Understanding Intermolecular forces

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Lecture-29

Types of forces; Mie potential; LJ potential

Welcome back ,so in today's video lecture we will look at the topic you know that involve intermolecular forces right so we will look at various types of forces we list the various types of forces and after that we will look at the some of the Power law being used from the context of intermolecular or interaction pair potential okay And after that, we can look at the Leonard-Jones potential, Mie potential Leonard-Jones potential is the special case of Mie potential. We will look at the minimum potential, right, based on the Leonard-Jones pair potential, right. So, we will begin our lecture. Let us begin. Yeah,

(Time: 1:15 min)

So, as we have just described, we will look at different types of forces. Remember, when we dealt with some lecture in Module 3, sorry, Module 2, we described some of these forces, right, using some, you know, schematics, right? For example, we talked about Van der Waals forces of attraction. In that, we looked at them. The induced dipole-permanent dipole based on, you know, few molecules type and permanent-permanent dipole, right? So, this comes from the, uh, polarity and, uh, uh, asymmetrical, uh, uh, you know, shape. I mean, the molecule, which, which has the asymmetry, right. Either due to polarity or due to the molecular structure. Okay. Uh, and the London dispersion force. So, these three forces come under the, uh, you know, the umbrella called Van der Waals force, right? So, this is a physical force, okay? Van der Waals force, you know, refers to the attractive force, right? Which is very short range, okay? And between molecules, so it, you know, it is applicable between noble gas atoms or any non-polar molecules, right? Okay.

So at least we have got about three forces under Van der Waals forces, which is nothing but London or dispersion. So, London force or dispersion force, which are often interchangeably used. Okay. This force, London or dispersion force is always there. No matter whether we deal with a neutral atom or charge in the system. So this Van der Waals force always exists. Okay. It is because of the fluctuation in the electron, right? Electron cloud. So due to which there will always be, you know, interactions. I mean, attraction between the atom or molecules, right? So important point to be noted is this is not same as the covalent bond or ionic bond that we often talk about. In fact, this is weaker than covalent or ionic bond, right? So, there's no reaction involved. These are physical forces, right? yeah so apart from van der Waals forces we also have you know electrostatic force so we also will also be dealing with electrostatic force so as the name suggests this electrostatic force comes from the it is a manifestation of coulombic interaction right so let's say if you have got two point charge let's say you have about two point charge and if they are equal in magnitude okay You can say either they can be equal in magnitude or they may be different in magnitude, right? As well as the charge, right? It can be positive charge also, it can be negative charge also. But we are talking about two-point charges, right? You know, kept apart a distance, right? Which is nothing but r. Okay. So, in such case, we know what is known as the Coulombic law, which says that it is proportional to product of two-point charges, right? Okay. Or inversely proportional to square of, I mean, inversely proportional to r^6, right? Yeah. Or square of the distance, correct? Yeah. Right. So, $q_1 q_2 / r^2$, right? So, we know that from the Coulombic interaction, Coulomb's law, we know it is $q_1 q_2 / r^2$, right? It depends on the distance as well. It depends on the magnitude of the charge as well. Okay. So that we know. And we talk about a steric force, which is also a force due to a steric hindrance, right?

So, let's say we talk about, let's say we have the, we deal with particle system. Let's say you have a sphere, okay? And sometimes the sphere can be grafted using some polymer, right? Right? this can be polymer brushes, so you can expect some sort of polymer brushes on the surface. Now, when another sphere of particle, right, interacts, right, so like you have polymer brushes, on top of this, okay, remember when these two polymers you know particle grafted with polymer when they approach each other they cannot approach you know very close to each other because there will be a hindrance between the polymer brush. So, this polymer overlap will be there. So, when overlap between two molecules, polymer molecules take place, there will be a steric hindrance. So, because of which they will not be able to penetrate further. On the other hand, there is something called depletion attraction, which is purely because of the osmotic imbalance.

So let's say no two particle will have symmetrical distribution of the polymer density right so in such case you will expect that there will be imbalance in the you know what you call asthmatic there will be asthmatic imbalance which will push the particle right uh towards each other right because of which there can be depletion attraction so so there can be two type of forces one is the steric repulsion because of the steric hindrance the other one is depletion attraction that is because of the uh force due to osmotic imbalance because we know that no two particle system will have symmetrical distribution of polymer brushes on the surface so you might expect depletion attraction so we will see them maybe one by one in detail sometime i mean in detail as we move along right yeah

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First successful phenomenological theories

❑ In an attempt to explain why real gases did not obey the ideal gas law, Van der Waals equation of state, the Dutch physicist van der Waals (1837-1923) considered the effects of attractive forces b/w molecules.

1)Van der Waals force
a. Induced dipole-induced dipole (London or dispersion)

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

❑ In 1903, Mie proposed an empirical form of interaction pair potential which for the first time included a repulsive and as well as attractive term.

c. Permanent-permanent dipole (Kesom)

Attraction between noble gas atoms or non-polar molecules

2) Electrostatic force $W(r) = \frac{-B}{r^n} + \frac{A}{r^m}$ ve or Repulsive force   2. Stronger than vdw

Columbic interaction between charged particles

❑ In 1924, Leonard-Jones proposed a special case of Mie potential.

3) Steric force

When the emulsifier $W(r) = \frac{-B}{r^6} + \frac{A}{r^{12}}$ eric. An electric charge with its associated boundary layer is not necessary.

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INTERFACIAL ENGINEERING

Yeah, so next we will look at the, you know, phenomenological theories, various theories, power law theories, right? So, the first successful phenomenological theory was proposed by Van der Waals, right? Who is a Dutch physicist, right? Who has contributed to these attractive forces between molecules, okay? uh so in the 18th century right and so you know this form of equation very famous equation this is van der Waals equation of state for real gas, so this was the first uh uh you know uh theory that came into existence when for you know predicting the pvt relations of real gas right so it was a it was modified from the ideal gas law right And so in this equation, two aspects was covered. One is the attractive force between molecules and another one is the excluded volume concept, right? So, the attractive force between molecules was first proposed by Van der Waals in his equation of state, right? After that came Mie potential theory, interaction pair potential theory. This was actually modified, you know, empirical, you know, interaction pair potential. So, this uses compact, you know, this was proposed in a very compact form. You can see there are two terms, right? One is the attractive term.

 I'm sorry this is attractive term so attractive force is often denoted using the convention negative convention right whereas repulsive force is often described using positive sign convention right So here you have the negative force as well as positive repulsive force and the constant which is B and A, this is nothing but the strength of attraction as well as strength of repulsion, right? Okay. And you can see this exponent which is n and m. Okay. m takes very large values whereas n is very, exponent of n is, you know, very small.

 So... So, this form of equation, this came after the, you know, in the form of Mie interaction pair potential theory. But this was not very useful. Later, 1924, Leonard Jones actually proposed a special case of Mie potential. Here, he has used explicitly the exponent for attractive term and repulsive term. So, you can see this is coming from the attractive term. Uh because uh attractive term if you look at in the van der waals equation it is a volume dependent right so v is uh you know uh as equal to r^3 right so since V^2 term was used in attractive term the volume dependent term is can be also expressed in the form of a distance dependent that is a you know r^6 term right okay. So, because V^2 is now converted into distance dependent term, which is r^6, right? So, this comes from the molecular theory of Van der Waals attractive force. Whereas this one comes from the, this doesn't have any molecular origin. Why the exponent of 12 was chosen? There is no specific reason to it. But, you know, the simplest, you know, the accepted reason is this is very easy to compute, right? If you want to compute, you know, using, I mean, computationally, because r^{12} is easy to express, which is just a square of the attractive term.Otherwise the exponent of m can be as large as possible okay so this actually indicates the indicates that the repulsive force you know goes something like this which is very steep right so this is something like your hot spear potential right

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First successful phenomenological theories

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

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$$W(r) = \frac{-B}{r^n} + \frac{A}{r^m}$$

❑ In 1924, Leonard-Jones proposed a special case of Mie potential.

$$W(r) = \frac{-B}{r^6} + \frac{A}{r^{12}}$$

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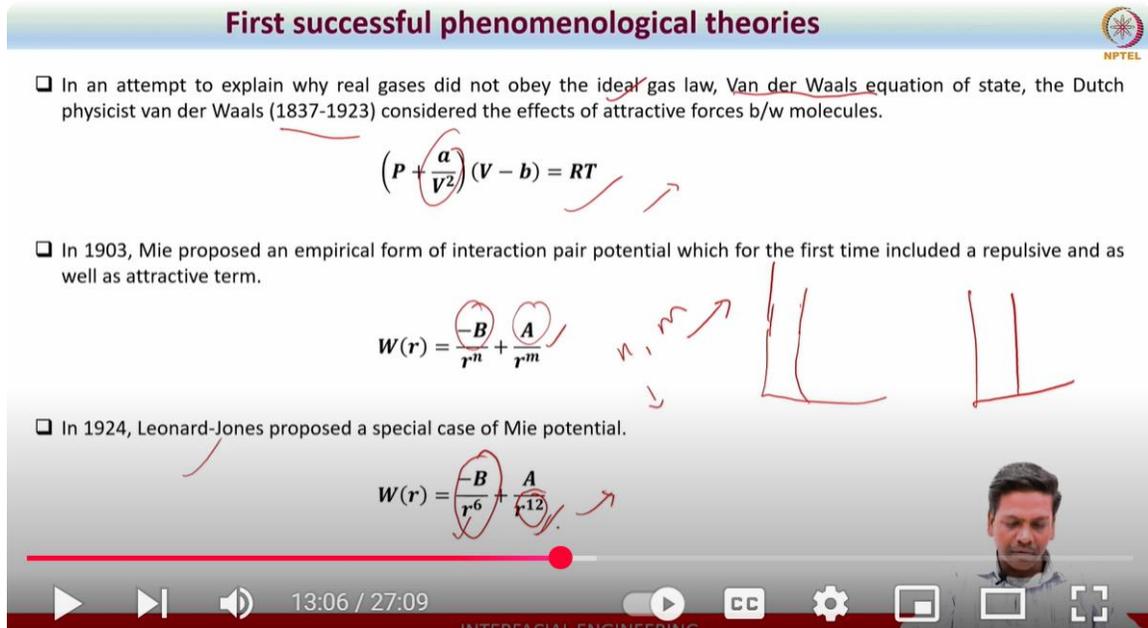
So here r^m can be any number as large as possible right but this r^{12} was just used to make it easier you know to calculate the potential computationally right okay yeah so this is about the Leonard-Jones potential. So $(-B/r^6)$ is basically attractive term. (A/r^{12}) is basically a repulsive term.

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Molecular interactions and power laws

In general, the combined effect of van der Waals attraction and interparticle repulsion at the molecular level

$$\phi = AX^{-12} - BX^{-6}$$
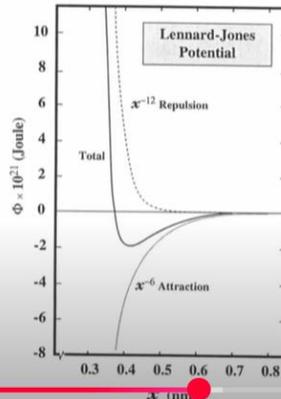
Now we know the combined effect of Van der Waals attraction and repulsion at the molecular level so if you plot the potential versus distance, okay, as a function of distance, center to center distance between molecules, you can see that the repulsion force, the repulsive force as such is going steeper, right, after some point, right? So this is going steeper. Because of this mathematical, you know, the. ... the Power law which we have used as x-^{12} this the repulsive the yeah so it reflects in this fashion right, the repulsive force reflects in this fashion whereas the attractive force is nothing but the long range , you know, interactive force right and this part is nothing but your attractive strength okay right so this represents the minima right it passes through minima okay van der Waals force which is very long range force in this case compared to the repulsive force okay so we know that the sum total of the attraction plus repulsion. If you plot on the same graph you will see this the solid line is nothing but this total force which is sum total of attractive force as well as repulsive force and the dotted line is the repulsion force alone in this case or attractive force alone in this case right yeah so now we can look at how to understand the minimum potential or minimum coordinates right so we know the

$$\phi = -\frac{B}{r^6} + \frac{A}{r^{12}}$$

Remember this B, we want to denote this parameter B because it comes from the β which we will see we will see later,

$$\beta \Rightarrow Debye + kesom + London \; contant$$

okay, which we will see later, so this is very easy to connect β with B that's why we often use this you know B in this I mean we use this notion B, okay right now, we know that from calculus if you differentiate this potential with respect to you know r, right because distance and set that to zero you would be able to get what is known as minimum radius ,I mean minimum distance right so which we will see now let's say

$$\frac{d\phi}{dr} = 0$$

$$\frac{d\phi}{dr} = -6 \times (-B) \times r^{-7} + (-12) \times A \times r^{-13}$$

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$$0 = -6 \times (-B) \times r^{-7} + (-12) \times A \times r^{-13}$$

$$12 \times A \times r^{-13} = 6 \times B \times r^{-7}$$

$$2 \times A \times r^{-13} = B \times r^{-7}$$

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$$r_m{}^6 = \frac{2A}{B}$$

$$r_m = \left(\frac{2A}{B}\right)^{1/6}$$

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$$\phi_m = -B \cdot r_m^{-6} + A \cdot r_m^{-12}$$

$$\phi_m = -B \cdot \left[\left(\frac{2A}{B}\right)^{1/6}\right]^{-6} + A \cdot \left[\left(\frac{2A}{B}\right)^{1/6}\right]^{-12}$$

$$\phi_m = -B \cdot \left(\frac{2A}{B}\right)^{-1} + A \cdot \left(\frac{2A}{B}\right)^{-2}$$

$$\phi_m = -B \cdot \frac{(2A)^{-1}}{B^{-1}} + A \cdot \frac{1}{2^2} \cdot \frac{1}{A^2} \cdot B^2$$

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$$\phi_m = -B \times \gamma_m + A \times \gamma_m$$

$$\phi_m = -B \times \left[\left[\frac{2A}{B}\right]^{1/6}\right]^{-6} + A \times \left[\frac{2A}{B}\right]^{1/6}$$

$$= -B \times \frac{(2A)^{-1}}{B^{-1}} + A \times \frac{1}{2^2} \times \frac{1}{} \times \frac{B}{}$$

$$= \frac{-B^2}{2A} + \frac{B^2}{4A}$$

$$= \frac{-2B^2 + B^2}{4A} = \frac{-B^2}{4A}$$

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$$\phi_m @ x_m = \frac{-B^2}{4A}$$

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Okay, so what does it represent is, if you look at our equation, so this part is nothing but your x_m and this part is nothing but your Φ_m, right? Okay, so this is the minimum potential and minimum coordinate, right? So here we will do some exercise so that, you know, we will be able to understand the, you know, the interactive energy, right? you will be able to relate quite well. So, let's talk about, you know, methane molecule. Let's say we have two methane molecules. They are approaching with each other, right? Okay. Very closely with each other. Then you know that as they move very closely with each other, they will be, you know, there will be Van der Waals molecules. right uh attraction, attractive energy they will experience van der Waals force and then repulsive force right

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So now we want to understand,you know, what is minima right ,when they ,what is the minimum coordinate when they pass through the minima that is total energy which is sum total of van der Waals and attractive and repulsive energy right ,so that's that's exactly what we are going to now look at as you can see as soon as you know it crosses this the energy goes into repulsive, you know, domain, you can see that they move very steeply. They grow very steeply. That's because as soon as they were, so that indicates that as soon as they, you know, cross that distance, right, So due to Pauli's exclusion principle, right, because there can be, you know, electron cloud cannot overlap with each other. So, this, you know, the infinite, because this repulsion energy is not finite, it indicates that the molecules cannot, you know, penetrate further. So that is exactly what it

indicates, right? So, the value, the repulsive energy cannot be finite value, right? It's infinity because it tells us that molecules cannot penetrate further, any further, right? So you can understand further by calculating what is the x_m, the minimum coordinate, right? at which it will experience you know minima right will pass through minima so this you can calculate we know

$$x_m = \left(\frac{2A}{B}\right)^{1/6}$$

So this is nothing but if you substitute these values so remember the value the A and B has units

$$A = 10^{-134} \text{ J·m}^{12}$$
$$B = 2.3 \times 10^{-77} \text{ J·m}^6$$

So, if you substitute these values,

$$x_m \approx 0.42 \text{ nm}$$

So that is the minimum distance, the minimum coordinate for this case, especially when we deal with a molecule that is methane.

$$\phi_m \approx -2.1 \times 10^{-21} \text{ J}$$

Remember this Φ here is expressed in the unit called joule, right, which is energy so it is nothing but interactive energy itself

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So if you want to understand or appreciate this number what is, the how will you relate so you can relate, this number with what is known as k_BT right, which is thermal energy so we know that There is something called k_BT, right? Boltzmann constant multiplied by temperature gives you thermal energy, right?

$$k_BT \rightarrow \text{thermal energy}$$

This is nothing but thermal energy. So when you divide this number with the thermal energy, which is k_BT, right?

$$k_B = 1.38*10^{-23} \text{ J/K}$$

So, when you into temperature, right? Multiply by temperature. right if you do that you will get this quantity dimensionless quantity right

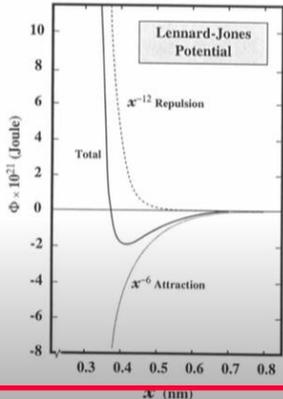$$\frac{\phi_m}{k_BT} = \frac{2.1 \times 10^{-21}}{k_BT}$$

$$\phi_m = 154. \, k_BT$$

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Molecular interactions and power laws

So this in this way you can understand what is their uh strength right what is the strength of energy, so the strength of energy in this case is 154 times the thermal energy which is nothing but uh you know uh k_BT right so this will help you to quickly relate uh you know uh about the Leonard- jones interactive energy right that we talked about right we will stop here we will continue from the next lecture thank you