Advanced Thermodynamics
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Lecture – 8
Intermolecular Forces – Potential Energy Functions

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is Intermolecular forces and potential energy functions. We have been discussing several kinds of intermolecular forces which may induce some kind of non-ideality in the system, right? So, since it is a continuation of previous lecture, we will be having a kind of a recapitulation of what we have seen in previous lecture.

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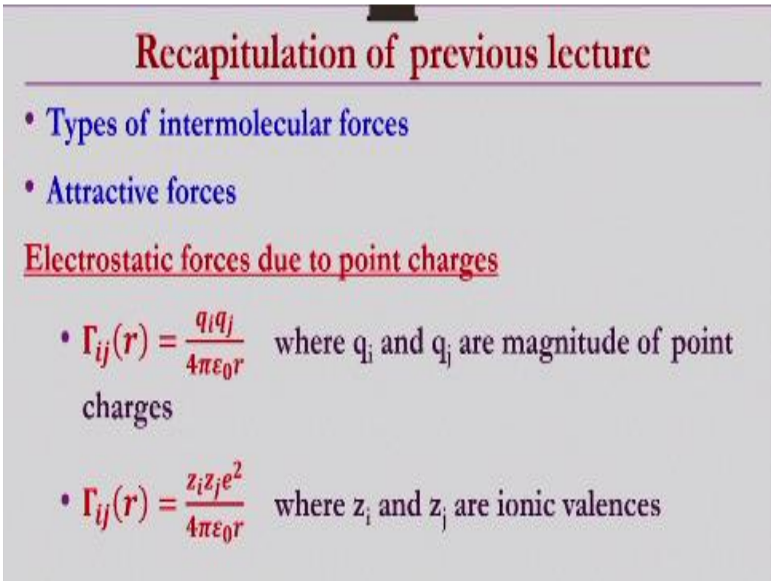

Recapitulation of previous lecture

- Types of intermolecular forces
- Attractive forces

Electrostatic forces due to point charges

- $\Gamma_{ij}(r) = \frac{q_i q_j}{4\pi\varepsilon_0 r}$ where q_i and q_j are magnitude of point charges
- $\Gamma_{ij}(r) = \frac{z_i z_j e^2}{4\pi\varepsilon_0 r}$ where z_i and z_j are ionic valences

In the previous lecture, we have seen different types of intermolecular forces out of which you know we started with discussing about the attractive forces because attractive forces are kind of long range forces compared to the repulsive forces. Under the attractive forces we have seen 2 different types of attractive forces, one is the electrostatic forces due to point charges, where we have seen the intermolecular potential Γ_{ij} is function of r and it is given us $\frac{q_i q_j}{4\pi\epsilon_\circ r}$, where r is the separation distance between 2 point charges q_i, q_j.

The q_i, q_j are the magnitudes of these 2 point charges between which we are trying to find out the attractive forces between these 2. So, this one we have already seen. Let us say if you have ionic molecules, then Γ_{ij} is function of r and then it is given as $\frac{q_i q_j}{4\pi\epsilon_{\circ} r^2}$, where z_i and z_j are nothing but ionic valances, right?

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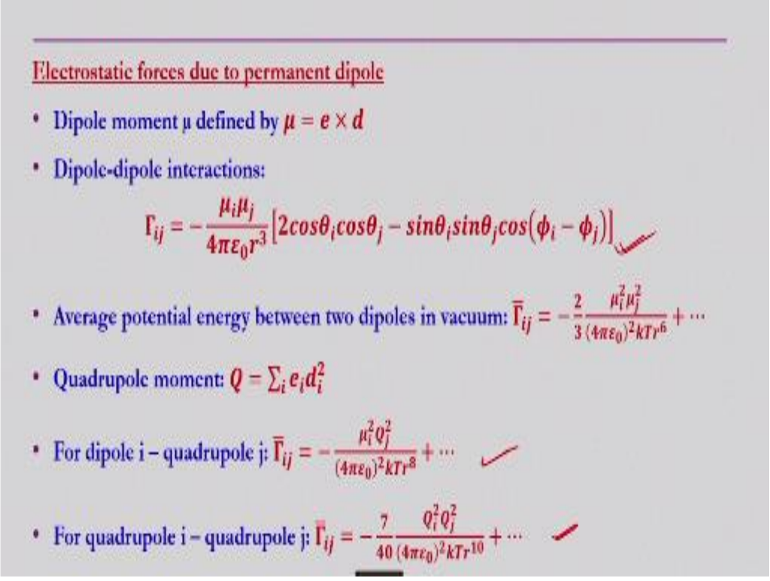

Electrostatic forces due to permanent dipole

- Dipole moment μ defined by $\mu = e \times d$
- Dipole-dipole interactions:

$$\Gamma_{ij} = -\frac{\mu_i \mu_j}{4\pi\varepsilon_0 r^3}\left[2cos\theta_i cos\theta_j - sin\theta_i sin\theta_j cos(\phi_i - \phi_j)\right]$$

- Average potential energy between two dipoles in vacuum: $\bar{\Gamma}_{ij} = -\frac{2}{3}\frac{\mu_i^2 \mu_j^2}{(4\pi\varepsilon_0)^2 kTr^6} + \cdots$
- Quadrupole moment: $Q = \sum_i e_i d_i^2$
- For dipole i – quadrupole j: $\bar{\Gamma}_{ij} = -\frac{\mu_i^2 Q_j^2}{(4\pi\varepsilon_0)^2 kTr^8} + \cdots$
- For quadrupole i – quadrupole j: $\bar{\Gamma}_{ij} = -\frac{7}{40}\frac{Q_i^2 Q_j^2}{(4\pi\varepsilon_0)^2 kTr^{10}} + \cdots$

Then we have also seen electrostatic forces due to permanent dipole. Dipole moment is nothing but μ = e * d, d is the separation distance between the 2 charges that is 1 + and 1 - charge if you take, the net charge is 0. They are separated by distance d. However, the electrons are shared between these 2 atoms where we have taken the charges unequally shared, so because of that kind of dipole moment is existing. The unit for dipole moment is nothing but Debye. So, there may be different dipoles.

There may be one dipole or between 2 point charges + -. There may be another dipole between another pair of + - charges. There may have a kind of dipole moment between 2 dipole moments, right? And then let us say separation distance under each condition is d_i, d_j and these 2 dipole moments are separated at a distance r. If r is larger than this d_i d_j, then these dipoles, 2 different type of dipoles, which may be orientating in different direction and then there may be a kind of interaction, right?

Those things we have seen and then under those conditions, the intermolecular potential Γ_{ij} is given by these things, right? So, there may be n number of orientations are possible. So, if you wanted to find out the overall average potential, so you have to do the averaging for all possible combinations of orientations and the separation distance and then we can find out average potential energy between 2 dipoles in vacuum as $\overline{\Gamma}_{ij}$ is given by this one, this is also we have seen.

So, like dipole moment is possible between 2 point charges of different opposite signs. Then similarly qudrupole moments also possible for 2 pairs of charges, like that is 4 different charges, 2 -, 2 +. Then net charge is again 0, but under such conditions also because of the imbalance or unequal sharing of the electrons, electronegative charges may be higher for one particular side compared to the other side, then because of that one again qudrupole moments are also possible.

If we have the qudrupole moments, then qudrupole moment that we have defined as $Q = \Sigma_i e_i\, d_i^2$ and then if you have 1 dipole and then 1 qudrupole, then average intermolecular potential that we have seen given by this equation. Likewise, if you have 2 qudrupoles, qudrupole i and qudrupole j and they are interacting amongst themselves, then we can have this $\overline{\Gamma}_{ij}$, given this equations. This is what we have seen in our previous lecture. Now, in this lecture what we do? We see the attraction forces because of the induction. So, that is induction forces.

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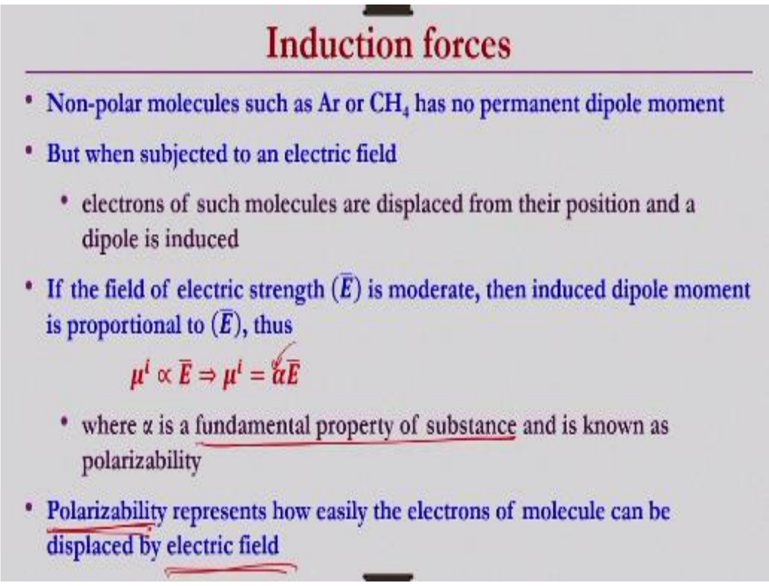

Induction forces

- Non-polar molecules such as Ar or CH_4 has no permanent dipole moment
- But when subjected to an electric field
    - electrons of such molecules are displaced from their position and a dipole is induced
- If the field of electric strength $(\bar{E})$ is moderate, then induced dipole moment is proportional to $(\bar{E})$, thus

$$\mu^i \propto \bar{E} \Rightarrow \mu^i = \alpha\bar{E}$$

    - where α is a fundamental property of substance and is known as polarizability
- Polarizability represents how easily the electrons of molecule can be displaced by electric field

Non-polar molecules such as argon or methane has no permanent dipole moment in general, but however, when an electric field is applied to them, then it is possible that they may also display a kind of a dipole moment that may not be permanent, okay? Because of this induction, because of applying this electric field, a kind of a dipole moment would be induced that is the reason these dipole moments are known as the induced dipole moments and they are not a permanent dipole moment, but when subjected to an electric field, electrons of such molecules are also displaced from their position and a dipole is induced.

This displace may be temporary or short range of kind of thing. If the electric field strength is moderate, then this dipole moment is proportional to whatever this dipole moment there that is the induced dipole moment is there because of subjecting to the electric field that induced a dipole moment is proportional to the electric field strength, provided electric field strength is moderate. Then μ_i, i stands for the dipole moment because of the induction or induced dipole moment is proportional to $\overline{E}$ or $\mu_i = \alpha \overline{E}$, α is nothing but polarizability.

Alpha is a proportionality constant and it is known as the polarizability, it is a fundamental property of the substance, okay? It one of the fundamental properties of the substance, okay? What is this polarizability means then? Polarizability represents how easily the electrons of molecule can be displaced by applying electric field. So, how easily the electrons of a molecule can be displaced by applying the electric field that is represented by the polarizability, and this polarizability is a fundamental property of the material or of a given substance.

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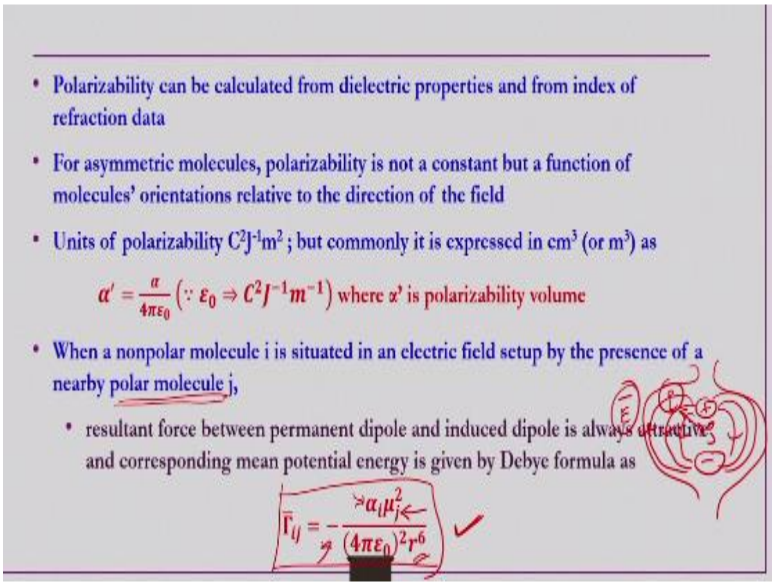

- Polarizability can be calculated from dielectric properties and from index of refraction data
- For asymmetric molecules, polarizability is not a constant but a function of molecules' orientations relative to the direction of the field
- Units of polarizability $C^2J^{-1}m^2$; but commonly it is expressed in cm^3 (or m^3) as

$$\alpha' = \frac{\alpha}{4\pi\varepsilon_0} (\because \varepsilon_0 \Rightarrow C^2J^{-1}m^{-1})$$ where α' is polarizability volume

- When a nonpolar molecule i is situated in an electric field setup by the presence of a nearby polar molecule j,
  - resultant force between permanent dipole and induced dipole is always attractive and corresponding mean potential energy is given by Debye formula as

$$\boxed{\overline{\Gamma}_{ij} = -\frac{\alpha_i \mu_j^2}{(4\pi\varepsilon_0)^2 r^6}} \checkmark$$

Polarizability can be calculated from dielectric properties and from indexation of refraction data. By experimental measurements, it is straightforward to get these calculations. For asymmetric molecules, polarizability is not a constant, but a function of molecules' orientation related to the direction of the field. In general, because of the asymmetric structure, it is possible that there may be a kind of permanent dipole moment as well. So that is the reason because of this symmetric molecules, the polarizability is not a constant, but a function of molecules orientation.

Because when there is a dipole moment, then orientations will come into the picture and then the orientation should also be taken into the consideration when we calculate these properties. Units of polarizability are Coulomb square joule inverse meter square, but commonly it is represented as volume units that is meter cube or centimeter cube because this alpha is represented as alpha prime in such a way that $\alpha' = \frac{\alpha}{4\pi\epsilon_\circ}$ and then this α' is known as the polarizability volume.

That is the reason in the results of this polarizability in general as a kind of presenting it as a kind of polarizability, it is presented as a kind of polarizability volume that is α'. When a non-polar molecule i is situated in an electric field set up by the presence of nearby polar molecule j, then also it is possible that some kind of induced dipole moment will take place for the non-polar molecule, okay? Let us say if you have a kind of + charge and then - charge, so then + to - these electric fields are being formed, something like this and this is what we have seen.

So, this is let us say a polar molecule j, okay? So, whatever the + - charges of this molecule if the sharing of electrons is not equal, then imbalance is there in sharing of valence electrons, then what happens, electric field is developed like this. So, if you assume there is a kind of a non-polar molecule i near to this polar j molecule, what happens? This polar molecule is having some electric field because of the imbalance sharing of electrons.

So, this electric field is affecting the or it is showing some kind of effect on this non-polar molecule or this nonpolar molecule is coming to a kind of electric field which is developed because of the polar molecules So, in general this electric strength of such polar molecules is very small compared to the external field that we apply, but this small electric strength also sufficient enough to induce some kind of a dipole moment in non-polar molecules, right?

So, in such cases also the resultant force between that i^{th} non-polar molecule and j^{th} polar molecule is attractive force and then corresponding mean potential energy is given by Debye formula. This is $\overline{\Gamma}_{ij} = \alpha_i$, α_i because of the polarizability of i^{th} molecule and non-polar i^{th} molecule, right? And then μ_j is nothing but the dipole moment of j^{th} polar molecule, okay?

Then the average potential between these 2 is given by this equation, $\bar{\Gamma}_{ij} = -\frac{\alpha_i \mu_j^2}{(4\pi\epsilon_\circ)^2 r^6}$ and then this - indicates the attractive force.

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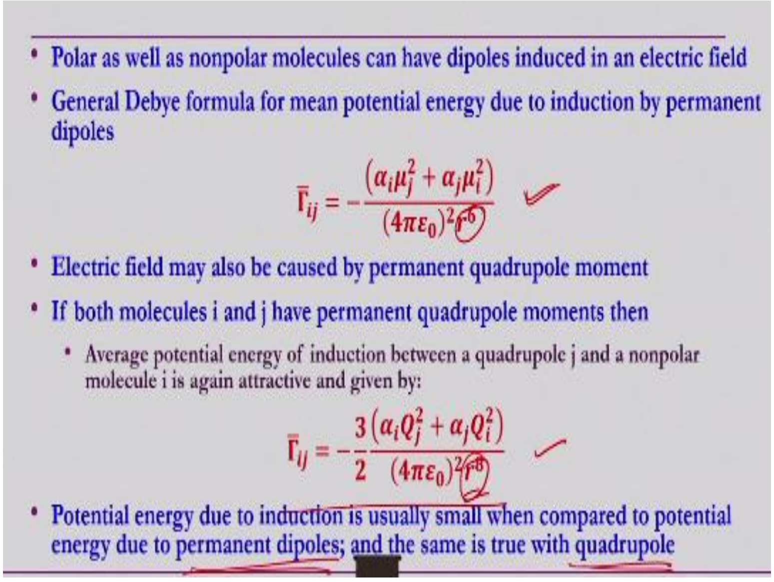

- Polar as well as nonpolar molecules can have dipoles induced in an electric field
- General Debye formula for mean potential energy due to induction by permanent dipoles

$$\bar{\Gamma}_{ij} = -\frac{\left(\alpha_i \mu_j^2 + \alpha_j \mu_i^2\right)}{(4\pi\varepsilon_0)^2 r^6} \checkmark$$

- Electric field may also be caused by permanent quadrupole moment
- If both molecules i and j have permanent quadrupole moments then
  - Average potential energy of induction between a quadrupole j and a nonpolar molecule i is again attractive and given by:

$$\bar{\Gamma}_{ij} = -\frac{3}{2}\frac{\left(\alpha_i Q_j^2 + \alpha_j Q_i^2\right)}{(4\pi\varepsilon_0)^2 r^8} \checkmark$$

- Potential energy due to induction is usually small when compared to potential energy due to permanent dipoles; and the same is true with quadrupole

So, polar as well as nonpolar molecules can have dipoles induced in an electric field or when these polar or non-polar molecules are brought into the contact with an external electric field, then kind of dipole moment may be induced for both the polar as well as non-polar molecules. Then under such conditions, general Debye formula for mean potential energy due to induction by permanent dipoles is given by this expression average intermolecular potential $\bar{\Gamma}_{ij}$ is given as $-\frac{\left(\alpha_i \mu_j^2 + \alpha_j \mu_i^2\right)}{(4\pi\epsilon_\circ)^2 r^6}$.

So, here again r power 6, what we have been seeing that in the previous lecture as well as this lecture this intermolecular potential is inversely proportional to separation distance or some power to the separation distance, okay? So, now here separation distance it is inversely proportional to the separation distance r power 6. Electric field may also be caused by permanent qudrupole moment as well, not only permanent dipole moment because of permanent qudrupole moment also an electric field may be developed.

If both molecules i and j have permanent qudrupole moments, then also it is possible to have a kind of electric field and because of that one also there will be kind of interaction between them and because of that interaction, there will be a kind of intermolecular potential and that intermolecular potential is again positive for this case also, okay? So, average potential energy of induction between a qudrupole j and non-polar molecule i is again attractive and given by this expression $\bar{\Gamma}_{ij} = -\frac{3}{2}\frac{\left(\alpha_i Q_j^2 + \alpha_j Q_i^2\right)}{\left(4\pi\epsilon_\circ\right)^2 r^8}$.

So, now here it is inversely proportional to r^8. So, potential energy due to induction is usually small when compared to the potential energy due to permanent dipoles and the same is true with the qudrupoles also. Whatever the induced dipole there because of the qudrupole moments that is also very small compared to the permanent qudrupole moments.

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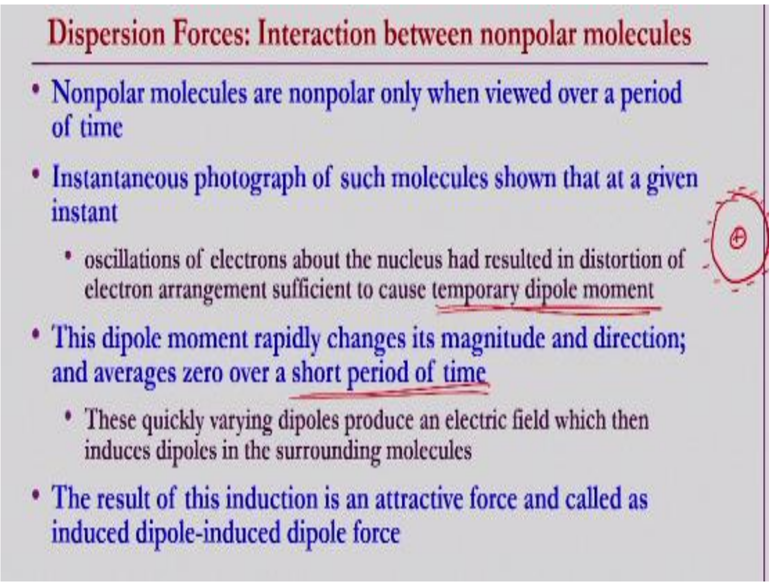

Dispersion Forces: Interaction between nonpolar molecules

- Nonpolar molecules are nonpolar only when viewed over a period of time
- Instantaneous photograph of such molecules shown that at a given instant
  - oscillations of electrons about the nucleus had resulted in distortion of electron arrangement sufficient to cause temporary dipole moment
- This dipole moment rapidly changes its magnitude and direction; and averages zero over a short period of time
  - These quickly varying dipoles produce an electric field which then induces dipoles in the surrounding molecules
- The result of this induction is an attractive force and called as induced dipole-induced dipole force

Now, we take dispersion forces or interaction between non-polar molecules. So, interaction between nonpolar molecules may also have some kind of intermolecular potential, right? And then those forces are also attractive forces and they are also known as the dispersion forces or London forces, right? So, whatever the nonpolar molecules are there, they are in general non-polar for a sufficiently large time of period, but instantaneously if one can observe the molecular structure of these molecules, then what one can see that the electrons are vibrating slowly, vibrating and then have some kind of motion kind of thing.

So, they are very quick and then of short range, but though they are quick, they are inducing some kind of interaction amongst the molecules. Non-polar molecules are non-polar only when viewed over a period of time. However, instantaneous photograph of such molecules shown that at a given instant, oscillations of electrons about the nucleus had resulted in distortion of electron arrangement and sufficient to cause temporary dipole moment. Here also some kind of temporary dipole moment happens. What happened?

We have a kind of positive nuclear and then surrounded by the electrons. These electrons, they keep oscillating, right? For a small time if you observe they are oscillating kind of things you can see. Because of that, oscillations of electrons about the nucleus results in some kind of distortion of electron arrangement. When these electrons are oscillating, whatever the electron arrangement is there that gets distorted and then because of that distortion a kind of temporary dipole moment is being induced in the case of non-polar molecules as well but they are only for a very short span of time, if you observe.

But if you see over a period of time, you do not find or whatever the oscillations are there they are balanced and then whatever the distortions are there, they may be seen as a kind of balanced and there may not be any kind of dipole moment. But however, this temporary dipole moment that caused because of the distortion of electron due to the oscillations of the electron, so this dipole moment rapidly changes its magnitude and direction as well and averages to 0 over a short period of time.

Instantaneously if you see, they may be changing their magnitude as well as the direction, okay? If they change the direction opposite keeping the same magnitude, then it averages to the 0. So, like that whatever the changes they cause in magnitude, whatever the changes occur in the magnitudes, and then whatever the directions they take, overall if you observe them in a short period of time, then what happens? It average to be 0, right? Instantaneously if you see, these are having some kind of temporary dipole moment and they are having some magnitude as well.

These quickly varying dipoles produce an electric field which then induces dipoles in the surrounding molecules. The result of this induction is again attractive force and called as induced dipole- induced dipole force.

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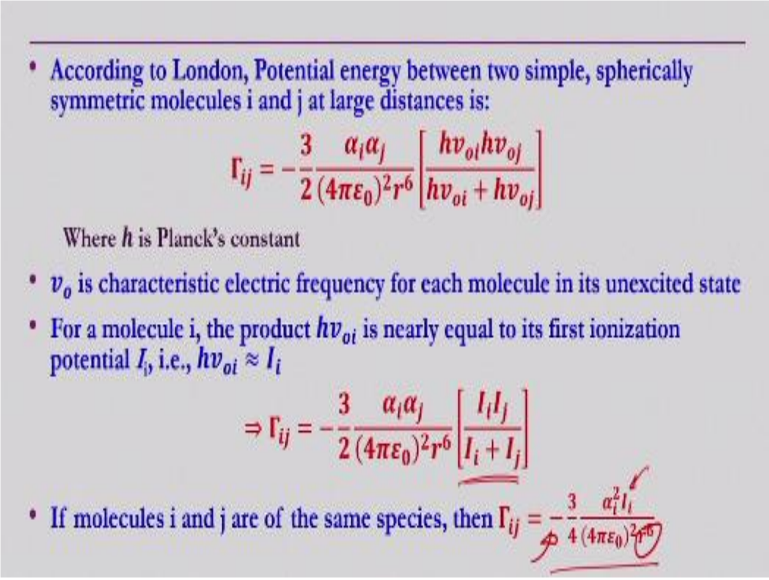

- According to London, Potential energy between two simple, spherically symmetric molecules i and j at large distances is:

$$\Gamma_{ij} = -\frac{3}{2}\frac{\alpha_i\alpha_j}{(4\pi\varepsilon_0)^2 r^6}\left[\frac{hv_{0i}hv_{0j}}{hv_{0i}+hv_{0j}}\right]$$

Where h is Planck's constant

- v_0 is characteristic electric frequency for each molecule in its unexcited state
- For a molecule i, the product hv_{0i} is nearly equal to its first ionization potential I_i, i.e., $hv_{0i} \approx I_i$

$$\Rightarrow \Gamma_{ij} = -\frac{3}{2}\frac{\alpha_i\alpha_j}{(4\pi\varepsilon_0)^2 r^6}\left[\frac{I_iI_j}{I_i+I_j}\right]$$

- If molecules i and j are of the same species, then $\Gamma_{ij} = -\frac{3}{4}\frac{\alpha_i^2 I_i}{(4\pi\varepsilon_0)^2 r^6}$

Now, according to London, the potential energy between 2 simple spherically symmetric molecules i and j at large distance is given by this, that is, $\Gamma_{ij} = -\frac{3}{2}\frac{\alpha_i\alpha_j}{(4\pi\epsilon_{\circ})^2 r^6}\left[\frac{h\vartheta_{0i}\,h\vartheta_{0j}}{h\vartheta_{0i}+h\vartheta_{0j}}\right]$, where h is nothing but the Planck's constant, ϑ_0 is nothing but characteristic electric frequency for each molecule in its unexcited state.

For a molecule i, the product whatever $h\vartheta_{0i}$ is there that is approximately equal to the first ionization potential that is I_i, I stands for the first ionization potential and then suffixed i is for the ith molecule. That means, $h\vartheta_{0i}$ is approximately I_i, I suffix i, that is the first ionization potential of molecule i. So, then this equation we can write it as $\Gamma_{ij} = -\frac{3}{2}\frac{\alpha_i\alpha_j}{(4\pi\epsilon_{\circ})^2 r^6}$ is same and then $h\vartheta_{0i}$ can be replaced by I_i, and then $h\vartheta_{0j}$ can be replaced by I_j.

Then we have I_i I_j divided by $I_i + I_j$. If molecules i and j are of the same species, then I_i should be equals to I_j and then we have I_i square by 2 I_i, so then I_i square by I_i is nothing but I_i and then these 2 and then 2 multiplied by 4 that is $-\frac{3}{4}$, $\alpha_i = \alpha_j$. So, $\frac{\alpha_i^2 I_i}{(4\pi\epsilon_{\circ})^2 r^6}$, again inversely proportional to r power 6, and then it is an attractive force and then the because of that one there is a -.

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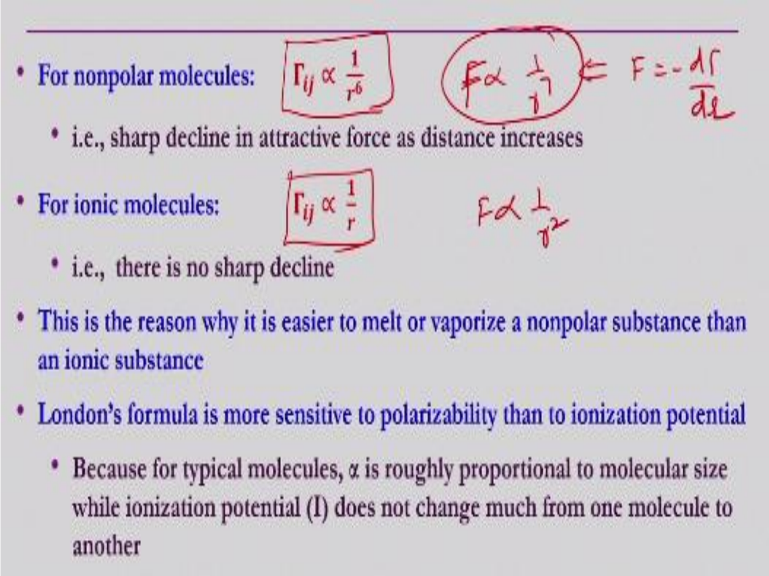

- For nonpolar molecules: $\boxed{\Gamma_{ij} \propto \frac{1}{r^6}}$ $F \propto \frac{1}{r^7}$ ⇐ $F = -\frac{d\Gamma}{dr}$
  - i.e., sharp decline in attractive force as distance increases
- For ionic molecules: $\boxed{\Gamma_{ij} \propto \frac{1}{r}}$ $F \propto \frac{1}{r^2}$
  - i.e., there is no sharp decline
- This is the reason why it is easier to melt or vaporize a nonpolar substance than an ionic substance
- London's formula is more sensitive to polarizability than to ionization potential
  - Because for typical molecules, α is roughly proportional to molecular size while ionization potential (I) does not change much from one molecule to another

So what we understand for non-polar molecules just now from the London's expression, we have seen $\Gamma_{ij} = -\frac{3}{4}\frac{\alpha_i^2 I_i}{(4\pi\epsilon_{\circ})^2 r^6}$ that is Γ_{ij} is inversely proportional to r^6. That means whatever the forces are there, they are rapidly decreasing, a sharp decline in attractive force as distance increases, $\frac{1}{r^6}$, so that is what does it mean by increasing distance, that is if r increases, that is r is the distance between 2 molecules.

So that if it increases, a small increase in r is going to reduce this attractive forces sharply, right? So, then force should be proportional to $\frac{1}{r^7}$ because F = - $\frac{d\Gamma}{dr}$. So, whatever the attractor force is there that is decreasing inversely and with the r^7 if r is increasing, okay? But in the case of ionic molecules in the previous lecture, we have seen that Γ_{ij} is inversely proportional to r. That means the decline is not very sharp and then F is proportional to $\frac{1}{r^2}$.

That is, this gamma indicates the intermolecular potential energy, F indicates the intermolecular force. So, now here that force is attractive force that attractive force in the case of ionic molecules is not decreasing very sharply. Whatever the attractive forces whichever molecules you take, the distance between the molecule increases, the attractive forces gradually decreases and then becomes 0 at very long distance, right? But the decrease is not very sharp in kind of ionic molecules.

Whereas in the case of non-polar molecules, it is very sharp and then this is the reason it is very easy to melt or vaporize the nonpolar molecules than the ionic molecules because in the case of ionic molecules, the attractive forces are strong and they are not decreasing rapidly with increasing the distance, okay? Whereas the non-polar molecules attractive forces are short range and then decreasing very sharply with the increasing the separation distance.

So, London's formula is more sensitive to polarizability than ionization potential. The same London's formula now for dispersion forces we can write in terms of polarizability as well as the ionization potential, but you know it is more sensitive to polarizability than to ionization potential because for typical molecules, this alpha is roughly proportional to molecular size while the ionization potential does not change much from one molecule to the other molecules. That is the reason this London's dispersion potential is more sensitive to the polarizability than the ionization potential because ionization potential is more or less same for different molecules, whereas alpha changes and then it depends on the molecular size as well.

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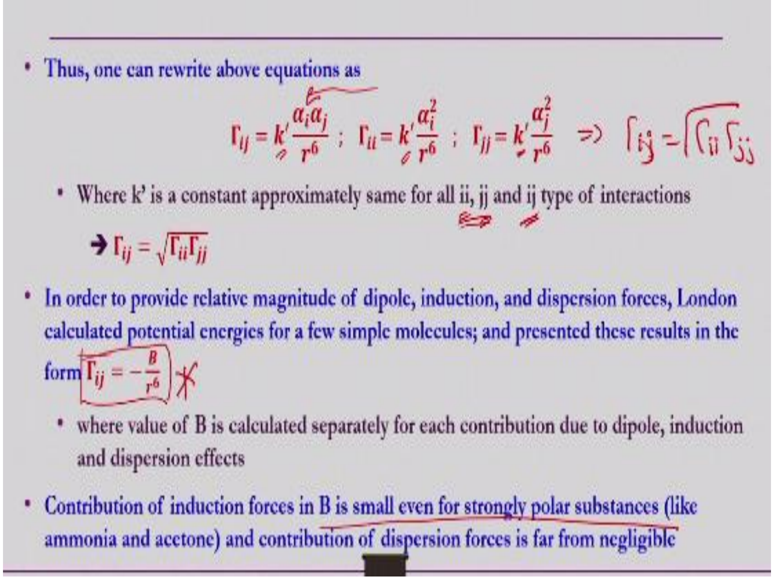

- Thus, one can rewrite above equations as

$$\Gamma_{ij} = k'\frac{\alpha_i\alpha_j}{r^6} \; ; \; \Gamma_{ii} = k'\frac{\alpha_i^2}{r^6} \; ; \; \Gamma_{jj} = k'\frac{\alpha_j^2}{r^6} \Rightarrow \Gamma_{ij} = \sqrt{\Gamma_{ii}\Gamma_{jj}}$$

  - Where k' is a constant approximately same for all ii, jj and ij type of interactions

$\rightarrow \Gamma_{ij} = \sqrt{\Gamma_{ii}\Gamma_{jj}}$

- In order to provide relative magnitude of dipole, induction, and dispersion forces, London calculated potential energies for a few simple molecules; and presented these results in the form $\boxed{\Gamma_{ij} = -\frac{B}{r^6}}$ *
  - where value of B is calculated separately for each contribution due to dipole, induction and dispersion effects
- Contribution of induction forces in B is small even for strongly polar substances (like ammonia and acetone) and contribution of dispersion forces is far from negligible

Thus, whatever the equations that we have for nonpolar molecules, we can rewrite them like Γ_{ij} = some constant $\frac{\alpha_i\alpha_j}{r^6}$ and then α_{ii} is some constant k′ again, $\frac{\alpha_i^2}{r^6}$, and then the Γ_{jj} = k′ $\frac{\alpha_j^2}{r^6}$. This k is a constant and it is almost same for all molecules, it does not change much actually. So, whatever that $-\frac{3}{4}\frac{1}{(4\pi\epsilon_\circ)^2 r^6}$ etc. those kind of things are there, they are taken as a kind of constant and that constant does not change much for different types of interactions.

What do you mean by ii interactions? The ii interactions that means, the interaction between same molecules of the same substance, pure substance i you take whatever the interaction between molecules of the substance i is there that is known as the ii interaction. Similarly, jj interaction is nothing but the interaction between the same molecules of species j, you take species j or substance j, whatever the molecules are there the interaction may be there.

So, since all the molecules are same in a given pure substance, so they are known as the jj interaction or these are also known as the like interactions. The ij interaction is the interaction between one molecule of substance i and then one molecule of substance j something like that, so they are different molecules, right? So, that is the reason they are known as the ij interactions or they are also known as the unlike interactions. If these are like interactions, this ij is unlike interaction, okay?

This constant is approximately same whether the interactions are like interactions or unlike interaction, so then we can write like this. So, then we can write from here $\Gamma_{ij} = \sqrt{\Gamma_{ii}\Gamma_{jj}}$, right? So, if this k prime constant is almost same for all type of interactions, then we can write $\Gamma_{ij} = \sqrt{\Gamma_{ii}\Gamma_{jj}}$ that you can simply here in place of α_i what you can do, you can substitute $\sqrt{\Gamma_{ii}}$ and some constant and then in place of Γ_j, you can substitute $\sqrt{\Gamma_{jj}}$ and some constant. So, that means $\Gamma_{ij} = \sqrt{\Gamma_{ii}}\sqrt{\Gamma_{jj}}$.

In order to provide relative magnitude of dipole, induction, and dispersion forces, London calculated potential energies for a few simple molecules and presented these results in a simpler form. Because now what we have seen, so this Γ_{ij} especially for a non-polar molecule, it is inversely proportional to r^6, the intermolecular potential is inversely proportional to r^6 and this intermolecular potential are attractive potential but non-polar molecules that is what we have seen.

Whatever the dispersion forces are there, they are attractive, so that there is a - and also there is a constant. So, all those constants may be changing whether depending on the type of interaction whether it is dipole induction or dispersion force, what is there depending on the type of force, the constant may be changing and then so but that inversely proportional to r^6 and then being attractive force are common.

So, keeping them as a common, so he has written a kind of a constant B that is $\Gamma_{ij} = -\frac{B}{r^6}$ and then for different molecules, he experimentally measured the influence of this dipole, induction, and dispersion forces in this B. How much it is important? How much each type of this interaction dipole interaction, induction, and then dispersion forces are contributing towards the value of B, that he has calculated, whereas value of B is calculated separately for each contribution due to dipole, induction, and dispersion effects.

Then he found that contribution of induction forces in B is small even for strongly polar substance like ammonia and acetone and contribution of dispersion forces is far from negligible that is what he has observed, right? So, this is about the attractive forces. Different types of attractive forces we have seen electrostatic force, induction forces, and dispersion forces we have seen. So, if it is electrostatic forces, then we have seen that intermolecular potential is inversely proportional to r for any molecule.

But if we have a kind of non-polar molecules, then we have seen that intermolecular potential is inversely proportional to r power 6, right? So, that means this attractive forces whatever are there that can be general way represented at the Γ_{ij} is proportional to $\frac{1}{r^n}$, n may be changing depending on the type of the attractive forces that is existing for a given system, right?

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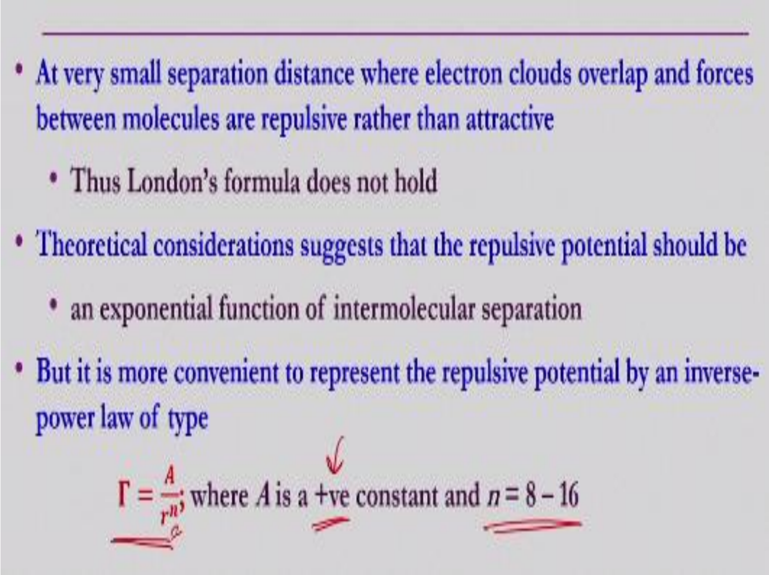

- At very small separation distance where electron clouds overlap and forces between molecules are repulsive rather than attractive
  - Thus London's formula does not hold
- Theoretical considerations suggests that the repulsive potential should be
  - an exponential function of intermolecular separation
- But it is more convenient to represent the repulsive potential by an inverse-power law of type

$$\Gamma = \frac{A}{r^n};\ \text{where } A \text{ is a +ve constant and } n = 8 - 16$$

So, at very small separation distance where electron clouds overlap and forces between molecules are in general repulsive, right? Obviously, when these 2 same molecules are touching each other, so basically there will be a kind of repulsive forces, there will not be any attractive forces, but whatever the London forces associated those things we have seen, so they are only for the attractive forces.

So, obviously at small separation distance, there will be kind of not only when touching, but even there is a small distance between 2 molecules for that small gap also or for small separation distance also, there will be a kind of a repulsive force. Whereas, this London forces, etc., all those things they consider only attractive forces. So, that means this whatever the London formula, etc., that we have seen, they are not valid for very small separation distance.

So, but theoretical consideration suggests that the repulsive potential should be an exponential function of intermolecular separation because when they are touching each other, it is infinite and then when they are moving slightly apart from each other, this repulsive forces sharply decreases, right? And then further increasing the distance, then attractive forces will start developing like that, right?

So, it is expected theoretically that repulsive force should be a kind of exponential function of intermolecular separation distance, but it is more convenient to represent repulsive potential in a kind of form like inverse power law type. Because the attractive forces are also in the similar form, so doing mathematical calculations, etc., may become convenient, easier as well, right? So, further we have seen these repulsive forces are very short range, only for a small distance only they are existing, after that no, attractive forces will start dominating, okay?

Then attractive forces are of long range, right? So, in order to have similarity with the attractive forces one can have a kind of repulsive forces of this form, same power law type form that is $\Gamma = \frac{A}{r^n}$, n is some constant between 8 to 16 and A is positive constant, positive because it is for the repulsive forces.

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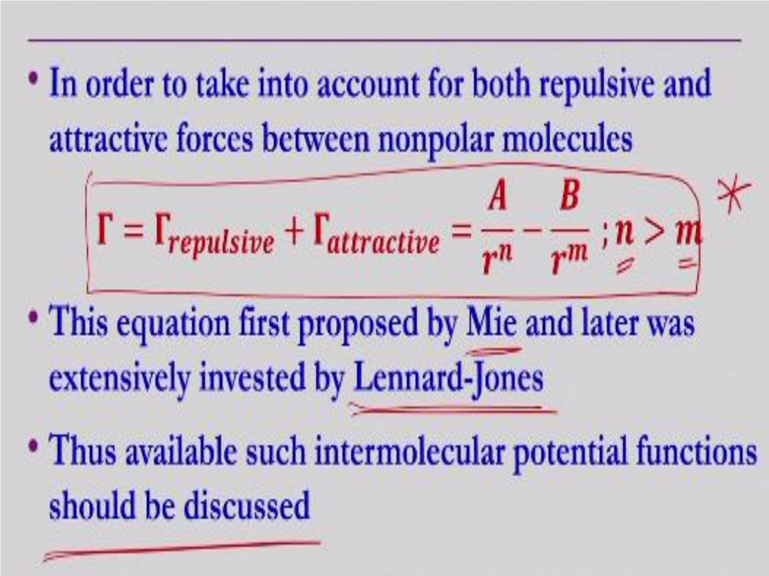

- In order to take into account for both repulsive and attractive forces between nonpolar molecules

$$\boxed{\Gamma = \Gamma_{repulsive} + \Gamma_{attractive} = \frac{A}{r^n} - \frac{B}{r^m} ; n > m} \ \ast$$

- This equation first proposed by Mie and later was extensively invested by Lennard-Jones
- Thus available such intermolecular potential functions should be discussed

So, in order to take into account for both repulsive and attractive forces between non-polar molecules, what we can have? We can add them together. The repulsive forces and attractive forces we can add them together. Repulsive forces are nothing but in the form A by r power n and then attractive forces are in the form - $\frac{B}{r^m}$, okay? So that we write, so generalized Γ, it is intermolecular potential, we can write in this form that is $\frac{A}{r^n}$- $\frac{B}{r^m}$, where A is a positive constant, B is also a positive constant.

There is a - between these two and then here n is larger than m, why because n has to be larger than m because repulsive forces are of a short range and then they sharply decreases when the separation distance increases that is one reason and these repulsive forces are there only for a very short separation distance. That is the reason n has to be large compared to m. So, this is proposed by Mie, this kind of form that is $\Gamma = \frac{A}{r^n} - \frac{B}{r^m}$, but has been extensively investigated by Lennard and Jones.

They have taken several systems, they have found the intermolecular potential because of different types of forces, and then they try to put them in this form and they have developed their own intermolecular potential function as well, okay? But this is the basis. Basis is the Mie's potential function, this is known as Mie's potential function and a much generalized one, okay? Thus available such intermolecular potential function should be discussed. So, now we see different types of intermolecular potential models.

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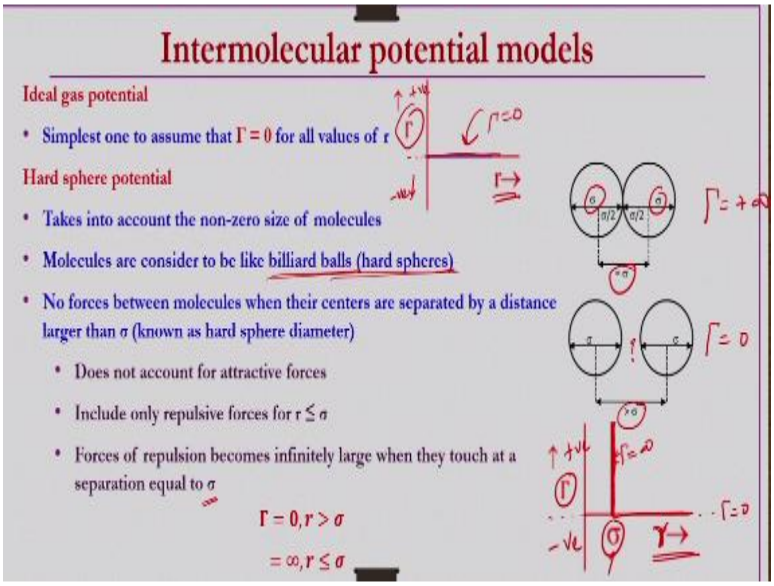

Intermolecular potential models

Ideal gas potential

- Simplest one to assume that $\Gamma = 0$ for all values of r

Hard sphere potential

- Takes into account the non-zero size of molecules
- Molecules are consider to be like billiard balls (hard spheres)
- No forces between molecules when their centers are separated by a distance larger than σ (known as hard sphere diameter)
  - Does not account for attractive forces
  - Include only repulsive forces for $r \leq \sigma$
  - Forces of repulsion becomes infinitely large when they touch at a separation equal to σ

$$\Gamma = 0, r > \sigma$$
$$= \infty, r \leq \sigma$$

So, obviously, it is better to start with the easy one that is the ideal gas potential where there is no intermolecular potential. That is simplest one to assume that Γ = 0 for all values of r, whether r = 0 or r = r_1, r $_2$ or r = ∞ whatever, there is no intermolecular potential according to this ideal gas behavior and then it is valid only in the limit of P tends to 0, okay? Then pictorially if you represent this gamma as function of separation distance or distance between the molecules or atom between which we are trying to find out the potential.

So, then we can see this is constant and this = 0, Γ = 0, here Γ is positive and then downside Γ is negative, and then this line is Γ = 0, right? So, this is the simplest case one, but obviously, we know there are attractive forces and repulsive forces also. Then we have to see the models which are including this effect. So, let us start with the model hard sphere potential model, which includes the repulsive forces only, how it incorporate repulsive forces? That we will see.

It takes into account the non-zero size of the molecules and molecules are considered to be like billiard balls or hard spheres. Why billiard balls? You might have observed that billiard balls, moment they touch each other they move, they immediately repel, right? So, that is when they are away from each other there is no interaction between these billiard balls in general, but when they touches each other immediately the repel, okay? So, that means, it does not take account about any of the attractive forces, but it takes only account of repulsive forces.

There are no forces between molecules when their centers are separated by a distance larger than sigma known as the hard sphere diameter. Because we are taking these billiard balls are hard sphere model, it does not account for the attractor forces, it includes only repulsive forces for r less than or equals to collision diameter or hard sphere diameter. Then forces of repulsion become infinitely large when they touch at a separation distance equal to size of these balls.

Pictorially if you see, so let us say you take 2 balls of size σ, right? So, the radius are $\frac{\sigma}{2}$ each. When they are touching each other, the center to center distance is σ = 1. The moment they touch each other, they immediately repel. So, that means it becomes + ∞, Γ becomes + ∞ immediately they touch each other, right? If the distance is more than this Γ, so it is $\frac{\Gamma}{2} + \frac{\Gamma}{2} = \Gamma$ and then there is some distance also there.

So, then there is no intermolecular potential at all, there should be some amount of attractive forces in reality but it does not account this model. So, this Γ will become 0. So, graphically if you represent this positive side Γ, this is negative side Γ, as the separation distance increases after sigma there is no force. This line is gamma is equal to 0 line, there is no force, but at r = σ, this value you know, the moment they come touching each other they start repelling immediately.

So, this line indicates Γ = + ∞. Shoots up immediately when they touch each other, okay? Repel, okay? This is what hard sphere model mathematically for r > σ, if Γ = 0, for r ≤ σ it is ∞, okay?

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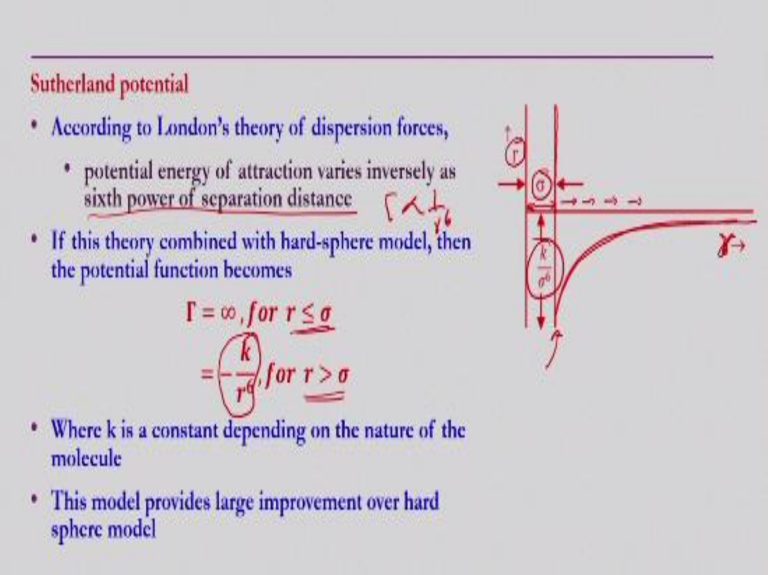

Sutherland potential

- According to London's theory of dispersion forces,
  - potential energy of attraction varies inversely as sixth power of separation distance $\Gamma \propto \frac{1}{r^6}$
- If this theory combined with hard-sphere model, then the potential function becomes

$$\Gamma = \infty, for\ r \le \sigma$$
$$= -\frac{k}{r^6}, for\ r > \sigma$$

- Where k is a constant depending on the nature of the molecule
- This model provides large improvement over hard sphere model

Next one is Sutherland potential. It is an improvement over hard sphere model. So, we are taking step by step. First we have taken ideal gas behavior, there are no intermolecular potential. Then there was a hard sphere model where there are kind of repulsive forces only.

Now, in addition to repulsive forces, there is further improvement done by Sutherland, where he has taken the contribution of attractive forces as well. According to London's theory of dispersion, the potential energy of attraction varies inversely as the sixth power of separation distance.

This is what we have seen, remember all these things we are doing for the non-polar molecules, okay? Because when we take the polar system, what happens there will be a kind of dipole moment and then the dipoles are having different free orientations, interactions, etc. So, then some additional terms will also come into the picture that we will see later anyway. So, if this theory combined with the hard sphere model, whatever the London's theory of dispersion forces is there if that is combined with the hard sphere model, then we can have the Sutherland potential.

Because hard sphere model talks about only repulsive forces and then London study of dispersion talks about only attractive dispersion forces. So, when we combine these two, then we can have a Sutherland potential. That is for $r \leq \sigma$, there is only $+\infty$ that is repulsive forces are there, but when the separation distance increases $r > \sigma$, there will be a kind of attractive forces of the form similar to London's dispersion forces.

That is - some constant divided by r power 6 according to London's theory. So, this talks about the attractive forces. So, here k is a constant depending on nature of the molecule obviously and this model provides large improvement over hard sphere model anyway. Because hard sphere model talks about only repulsive forces when the molecules are touching each other, but here it also takes attractive forces to some distance which are existing when $r > \sigma$.

So, pictorially if you represent, this is intermolecular potential Γ and this distance r intermolecular separation distance r. So, at $r = \sigma$ that is when the collision diameters, they are touching each other, so this molecules repelling, but slightly when you start moving, just slightly moving from each other, then attraction force will start so that attraction force at that point is maximum according to Sutherland potential and that is given by $\frac{k}{\sigma^6}$.

Further if you increase this r value gradually, then what happens? This attractive forces will start decreasing and then far away distance it becomes, 0 or close to the 0, okay? So, it is a combination of London's theory of dispersion and then hard sphere model.

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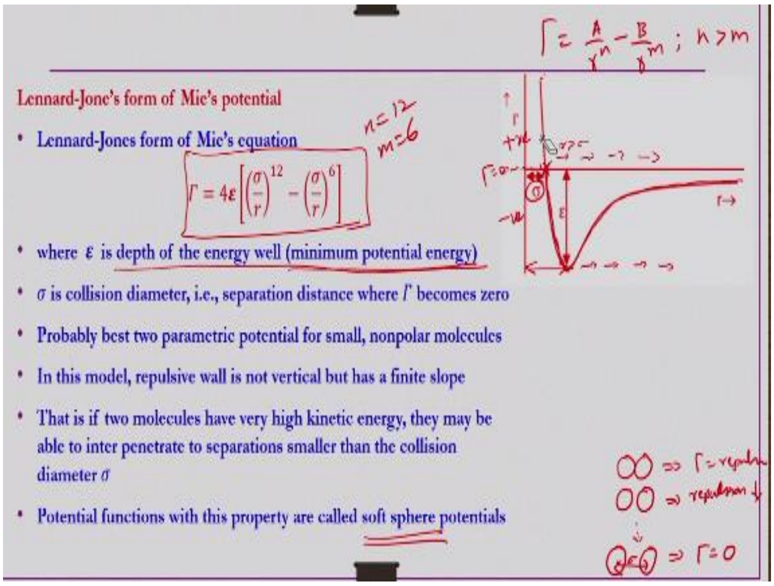

Lennard-Jone's form of Mie's potential

- Lennard-Jones form of Mie's equation

$$\Gamma = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

- where ε is depth of the energy well (minimum potential energy)
- σ is collision diameter, i.e., separation distance where Γ becomes zero
- Probably best two parametric potential for small, nonpolar molecules
- In this model, repulsive wall is not vertical but has a finite slope
- That is if two molecules have very high kinetic energy, they may be able to inter penetrate to separations smaller than the collision diameter σ
- Potential functions with this property are called soft sphere potentials

Now, we take a more generalized Lennard-Jones form of Mie's potential. Mie's potential we have seen it is have the form Γ = $\frac{A}{r^n}$ - $\frac{B}{r^m}$, where n > m and A and B are positive constants. Lennard-Jones have taken this Mie's potential and then have studied a variety number of systems and then they have applied this potential to check whether it is valid or not and then they have developed their own potential, but it is having same form like this.

It is given by Γ = 4 ε$\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$ that is n = 12 and m = 6, okay? And then A = 4 ε σ^{12} and B = 4 ε σ^{6}, if you compare with the Mie's potential that is what you understand, right? Here ε is nothing but the depth of the energy well or the minimum potential energy which is the maximum attractive force, σ is collision diameter, okay? That is the separation distance where this Γ becomes 0.

It is not the far away distance. When the molecules are touching each other, immediately repulsion force is there, but certain if you gradually move away this repulsive force decreases and there will be a kind of point this repulsive force decrease and there will be kind of a balance between repulsive and attractive forces this Γ becomes 0, right? So, that point is known as the sigma, okay? Or collision diameter and then further if you increase then attractive forces will start developing, right?

So, that is initially you have a molecule and then the other molecules, so then here repulsion is there, right? So, this molecule now if you increase the distance, so there may be repulsion, but it start decreasing. So, it decreases like that if you increase certain distance like this, then there will not be even repulsive force also, this will become 0, right? Further if you increase, then it starts increasing the attractive forces. So, this distance whatever this there, collision diameter is nothing but the center to center distance between these 2 molecules at which this gamma is becoming 0.

Probably best two parametric potential for small non-polar molecules is the LJ model. In this model, repulsive wall is not steep, is not vertical as in the kind of hard sphere model, okay? But it has a finite slope that is if 2 molecules have very high kinetic energy, they may able to interpenetrate to separation smaller than the collision diameter σ, right? Like what happens you know, when you have hard sphere model like a billiard balls, so the moment they touch they repel, they cannot interpenetrate.

But if you think of as a kind of molecules as a kind of soft balls, right? And then these are having very high kinetic energy that means they are moving very fast and they come and then touch each other, so then what happens? They may interpenetrate into each other to certain distance and then the distance may be even smaller than collision diameter σ, okay? Because in the case of this model, these molecules are not the kind of hard sphere balls, it is a kind of soft foam balls.

Foam balls kind of thing and then when they hit each other at high kinetic energy, it is possible that they interpenetrate into each other. So, then under such conditions, the intermolecule separation distance may be smaller than collision diameter σ. Collision diameter is nothing but the distance at which Γ becomes 0, between the 2 molecules. So, potential functions with these properties because of this interpenetrating nature of the molecules that soft ball kind of thing nature we are taking, this model is also known as the soft sphere potential model.

Pictorially if you see the same thing, so this is a positive Γ, this is negative Γ. So, here the Γ is 0 that means, there is no intermolecular potential. So, when the separation distance is very small that is their molecules are touching each other, there is a kind of repulsive forces, but this distance if you gradually increase, then what happens? This repulsive force decreases where here now, there will be a kind of point where the intermolecular potential is becoming 0 before starting this attractive forces and then this distance is known as σ.

This separation distance where Γ is becoming 0 after overcoming the repulsive forces and then before developing the attractive forces, the point at which this gamma is becoming 0 that is known as the collision diameter. Then now here further if you increase $r > \sigma$ gradually like this, this attractive forces then gradually increases, because these are the negative sign, so then this is magnitude wise decreasing, but this is the point you know where the attractive force is maximum, right?

So, this is the distance at which the attractive forces are maximum, but further if you increase this distance gradually here, these attractive forces are decreasing and then they are also again going towards the $\Gamma = 0$ line, right? Then we can see here they are not very steep like you know in the case of hard sphere model they are very steep like this, right? In the case of hard sphere model, they are very steep like this, but now there is a kind of slope here, okay? So that we can see clearly here from the picture.

That is that slope is there because of the interpenetrating nature of the molecules or considering the molecule as a kind of soft spheres.

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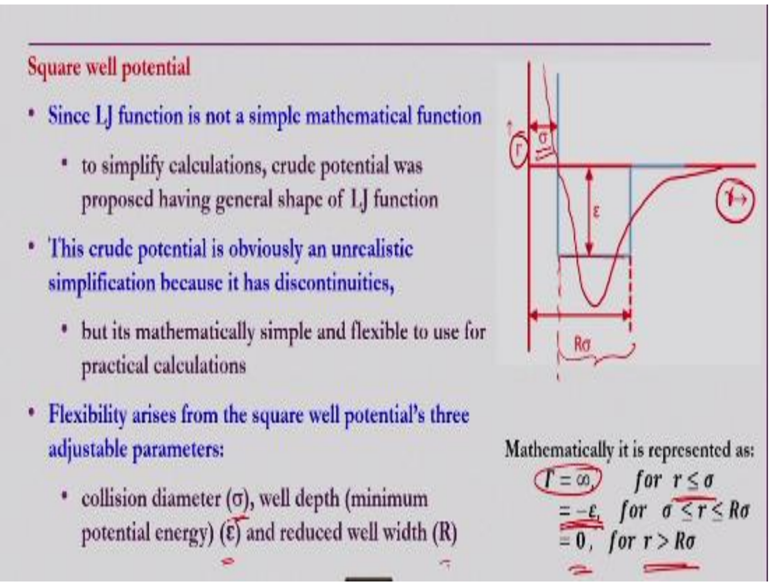

Square well potential

- Since LJ function is not a simple mathematical function
  - to simplify calculations, crude potential was proposed having general shape of LJ function
- This crude potential is obviously an unrealistic simplification because it has discontinuities,
  - but its mathematically simple and flexible to use for practical calculations
- Flexibility arises from the square well potential's three adjustable parameters:
  - collision diameter (σ), well depth (minimum potential energy) (ε) and reduced well width (R)

Mathematically it is represented as:

$$\Gamma = \infty, \quad for\ r \leq \sigma$$
$$= -\varepsilon, \quad for\ \sigma \leq r \leq R\sigma$$
$$= 0, \quad for\ r > R\sigma$$

Now, we take square well potential. So though the Lennard-Jones potential that we have seen it is very reliable and then fundamentally very acceptable, what happens the mathematical nature is not simple while doing the calculations. So, because of that reason, this square well potential is developed just to simplify calculations, whatever this crude potential was proposed having the general shape of LJ functions or Lennard-Jones potential functions, right? The square well it is having mathematically crude form we can say, it is similar to the LJ form

The purpose is just to simplify mathematical calculations. Why mathematical calculations? In the later courses, we can see whatever this intermolecular potential gamma, etc., are there, they will be used to calculate the some constant. Let us say if you have a Virial equation of state, second Virial coefficient, third Virial coefficients, etc., so those things can be calculated by using this intermolecular potential, right? So, this if intermolecular potential function is very complicated, then finding those Virial equation coefficients, etc., may become very difficult.

So, in order to avoid such kind of difficulties, LJ model has been replicated or simplified in such a way that you know it will be having a form of square well. This is crude potential, obviously an unrealistic simplification because it has discontinuities because when you go from the repulsive to the 0 intermolecular potential and zero intermolecular potential to the attractive side and then attractive force decreasing and then again decreasing like this, so all these things, there is no discontinuity.

Fundamentally there should not be discontinuity, but this model if you see pictorially it is having a discontinuity, but it is mathematically simple and flexible to use for practical calculations. You may be having some errors in the solutions, but the error may not be very high, but again we cannot guarantee for all the system that depends on the system to system, molecule to molecule. Pictorially if you see this y axis is Γ, intermolecular potential, x axis is nothing but intermolecular separation distance.

Now, the potential you can see here, the blue dotted line, this is a square well, remember this thing you know intermolecular potential by LJ model is having this one, which is more realistic obviously, like this. So, now, this is mathematically in order to simplify people have developed this square well potential kind of thing, that is the only advantage, otherwise nothing, okay? Obviously as I mentioned, LJ model is the best available model for this intermolecular potential for non-polar molecules till date.

Mathematically if you can see here, for r ≤ σ, we have Γ = ∞ and then r between σ, r = σ to r = R σ, we have - ε, - ε that is the maximum attractive force and then it is constant, this constant maximum attractive force there between σ to R σ without any changes.

Then after r > R σ, it suddenly becomes 0, okay? Flexibility arises from the square well potential because of the 3 adjustable parameters. So, collision diameter, well depth or the minimum potential energy and reduced well depth

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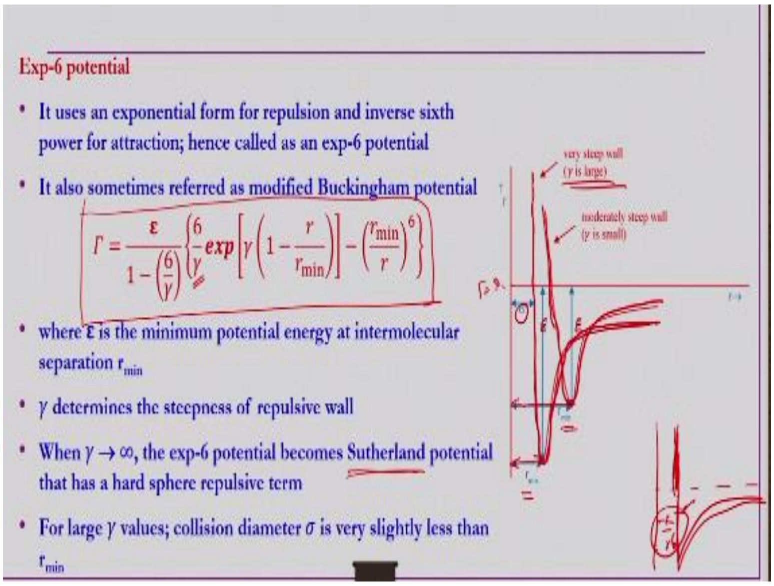

Exp-6 potential

- It uses an exponential form for repulsion and inverse sixth power for attraction; hence called as an exp-6 potential
- It also sometimes referred as modified Buckingham potential

$$\Gamma = \frac{\varepsilon}{1-\left(\frac{6}{\gamma}\right)}\left\{\frac{6}{\gamma}\exp\left[\gamma\left(1-\frac{r}{r_{\min}}\right)\right]-\left(\frac{r_{\min}}{r}\right)^{6}\right\}$$

- where ε is the minimum potential energy at intermolecular separation r_{min}
- γ determines the steepness of repulsive wall
- When γ → ∞, the exp-6 potential becomes Sutherland potential that has a hard sphere repulsive term
- For large γ values; collision diameter σ is very slightly less than r_{min}

Then exponential 6 potential. So, remember in one of the previous slides, we have seen this repulsive forces, fundamentally they have to be in a kind of exponential form because they are there in only for the short range and then suddenly drops from very large infinite repulsive force to the gamma is equal to 0 within a very small r separation distance. That is the reason fundamentally theoretically it is expected that repulsive forces should be exponential.

But people have taken power law type because to have a similarity with the attractive forces as well as to have a kind of mathematically simplicity while using these models for other calculations, okay? So, but now this model, exponential 6 model is the one where it considered exponential form for repulsive forces and then attractive forces are having London’s dispersion form, where it is having inversely proportional to r power 6 form. That is the reason it is known as the exponential 6 potential.

It uses an exponential form for repulsion and inverse the sixth power for attraction, hence called as an exponential six potential. It also sometimes referred as modified Buckingham potential and then you can see it is having this form. This γ is a kind of adjustable parameter which takes into account how steep is the repulsive forces, right? So, here ε is the minimum potential energy at intermolecular separation r minimum, okay? Anyway and then γ determines the steepness of repulsive wall.

This γ it determines the steepness of the repulsive wall. When γ tends to infinity, then exponential 6 potential becomes same as a kind of Sutherland potential, where we have Sutherland potential this is how we have, this kind of form, right? So, here it is - $\frac{k}{r^6}$. This is attractive force, this repulsive forces is there, - $\frac{k}{r^6}$ attractive force, maximum attractive force and then it decreases, like this form we can get if in this equation if you substitute γ =∞.

That is for Γ values, collision diameter σ is very slightly less than r minimum, how it is? Let us say this equation you take different values of γ and then try to pictorially represent, then we can have this kind of form. So, where if you have a γ very large, very large that is tends to infinity, so then you can have this kind of potential shown like this here. So, this is the εand then this ε is the maximum here, okay? And the attractive forces r - ε, right?

Then the distance at which this attractive force is becoming maximum is known as r minimum and this collision diameter sigma is the distance at which this γ becomes Γ or intermolecular potential becomes 0. Now, we can see here when it is large, it is very steep, okay? The same thing if you take a moderate value or the small value of gamma, then we can see the potential function would be something like this, it will becoming more or less quite similar to LJ model and then this is the r minimum distance.

Here, r minimum distance is the distance at which the attractive force is maximum, r Γ_{ij} is minimum, okay? Minimum Γ_{ij} indicates the maximum attractive force, okay? So, now, you can see in 2 cases, here in gamma is large, then we can say the difference between r minimum and then σ is very small, that is more or less like in the kind of Sutherland potential. If Γ is moderate, then it is more or less like a LJ model, okay?

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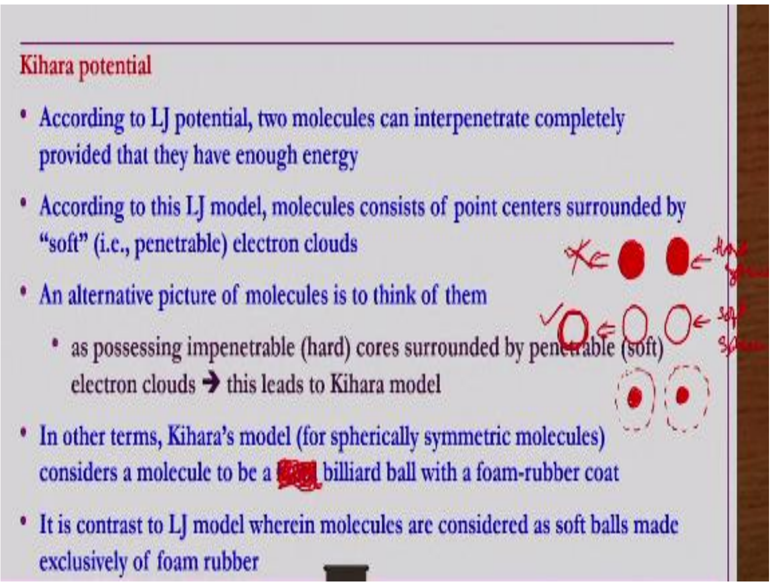

Kihara potential

- According to LJ potential, two molecules can interpenetrate completely provided that they have enough energy
- According to this LJ model, molecules consists of point centers surrounded by "soft" (i.e., penetrable) electron clouds
- An alternative picture of molecules is to think of them
    - as possessing impenetrable (hard) cores surrounded by penetrable (soft) electron clouds ➔ this leads to Kihara model
- In other terms, Kihara's model (for spherically symmetric molecules) considers a molecule to be a [redacted] billiard ball with a foam-rubber coat
- It is contrast to LJ model wherein molecules are considered as soft balls made exclusively of foam rubber

Then Kihara potential. According to LJ, 2 molecules can interpenetrate completely provided that they have enough energy, okay? According to this model, molecules consists of point centers surrounded by soft penetrable electron cloud, right? Okay? An alternative picture of molecule can we think of like this. Let us say if to explain this is hard sphere, hard sphere model it is completely like billiard ball kind of thing, right? I am making fully colored so that to indicate hard sphere model. So, this is what we have, hard sphere model.

What LJ model takes count, it takes soft sphere kind of molecules, right? Where these molecules can be when they are colliding each other, it is possible that there may be interpenetrated into each other completely like this. Where here moment they interact each other, they may be repelling, they may be going away, alright? So, there is no penetration at all, but we can think of something in between of this thing. You can take the molecular core which is hard sphere kind of thing and then covered by a kind of soft this thing electron cloud like this in between of these two things.

So, here first case, it is not at all penetrable, in the second case it is fully penetrable, whereas now this Kihara model it takes, molecule core center as a kind of hard sphere surrounded by the electron cloud as a kind of soft foam kind of material, alright? So, then this is in between, partially kind of thing. So, whatever the kinetic energy they have, so up to what distance they can penetrate, only they can penetrate the electron cloud part only, they cannot penetrate the core of the molecules. So, this is what the basis for a Kihara potential.

So, as possessing impermeable hard cores surrounded by permeable soft electron clouds, this leads to Kihara model. In other terms, Kihara's model for spherically symmetric molecules considers a molecule to be a billiard ball with foam rubber coat, right? So billiard ball with a foam rubber coat like in between of these kinds of thing, so that it is contrast to the LJ model wherein molecules are considered as a soft balls made of exclusively foam rubber and then completely interpenetrable.

In this case complete interpenetration is not possible, as well complete repelling as in the case of hard sphere ball is also not possible in the case of Kihara potential, it is in between of these two.

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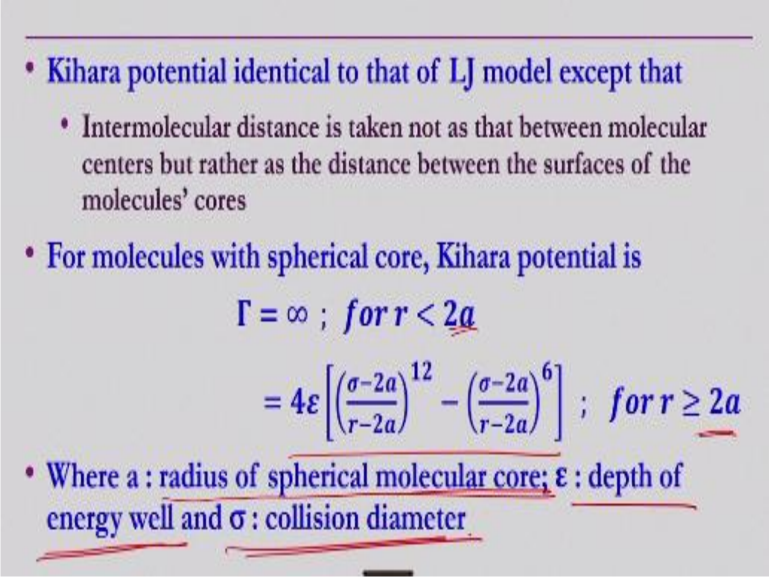

- Kihara potential identical to that of LJ model except that
  - Intermolecular distance is taken not as that between molecular centers but rather as the distance between the surfaces of the molecules' cores
- For molecules with spherical core, Kihara potential is

$$\Gamma = \infty \; ; \; for\, r < 2a$$

$$= 4\varepsilon\left[\left(\frac{\sigma-2a}{r-2a}\right)^{12} - \left(\frac{\sigma-2a}{r-2a}\right)^{6}\right] \; ; \; for\, r \geq 2a$$

- Where a : radius of spherical molecular core; ε : depth of energy well and σ : collision diameter

Then this model is exactly same as LJ model except only thing that this intermolecular distance is taken not as that between molecular centers but rather as the distance between the surfaces of the molecules' cores and then for molecules with spherical core Kihara potential is given as $r < 2a$, $\Gamma = \infty$. Then for $r \geq 2a$, it is exactly same to the LJ model. What LJ model is having, $4\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$, but now σ and r are being subtracted with - 2a that is Kihara model.

That is $4\,\varepsilon\left[\left(\frac{\sigma-2a}{r-2a}\right)^{12} - \left(\frac{\sigma-2a}{r-2a}\right)^{6}\right]$, so where a is the radius of spherical molecular core that is central hardcore and then epsilon is obviously depth of energy well, the minimum energy potential, and then sigma is nothing but the collision diameter.

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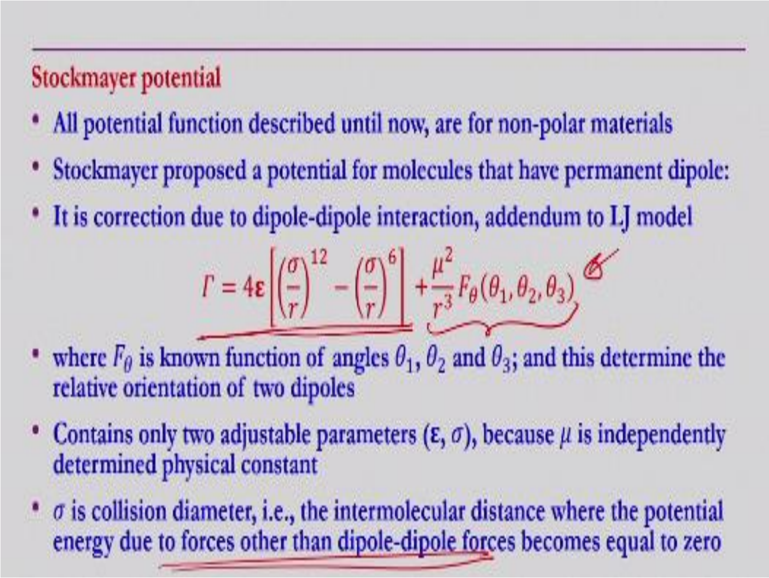

Stockmayer potential

- All potential function described until now, are for non-polar materials
- Stockmayer proposed a potential for molecules that have permanent dipole:
- It is correction due to dipole-dipole interaction, addendum to LJ model

$$\Gamma = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \underbrace{\frac{\mu^2}{r^3}F_\theta(\theta_1,\theta_2,\theta_3)}$$

- where F_θ is known function of angles θ_1, θ_2 and θ_3; and this determine the relative orientation of two dipoles
- Contains only two adjustable parameters (ε, σ), because μ is independently determined physical constant
- σ is collision diameter, i.e., the intermolecular distance where the potential energy due to forces other than dipole-dipole forces becomes equal to zero

So, the last one is the Stockmayer potential. All potential function whatever we have seen until now, they are for non-polar materials. Stockmayer proposed a potential for molecules that have a permanent dipole and then it is correction to dipole-dipole interaction and then addendum to LJ model, okay? Whatever the LJ model is there, for that model he has brought in some kind of additions, those additions are occurring because of the permanent dipole-dipole interactions right and then it is having this form.

So, if you take only this part gamma = 4 $\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$, this is nothing but LJ model, Lennard-Jones models, which is valid for non-polar molecules, but now because of the polar molecules, there are the kind of dipole moments are there and those permanent dipole moments are having some kind of interactions. So, those interactions are brought into this LJ model by a kind of addition and then addition is having this form $\frac{\mu^2}{r^3}$ and then function of θ_1, θ_2, θ_3.

This function F_θ is a known function and then it is function of angles θ_1, θ_2 and θ_3 and this determines the relative orientation of two dipoles at which they are interacting. It contains only 2 adjustable parameters, σ and ε, where μ is independently determined by physical constant because μ = e * d, μ is the dipole moment. σ is the collision diameter, that is, the intermolecular distance where the potential energy due to forces other than the dipole-dipole forces becomes equal to 0 because it is due to forces other than dipole-dipole forces.

Because otherwise Γ will never become 0 here, whatever the distance you take here because this additional term is there. So, that is the reason sigma is the collision diameter at which gamma becomes 0 due to the forces other than the dipole-dipole interactions.

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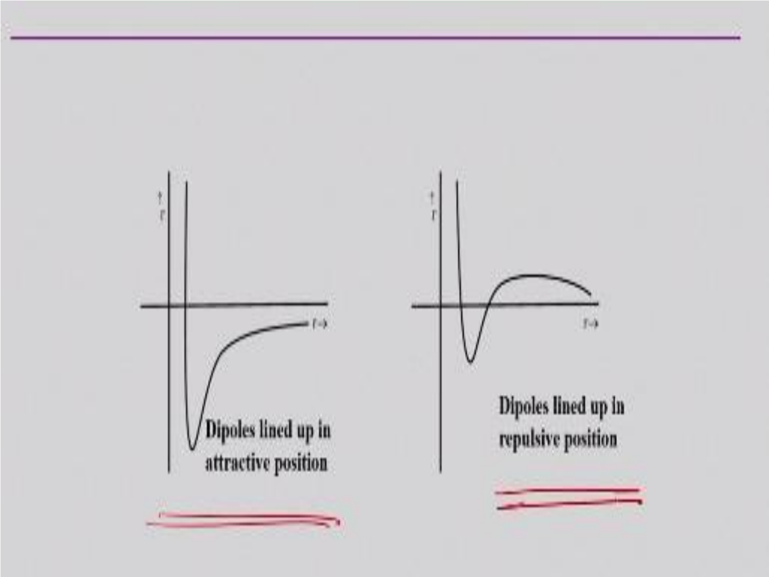

Then pictorially if you see if the dipoles are lined up in attractive positions, then Stockmayer potential will have this form and then dipoles if they are lined up in a repulsive position, then Stockmayer potential function will have this particular form. So, this is about the intermolecular potential.

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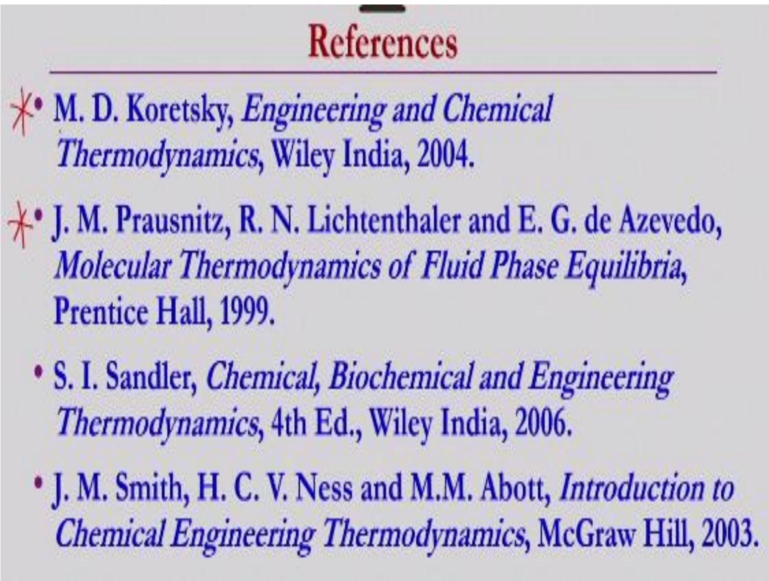

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The references for this lecture are Koretsky, Engineering and Chemical Thermodynamics. Prausnitz et al, Molecular Thermodynamics of Fluid Phase Equilibrium. Sandler, Chemical Biochemical and Engineering Thermodynamics. Smith et al, Introduction to Chemical

Engineering Thermodynamics. But the models are taken from here and then few details about the intermolecular potentials are also taken from this other book, Engineering and Chemical Thermodynamics by Koretsky.

Thank you.