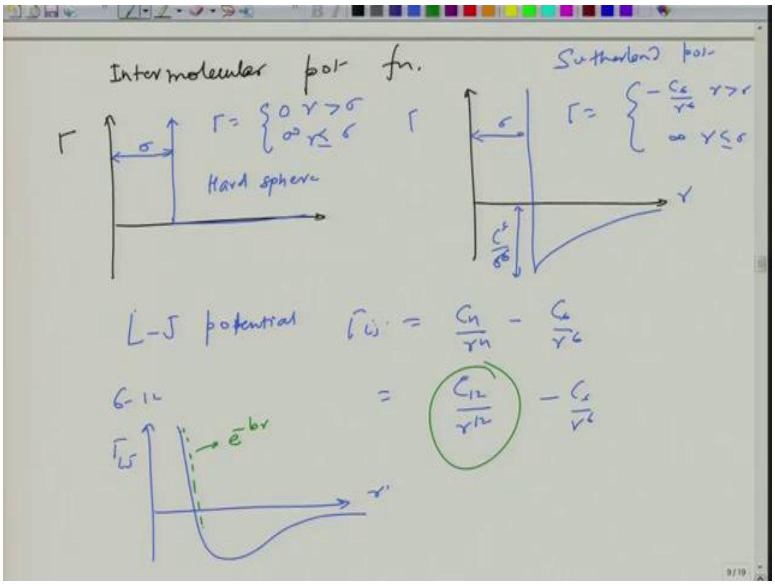
8/19

$$\Gamma_{ij}^{overlap} = Be^{-br} \quad \textit{Morse Plot}$$

But what about the repulsion, ok. So, with this is all attractive in nature. But of course there is a repulsion in molecule which originate due to the overlap of an electronic cloud principle, ok. So, this is basically this two practically this is the major reason for having an repulsion and in fact molecular beam experiments suggest a kind of an expression analytical expression for such repulsive force .

So, molecular experiment indicate that except at R almost equal to 0 for spherical symmetrical molecule Gamma overlap can be written as minus of a br overlap i and j or we can say Gamma ij can be approximated as e to the power minus br and some constant. So, this is this kind of potential model is also is something we should called sometimes Morse potential, ok. Now, combining this repulsive and attractive term we can come up with a intermolecular potential which can be of many times, we already discussed some aspects of that but let me just write down formulae, some popular potential models, ok.

(Refer Slide Time: 03:37)



$$\Gamma_{ij} = \frac{C_4}{r^4} - \frac{C_6}{r^6} = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6}$$

So, one is the hard sphere like this, distance is Sigma which could be the size of molecule, ok. So, potential module is the following is 0 when r is greater than Sigma ok and which essentially means that the distance between the particles are more than the size of the molecule and infinity which is less than when r is less than sigma, ok.

So, this is more like a kind of a billet ball kind of a concept here that as soon as the particles touch they have infinite repulsion and hence it cannot penetrate and otherwise there is not attraction, ok. So, this is a hard sphere model very popular in early days which is acted as reference for many systems then one can come up with a expression of a attractive forces and modify this intermolecular potential by considering something like this where still as a shock repulsion but then there is a attraction as well, ok.

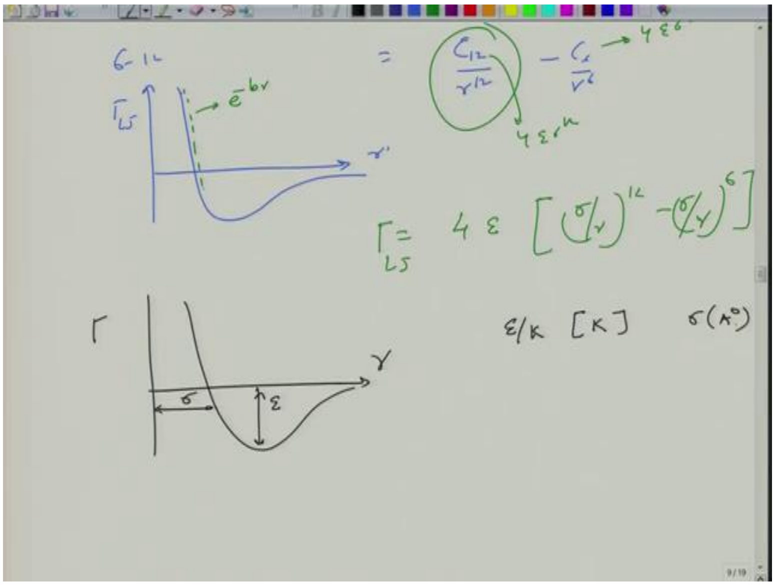
So, this is something which is called Sutherland potential, ok. Where you have the following for r greater than Sigma and of course infinity for r less than equal to Sigma, ok. So, this is the potential well ok which is nothing but c6 by r6, ok. And in this case since in this case r would be Sigma so this would be Sigma by 6. So, that is a maximum value it is, ok.

But this not of course a useful in analytical expressions for when you come up with the thermodynamic functions and so forth. But one can come up with a general expression which a called Lennard Jones kind of potential, ok. Well you can have repulsive part instead of using exponential ok, and can be written as this here cn, rn and then we have c6 r6.

Now, normal 6 -12 potential would be here to be c12 by r 12 minus c6 r6, right. And potential module may look like graphically look like this where it is something like here, ok. This particular repulsive one if you plot also along with this exponential then some exponential then this is very close to what seen in the molecular beam experiment, ok.

So, that is why this analytical you know the kind of expression which is very close to the molecular beam experiment leading to that Morse potential kind of a repulsive force or repulsive attraction is something which we can use because this way analytically this because much easier formulation which is useful theoretically to solve many other problems. So, this is one of the reasons why this become very very popular expression.

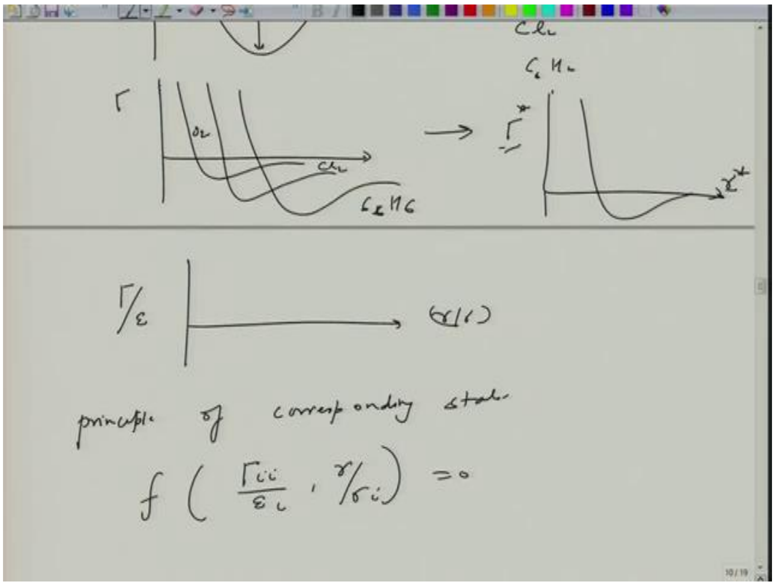
(Refer Slide Time: 07:32)



$$\Gamma_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

In fact one can write more in detail this Lennard-Jones potential by writing it like 4 epsilon Sigma by r to the 12 minus Sigma by r to the 6, ok. Here, of course c6 is 4 epsilon sigma 6 c12 is 4 epsilon sigma 12. So, this becomes a typical Lennard Jones potential 6-12 potential which can be written in this form. Now, one can plot this also and if you plot this ok, this would be your epsilon this would be your sigma, ok. Usually when you look at the data of Lennard-Jones of course many systems can be model here mostly gases and simple systems the usual data are be something like epsilon this is scaled by Boltzmann constant and this would be in the Kelvin unit as sigma are in the unit of A square.

(Refer Slide Time: 8:38)



So, now we try to look at what happens when you consider different system. Consider let say take for an example, if you change molecules let say cl2 o2 and c6h6 how does the Lennard-Jones potential looks like for all three different molecules here and the way it looks like is following this would be let say for o2 this is for cl2 and this is for c6h6, this is for cl2 this is for o2, ok.

Now, how do we generalize our treatment of intermolecular interaction that lead to let us say non idea behavior. But, one of the thing which we can do is of course we can if we try to scale this, ok in a way that this is reduced by epsilon and by kt this can be reduced by epsilon and essentially this can be reduced by sigma, then essentially what we can do is we can try to get very generic reduced property where all three of this curve may get to just one single value with a reduced let us say potential energy and distance here.

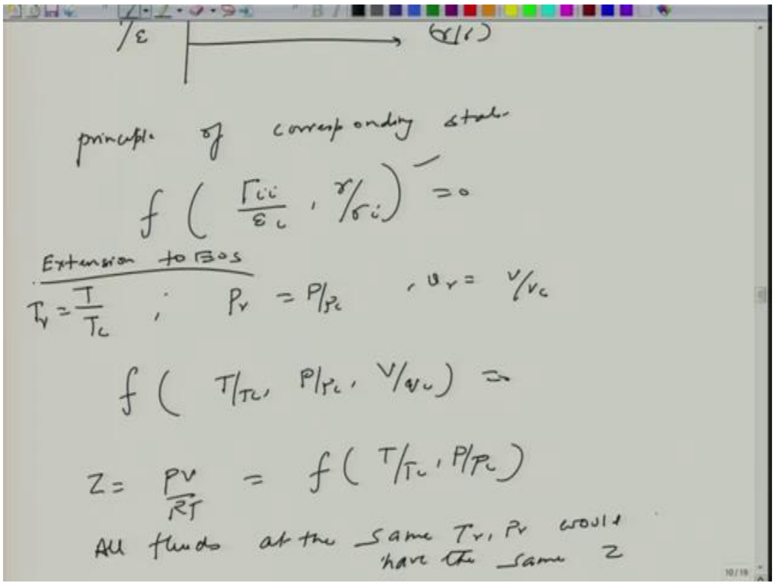
So, this is something which we can do as far as the reductions are concern ok, and this is also the curve something which will lead to something called principle of corresponding state. So, it tells you that if you reduced this potential energy appropriately then it leads to universal curve or universal expression for all molecules, ok. So, dimensionless potential energy apparently here can be applied to any species. Now, from here if you can plug in back sigma and epsilon for specific molecule you should be able to obtained the potential energy of that specific molecule.

So, this gives you a function of some quantity function of this cross-bedding state principle here which is something like this. So, this way we can obtain something like this kind of graph.

Now, we can extend the principle of cross bedding state to microscopic thermodynamic property so just like for example equation of state where we have tried we can apply equations on other by scaling it into right kind of a properties.

So, critical properties one of those which can allow us to reduce the thermodynamic property and since it the critical point is something which is very unique where the behaviors of the systems are almost similar ok, and is an unique state for given intermolecular potential and hence can be used in order to scale the variables which we are interested in.

(Refer Slide Time: 11:50)



/ε → (r/σ)

principle of corresponding state

$f\left(\frac{\Gamma_{ii}}{\varepsilon_i}, r/\sigma_i\right) = 0$

Extension to EoS

$T_r = \frac{T}{T_c}$; $P_r = P/P_c$, $v_r = V/V_c$

$f\left(T/T_c, P/P_c, V/V_c\right) =$

$Z = \frac{PV}{RT} = f\left(T/T_c, P/P_c\right)$

All fluids at the same T_r, P_r would have the same Z

10/19

$$f\left(\frac{\Gamma_{ij}}{\epsilon_i}, \frac{r}{\sigma_i}\right) = 0$$

$$Extension\ to\ equation\ of\ state:$$

$$T_r = \frac{T}{T_c};\ P_r = \frac{P}{P_c};\ V_r = \frac{V}{V_c}$$

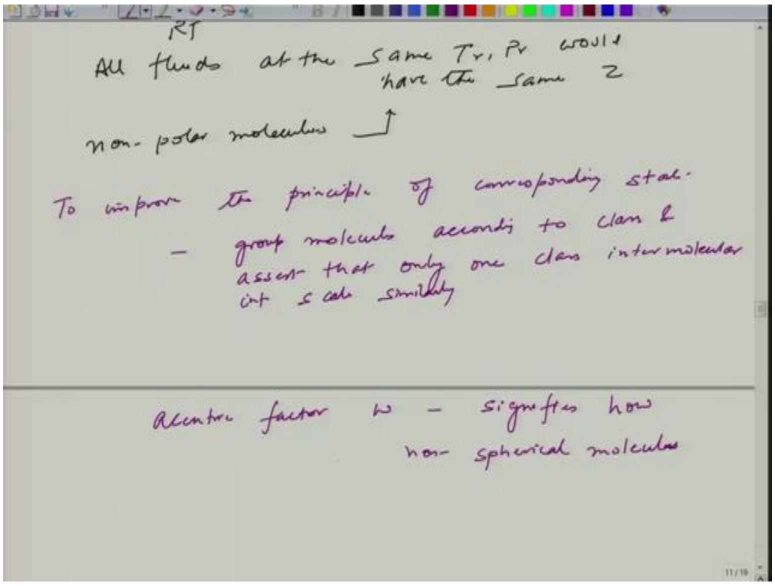
$$f\left(\frac{T}{T_c}, \frac{P}{P_c}, \frac{V}{V_c}\right) = 0$$

$$z = \frac{PV}{RT} = f\left(\frac{T}{T_c}, \frac{P}{P_c}\right)$$

So, if you reduce for example temperature by tc we can call it like tr, ok. And similarly pr would be p by pc and vr would be v by vc. So, that is a case I can now write just like an any so instead of saying intermolecular potential I am trying to now extend this two equations of state and then in that case I can write this as t by tc p by pc and v by vc, ok.

So, similarly we can try to have a or we can also consider different approach we can also try to generalize it in this way, we can consider it as a pv by rt which is non dimensional parameter. And then we consider this f function f t by tc p by pc. So, this will tell you that all the fluid at same tr and pr would have the same z we will have the same z, ok.

(Refer Slide Time: 13:09)



RT

All fluids at the same T_r, P_r would have the same Z

non-polar molecules

To improve the principle of corresponding state.

- group molecules according to class & assert that only one class intermolecular int scale similarly

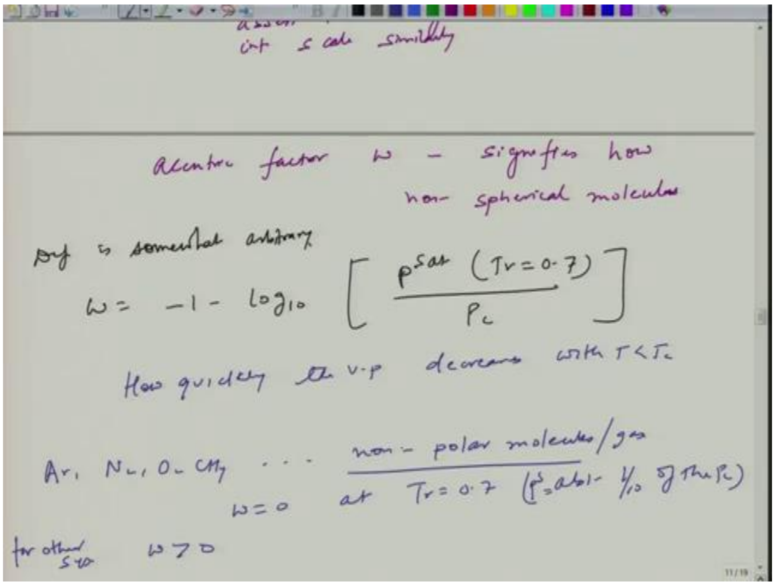
Acentric factor ω - signifies how non-spherical molecules

Now, this is for the case of a non polar molecule, ok. So, this was for non polar molecule, what about the polar molecules. Now, polar molecules due to the strong dipolar interactions would be here differently from non polar molecule. So, it will not only depends on the simple tr pr if you want to come up with the generalize equation of state or generalize behavior we have to also consider some kind of asperity some kind of non polar popularizibility of polar nature of molecule, ok.

So, to improve the principle of state corresponding state, it would be better if we can group molecules according to the class and assert that only one class intermolecular scale differ similarly. So, essentially the idea is that if we can group molecules according to class. So, if it is a polar you separate part if it is a non polar you separate part if it is of same size you separate it if it is you know same size can be consider as a one group, ok.

And I assert that only one class of intermolecular interaction scale similarly. So, scaling would be done for a group of a molecule having similar nature of interaction. So, thus in order to have different you know kind of non-spherical molecules, we need to introduced a different factor, where eccentric factor omega was introduced ok, which signifies how non spherical the molecule is so, it is kind of a more it is not exactly straight because it also capture the polar nature of it, ok. So, it is kind of arbitrary, ok.

(Refer Slide Time: 15:43)



int s cale similarity

acentric factor ω – signifies how non-spherical molecules

Def is somewhat arbitrary

$\omega = -1 - \log_{10}\left[\frac{P^{sat}(T_r = 0.7)}{P_c}\right]$

How quickly the v.p decreases with $T < T_c$

Ar, N_2, O_2, CH_4 . . . non-polar molecules/gas

$\omega = 0$ at $T_r = 0.7$ (P^s = about 1/10 of the P_c)

for other sys $\omega > 0$

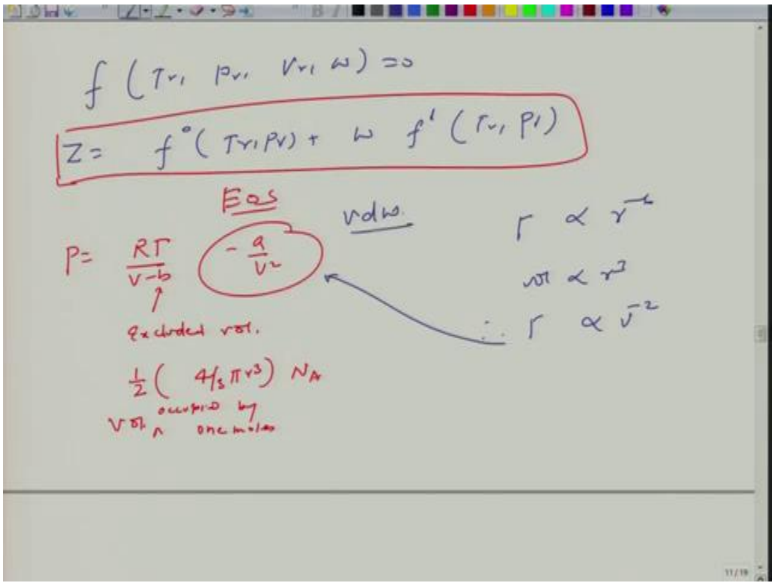
11/19

$$\omega = -1 - \log_{10}\left[\frac{P^{sat}(Tr = 0.7)}{P_c}\right]$$

So, the definition is omega is minus 1 minus log of tan, base tan p sat at tr is equal to 0.7 ok and pc, ok. So, as I said definition is somewhat arbitrary. So, if we look at this expression it tells you how quickly the vapor pressure decreases with t less than tc, ok. So, it is very loosely connected as far as the non-spherical nature is concern.

So, based on the observation if we look at the origin of the expression it turns out that the it is meant for the non-polar common gases such that at tr is equal to 0.7, ok. The value the vapor pressure is about 1 10 th of the pc. That means the Ar argon nitrogen oxygen and CH4 kind of non-polar molecules or gases, ok. We will have omega is equal to 0 at tr is equal to 0.7 because this is about 1 10 th of the pc, ok. So, based on this these was taken as a reference, ok. That this is p sat is nothing but 1 10 th of pc at tr is equal to 0.7 for non polar gases, ok. And thus for other system we expect w to be greater than 0 for other system.

(Refer Slide Time: 17:43)



$f(T_r, P_r, V_r, \omega) = 0$

$\boxed{Z = f^0(T_r, P_r) + \omega f^1(T_r, P_r)}$

EoS

vdw.

$P = \frac{RT}{V-b} - \frac{a}{V^2}$

excluded vol.

$\frac{1}{2}\left(4/3 \pi r^3\right) N_A$

vol occupied by one molec

$\Gamma \propto r^{-6}$

$v \propto r^3$

$\therefore \Gamma \propto v^{-2}$

So, now coming back further to get the generalize microscopic equation which would be now f as a function of tr pr vr and omega, ok. Or often we can write z as a two part now, f not function of tr pr and then we have this w factor which will now have some other function f1 which is a function of only pr and tr but w is now inserted to provide this non spherical nature of the molecule, ok.

$$f(T_r, P_r, V_r, \omega) = 0$$

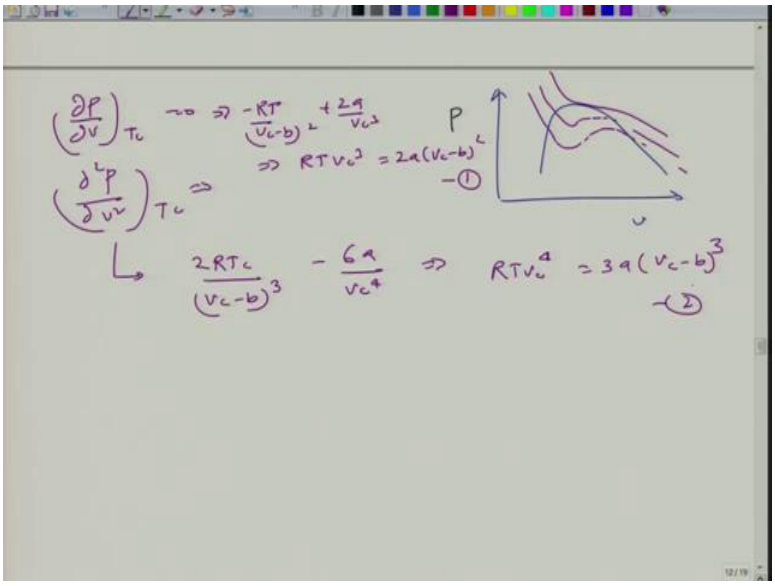
$$z = f^0(T_r, P_r) + \omega f^1(T_r, P_r)$$

So, let us now look at a generic van der waal equation first and then subsequently we will try to summarize some other equation of state. So, now we just concluded this corresponding statement basically z can be now segregated in two parts, one with basically non polar nature and because of the non-spherical nature of the molecules. So, this z and this function is usually drawn in a compressibility charge something which we will look at in a next lecture. But here let us go back again to the basic equation of a state which is your van der waal equation of state where this is the equation, right.

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

If we look at this part only this is nothing but a excluded volume, right where it is written as half 4 by 3 pie r cube times the number of moles and this comes directly from the basic geometry of the molecule which is nothing but the volume of volume occupied by one mole of molecule. Now, as far as this is concern this comes from our understanding of the intermolecular interactions where we say that gamma is proportional to minus r6. And now, we can convert this thing in the volume because volume is proportional to r to the power 3 that means gamma is proportional to v to the power minus 2 and that is where it comes here and this has to be negative and hence this is added here. So, with this now equation this was first of course given by Wander walls.

(Refer Slide Time: 20:17)

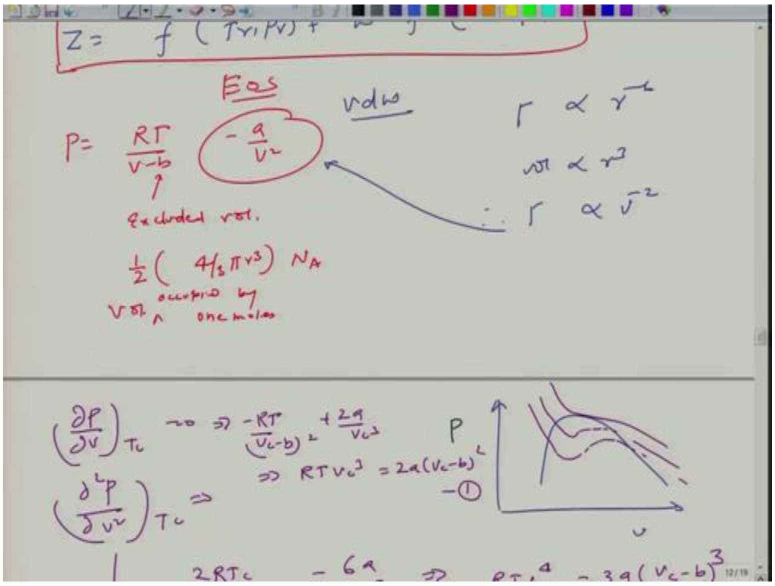


$\left(\frac{\partial P}{\partial v}\right)_{T_c} \to 0 \Rightarrow -\frac{RT}{(v_c-b)^2} + \frac{2a}{v_c^3}$

$\Rightarrow RTv_c^3 = 2a(v_c-b)^2$ —①

$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} \Rightarrow$

$\frac{2RT_c}{(v_c-b)^3} - \frac{6a}{v_c^4} \Rightarrow RTv_c^4 = 3a(v_c-b)^3$ —②



$Z = f(T_r, P_r) + \ldots$

EoS

vdw

$P = \frac{RT}{v-b} - \frac{a}{v^2}$

Excluded vol.

$\frac{1}{2}\left(4/3 \pi r^3\right) N_A$

vol. occupied by one molec

$\Gamma \propto r^{-6}$

$vol \propto r^3$

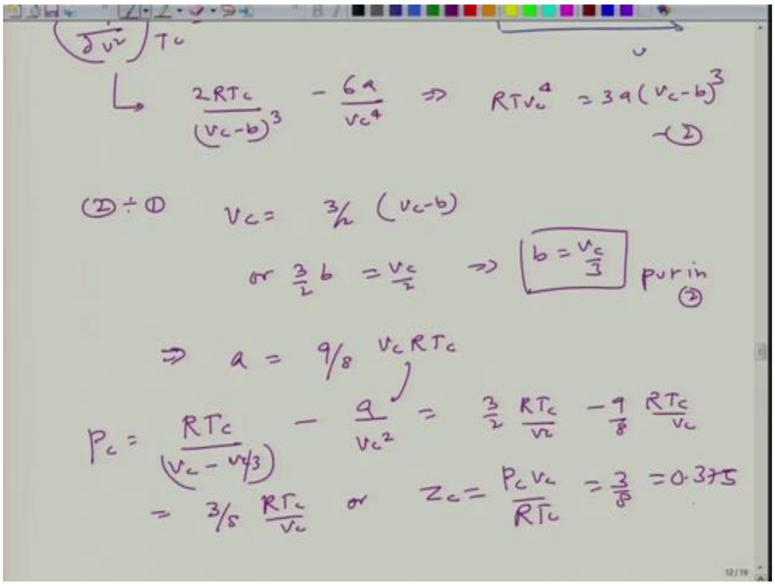
$\therefore \Gamma \propto v^{-2}$

$\left(\frac{\partial P}{\partial v}\right)_{T_c} \to 0 \Rightarrow -\frac{RT}{(v_c-b)^2} + \frac{2a}{v_c^3}$

$\Rightarrow RTv_c^3 = 2a(v_c-b)^2$ —①

$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} \Rightarrow$

(Refer Slide Time: 21:55)



$\partial v^2)_{T_c}$

$\hookrightarrow \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} \Rightarrow RTV_c^4 = 3a(V_c-b)^3$ — ②

② ÷ ① $V_c = \frac{3}{2}(V_c-b)$

or $\frac{3}{2}b = \frac{V_c}{2} \Rightarrow \boxed{b = \frac{V_c}{3}}$ put in ②

$\Rightarrow a = 9/8\ V_c R T_c$

$P_c = \frac{RT_c}{(V_c - V_c/3)} - \frac{a}{V_c^2} = \frac{3}{2}\frac{RT_c}{V_c} - \frac{9}{8}\frac{RT_c}{V_c}$

$= 3/8\ \frac{RT_c}{V_c}$ or $Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8} = 0.375$

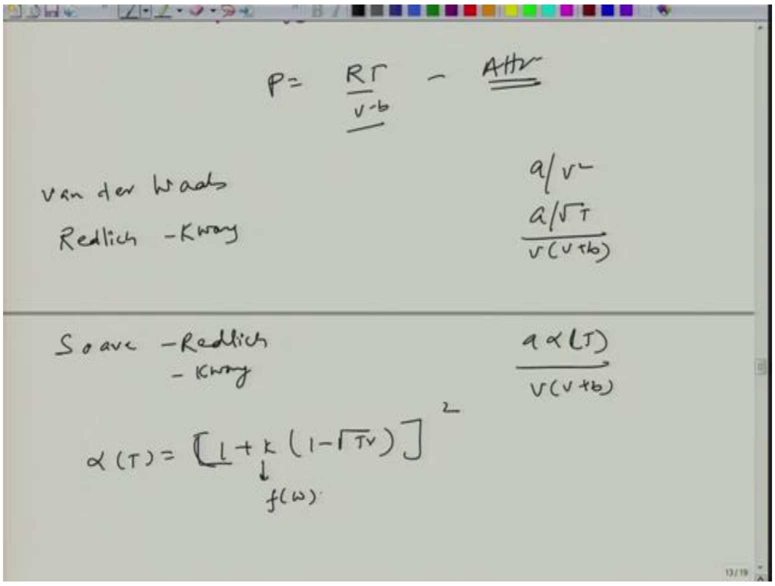
$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \ \ or, -\frac{RT}{(V_c-b)^2} + \frac{2a}{V_c^3} = 0 \ \ or, \ \ RTV_c^3 = 2a(V_c-b)^2$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \ \ or, \ \ \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0 \ \ or, \qquad RTV_c^4 = 3a(V_C-b)^3$$

$$V_c = \frac{3}{2}(V_c-b) \ \ or, \qquad b = \frac{V_C}{3} \quad or, \qquad a = (9/8)\ \ RT_cV_c$$

$$P_c = \frac{3}{8}\left(\frac{RT_c}{V_c}\right) \quad or, \qquad Z_c = \frac{P_cV_c}{RT_c} = \frac{3}{8} = 0.375$$

(Refer Slide Time: 23.31)



$$P = \frac{RT}{V-b} - \text{Attr}$$

Van der Waals a/V^2

Redlich - Kwong $\frac{a/\sqrt{T}}{V(V+b)}$

Soave - Redlich - Kwong $\frac{a\alpha(T)}{V(V+b)}$

$$\alpha(T) = [1 + \underset{\substack{\downarrow \\ f(\omega)}}{k}(1-\sqrt{Tr})]^2$$

$$Van\ der\ Waals: \ \frac{a}{V^2}$$

$$Redlich - Kwong: \ \frac{\frac{a}{\sqrt{T}}}{V(V+b)}$$

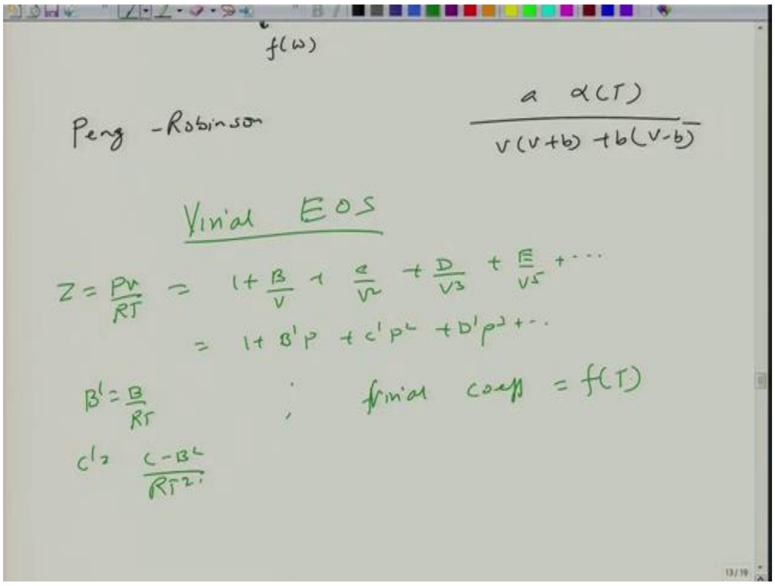
$$Soave - Redlich - Kwong: \ \frac{a\alpha(T)}{V(V+b)}$$

$$\alpha(T) = \left[1 + k\left(1 - \sqrt{Tr}\right)\right]^2 \quad k = f(\omega)$$

So, let me summarize the kind of a different attractive groups or terms which we get. So, most of the cases you will see the equation of state having the repulsive part in this following way or most of the cases you will find this ideal gas modified this exclusive volume will be in this way and then you have this attractive terms, ok.

So, this term keeps changing for various different equations of state for the case of the wander wall if we know this a by v square. Now, for the case of Redlich Kwong is modified bit here, ok. And this is added here and this all cubic equation of state by the way and the other one is Soave Redlich Kwong which is a alpha which is function of t v v plus b alright. Where alpha T is something like 1 plus K times 1 by under root square Tr square. Where k it is a function of omega, ok.

(Refer Slide Time: 25:02)



$f(\omega)$

Peng -Robinson $\frac{a\,\alpha(T)}{v(v+b)+b(v-b)}$

Virial EOS

$Z = \frac{Pv}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \frac{E}{V^5} + \cdots$

$= 1 + B'P + C'P^2 + D'P^3 + \cdots$

$B' = \frac{B}{RT}$; Virial coeff $= f(T)$

$C' = \frac{C-B^2}{RT^2}$

$$z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \frac{E}{V^5} + \cdots \quad = \quad 1 + B'P + C'P^2 + D'P^3 + \cdots$$

$$B' = \frac{B}{RT} \quad C' = \frac{C - B^2}{RT^2}$$

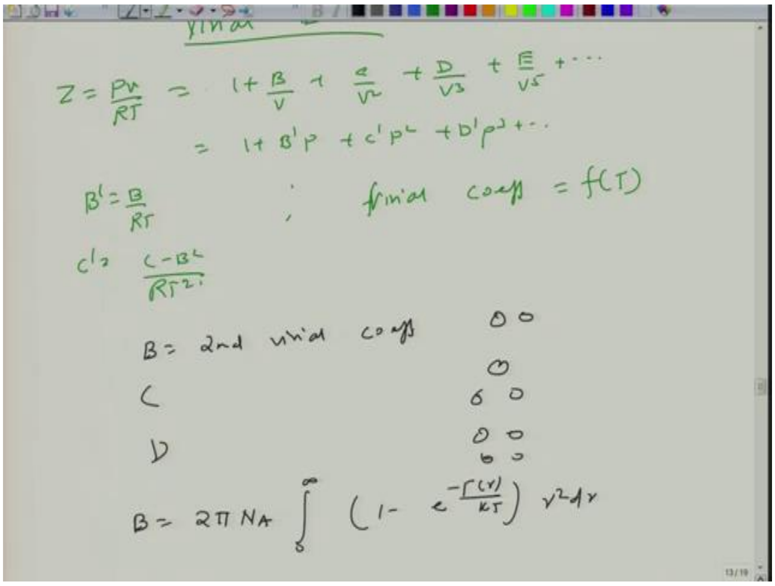
So, something which is available in the text book when you look at the details and the last one which is also popular is Peng Robinson. But this is more complicated. But these are all cubic equations of state, ok. So, something which one can use it and Peng Robinson is one of the most popular now which can be used for many systems and can be applied for real and practical situations as well where the complicated molecules are used, ok.

$$Peng - Robinson: \quad \frac{a\alpha(T)}{V(V+b) + b(V-b)}$$

So, before closing what we can do is we can also look at one another popular equation of state which has statistical mechanics origin. And this is something called Virial equation of state. So, as I said this originates from the statistical mechanics and hence this is an exact kind of expression, ok. Or this can be written as 1 by b dash p plus c dash p square D dash p cube and so for, ok.

So, one is as a volumetric form as well as in pressure form in fact this are related B dash is B by Rt C dash is C minus b square by Rt square. Now, in this case B, C, D, E these are called Virial coefficients and these are only function of, Virial coefficients are only function of temperature, ok. So, they only function of temperature. And it has some meaning and it is molecular in nature.

(Refer Slide Time: 27:13)



Virial

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \frac{E}{V^5} + \cdots$$

$$= 1 + B'P + C'P^2 + D'P^3 + \cdots$$

$B' = \frac{B}{RT}$; Virial coeff $= f(T)$

$C' = \frac{C - B^2}{RT^2}$

B = 2nd virial coeff

C

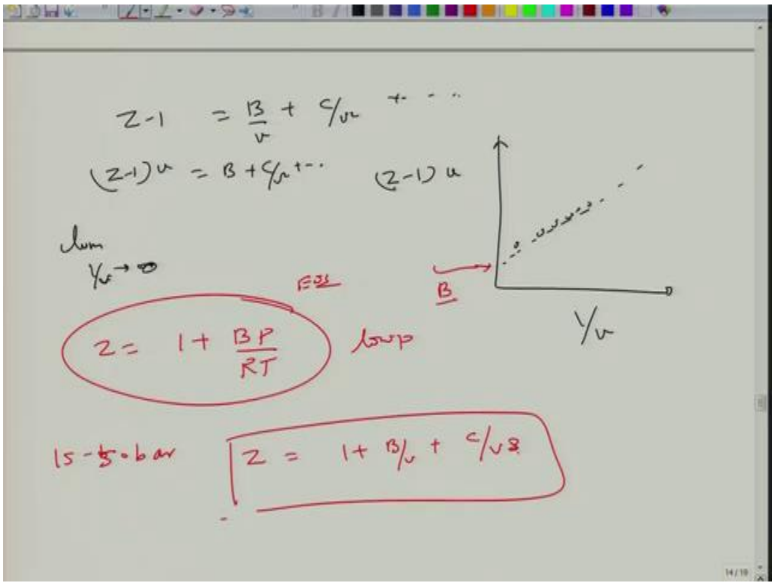
D

$$B = 2\pi N_A \int_0^\infty \left(1 - e^{-\frac{\Gamma(r)}{kT}}\right) r^2 dr$$

So, B for example is called 2nd Virial coefficient. So, it is something that this B represent the contribution of 2 particles, C is the contribution of 3 particles it like a contribution when they come closer and D would be contribution of 4 particles and so forth. Typical expression for B which comes directly from statistical mechanics and hence it is absolutely correct. 2 Pi NA 0 to infinity 1 minus e to the power minus potential energy by KT r square dr, ok. So, this is something which is an expression so essentially if you want find out what is a 2nd real coefficient for hard sphere or Lennard Jones we have to plug in the potential energy and obtain this integral, ok.

Now, you may ask like how do you calculate these coefficients from the experiment. Now, for that we can just consider one of the examples here, let us say this is Z ok.

(Refer Slide Time: 28.23)



$$Z-1=\frac{B}{V}+\frac{C}{V^2}+\cdots$$

$$(Z-1)V=B+\frac{C}{V}+\cdots$$

$$Z=1+\frac{BP}{RT}$$

$$Z=1+\frac{B}{V}+\frac{C}{V^2}$$

And this I can write this again what I can do is I can take one hale and I can write this as z minus 1 is B by v plus c by v square and so forth, right. And if I plot the z minus 1 v here then this is going to be B plus cv square and so forth. So, if I plot z minus 1 v as a functional v then at v limits of 1 by v goes to 0, when v is infinity that means extremely large volume or very less dense system, then this essentially I can find out the data and I can take this slope and this particular slope would give us 2nd Virial coefficient. And similarly, of course I can try to take it B other side and find out C also but, usually a this becomes much more easier particularly for 2nd Virial coefficient.

So, for the case if a low pressure which would be the case here, I can consider z I can trunked it and I can consider only the 2nd Virial coefficient, ok. But, for little bit higher pressure so this would be low pressure for little bit higher pressure let us say 15 to 50 bar, we may have to consider the 3rd viral coefficient also, ok.

So, this is a common equation of state for low pressure considerations, ok. So, I think with this a what we can do is we can stop here and we will take this understanding particularly try to do some problem solving sessions for the calculations of a viral coefficients and as well as will be making use of compressibility chart which I talked about where we will see how to make use of that to obtain a properties and compare that with equation of state so that understanding will be try to understand that particularly using example in the next lecture.

So, that would be, this would be end of the today lecture I will see you in the next lecture.