# Colloids and Surfaces
**Prof. Basavaraj Madivala Gurappa**
**Department of Chemical Engineering**
**Indian Institute of Technology-Madras**

## Lecture-13
## Vanderwaal Interactions Between Particles

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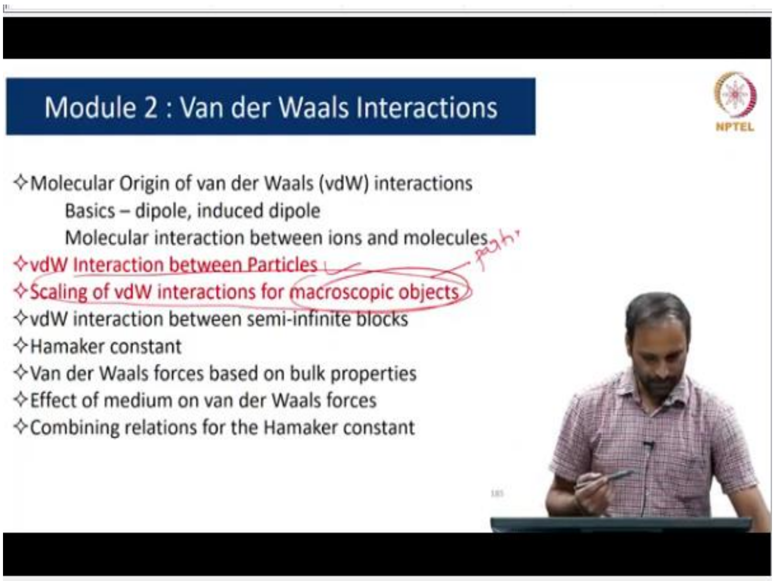

Module 2 : Van der Waals Interactions

- ✧Molecular Origin of van der Waals (vdW) interactions
  - Basics – dipole, induced dipole
  - Molecular interaction between ions and molecules path'
- ✧vdW Interaction between Particles
- ✧Scaling of vdW interactions for macroscopic objects
- ✧vdW interaction between semi-infinite blocks
- ✧Hamaker constant
- ✧Van der Waals forces based on bulk properties
- ✧Effect of medium on van der Waals forces
- ✧Combining relations for the Hamaker constant

So, far what you have done is we have looked at molecular origin of van der Waals interaction , we did a little bit of basics looking at dipole, induced dipole and then we talked about following that I showed you a table where you know we had listed several molecules or atoms and we were looking at molecular interactions and what is the contribution of the Debye interaction, the Keesom interaction and London dispersion forces to the overall van der waals interaction okay that is what we are done.

So, what we will try and do today is these 2 topics, one is looking at van der Waal interaction between particles now and we will look at a very simple and nice concept called scaling of van der Waals interaction for macroscopic objects, what I mean by that is, if you so macroscopic objects corresponds to particles right, you know or any you know colloidal length scale species right okay.

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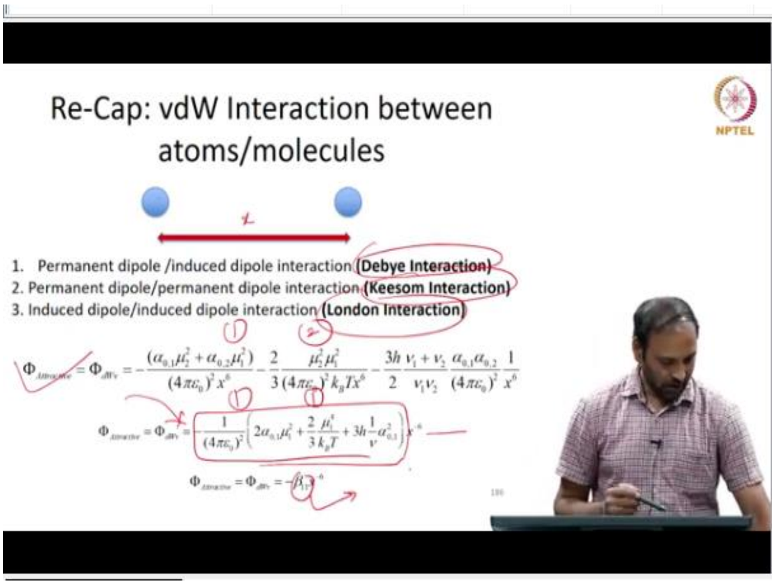

## Re-Cap: vdW Interaction between atoms/molecules

1. Permanent dipole /induced dipole interaction **(Debye Interaction)**
2. Permanent dipole/permanent dipole interaction **(Keesom Interaction)**
3. Induced dipole/induced dipole interaction **(London Interaction)**

$$\Phi_{Attractive} = \Phi_{vdW} = -\frac{(\alpha_{0,1}\mu_2^2 + \alpha_{0,2}\mu_1^2)}{(4\pi\varepsilon_0)^2 x^6} - \frac{2}{3}\frac{\mu_2^2\mu_1^2}{(4\pi\varepsilon_0)^2 k_B T x^6} - \frac{3h}{2}\frac{\nu_1+\nu_2}{\nu_1\nu_2}\frac{\alpha_{0,1}\alpha_{0,2}}{(4\pi\varepsilon_0)^2}\frac{1}{x^6}$$

$$\Phi_{Attractive} = \Phi_{vdW} = -\frac{1}{(4\pi\varepsilon_0)^2}\left(2\alpha_{0,1}\mu_1^2 + \frac{2}{3}\frac{\mu_1^4}{k_B T} + 3h\frac{1}{\nu}\alpha_{0,1}^2\right)x^{-6}$$

$$\Phi_{Attractive} = \Phi_{vdW} = -\beta_{11}x^{-6}$$

So, just to do a quick recap. So, this is what we had done in the last lecture. So, if I have 2 atoms or molecules which are separated by a distance x we said that the total contribution to the van der Waals forces or van der Waals interaction comes by the Debye interaction, Keesom interaction and London dispersion forces and this is what we wrote if we have 2 dissimilar you know atoms or molecules 1 and 2.

And that kind of simplifies to this equation if you have interaction between 2 similar atoms and we said that this all this constant here that is your beta, right that is what we had done and I also mentioned that this is analogous to you know the attractive term in the Leonard Jones potential right. That is what we are done okay.

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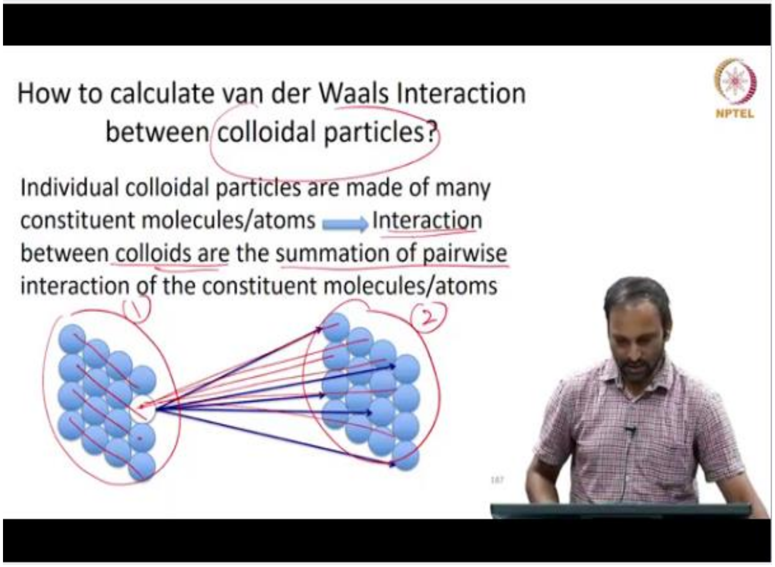

## How to calculate van der Waals Interaction between colloidal particles?

Individual colloidal particles are made of many constituent molecules/atoms → Interaction between colloids are the summation of pairwise interaction of the constituent molecules/atoms

Now so, if you want to calculate the van der Waals interaction between colloidal particles you know we can actually extend. So, here we are assuming that you know there are 2 atoms or 2 molecules which are interacting. Now you can consider a colloidal particle 1 and a colloidal particle 2 as consisting of collection of large number of atoms and molecules right. In fact we can calculate that right, if I know what is the size of the particle that I am dealing with.

And if I know you know the chemistry of the particle, if it is in a gold, silica or anything right I mean I should be able to calculate the number of atoms and molecules that constitute the colloidal particle that we are considering right. Now the interaction between colloidal particles are essentially summation of the pairwise interaction of the constituent atoms or molecules that make up the particle okay.

That means okay in this case I am considering a case where I have 4 ok 16 you know a particle which is made up of 16 atoms okay, similarly there is another particle which is again made up of similar number of atoms right. I take one particle and I look at you know its interaction with all of them okay, all the 16 right, then I go to the next one okay and again I look at the interaction with all the other 16 atoms of molecules.

And I sum them up okay. So, this pairwise addition of the interaction of every atom or the molecule that constitute a particle with the atoms and the molecules in the other particle is what gives rise to the total van der Waals force of interaction between colloidal particles okay.

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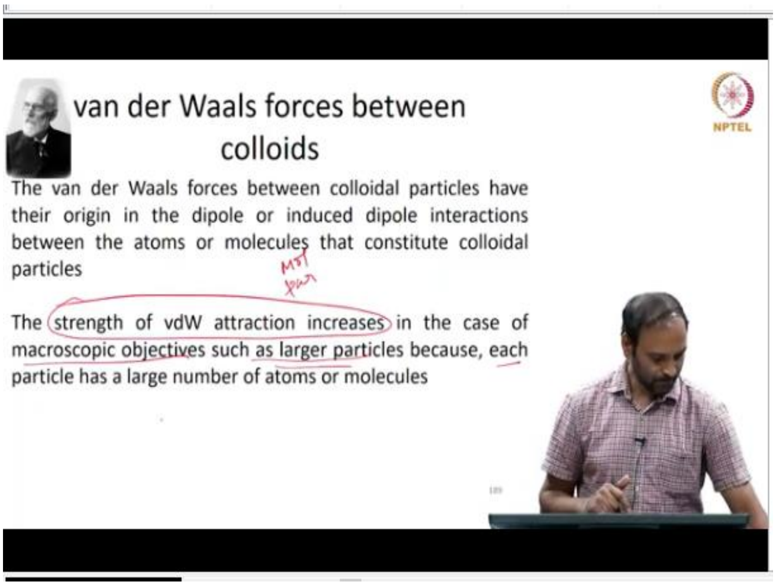

van der Waals forces between colloids

The van der Waals forces between colloidal particles have their origin in the dipole or induced dipole interactions between the atoms or molecules that constitute colloidal particles

The strength of vdW attraction increases in the case of macroscopic objectives such as larger particles because, each particle has a large number of atoms or molecules

So, that is again just like you know atoms and molecules the van der Waals force of interaction or van der Waals interaction between colloidal particles are again they have their origin in the dipole and the induced dipole interaction just like the atoms in the molecules, but one thing to keep in mind when you compare the interaction between molecules and particles is that the strength of van der Waals attraction okay.

In the case of macroscopic objects that is colloidal particles okay are much larger because each particle has a large number of atoms and molecules, that means if I were to calculate the strength of van der Waals interaction between atoms and molecules and compare that to the strength of van der Waals interaction between 2 macroscopic particles okay at a particular separation distance you will see that the strength of van der Waals interaction for the macroscopic particles is larger compared to that for the molecules and the atoms at the same separation distance okay.

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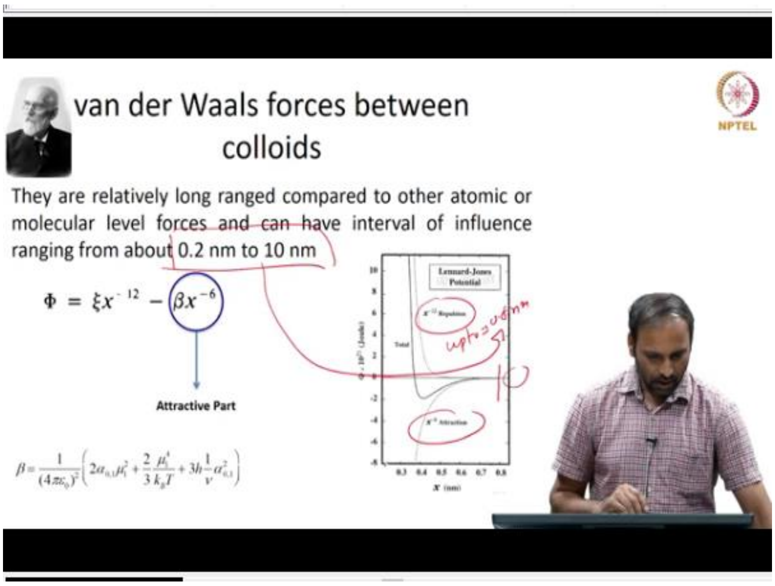

van der Waals forces between colloids

They are relatively long ranged compared to other atomic or molecular level forces and can have interval of influence ranging from about 0.2 nm to 10 nm

$$\Phi = \xi x^{-12} - \beta x^{-6}$$

Attractive Part

$$\beta = \frac{1}{(4\pi\varepsilon_0)^2}\left(2\alpha_{0,1}\mu_1^2 + \frac{2}{3}\frac{\mu_1^4}{k_BT} + 3h\frac{1}{\nu}\alpha_{0,1}^2\right)$$

So, the other thing to notice is that they are relatively long ranged compared to the atomic or molecular forces okay and they can have interval of influence ranging from about 0.2 nanometer to 10 nanometer okay, everybody understand the statement okay. Let us go back okay, I just want to make a point that they are long-ranged compared to the atomic or molecular forces okay.

For that I will again go back to this picture okay Leonard Jones potential okay, you look at both the repulsive part and the attractive part okay and if I were to write what is the range of interaction I can say it is up to about 0.8 nanometer right, beyond that distance you know you do not have to worry about the you know both the terms are essentially 0 that means you do not have to worry about these interactions beyond the distance okay.

But however if you take you know van der Waals forces between colloidal particles they have a range going from about 0.2 nanometer to 10 nanometer compared to 0.8 nanometer they are more long ranged right, that is the point that I want to make.

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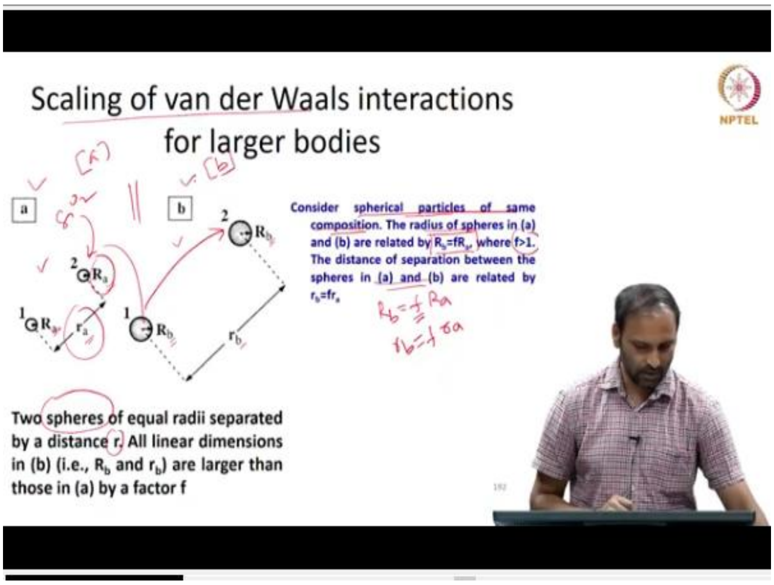

Scaling of van der Waals interactions for larger bodies

Consider spherical particles of same composition. The radius of spheres in (a) and (b) are related by $R_b=fR_a$, where f>1. The distance of separation between the spheres in (a) and (b) are related by $r_b=fr_a$

$R_b = f R_a$

$r_b = f r_a$

Two spheres of equal radii separated by a distance r. All linear dimensions in (b) (i.e., $R_b$ and $r_b$) are larger than those in (a) by a factor f

Now we will do a very simple exercise which is what is called as scaling of van der Waals interaction between large bodies or large particles okay. Good thing about this exercise is that it will also help you to think about how do people calculate van der Waals force of interaction between the particles okay or the macroscopic particles. So, what you have is a case a and case b okay.

That is you know there is a subscript a that corresponds to case a and there is a subscript b that corresponds to case b. So R is a radius of the particle and they are separated by distance r a in the first case and r b in the second case okay and both for case 1 or and case 2 or case a and case b the particles are of equal size okay and we are saying that they are spheres of equal size.

And they are separated by some distance okay, we will assume that the spherical particles are of same composition okay, that means if I were to think about a case a if I have taken say silica particles okay, the other particle will also be silica particle and then similarly all the particles will have the same composition okay. That is done just to keep things simple okay. You can do a similar kind of exercise also for you know the cases where the composition need not be same.

But you know for simplicity we have done that okay. So, these 2 individual cases case a and case b are in a way related because the radius of spheres in a and b are related by this R b is equal to f times R a okay, that means if you know because if f is greater than 1 the size of R b is greater than the size of the particles you know that you see in you know this R a by a factor f okay.

Similarly the distance of separation between the spheres in a and b are again related by a similar kind of way where r b is again f times r a okay. So, we will ask a question as to what can we say about the van der Waals force of interaction in the case a and what is the van der Waals you know force of interaction in the case b okay. That is a exercise that we will try and do okay.

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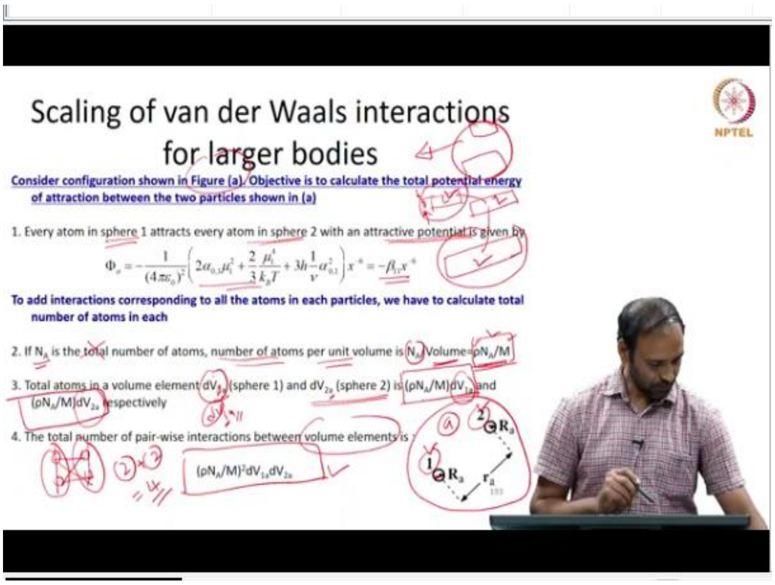

Scaling of van der Waals interactions for larger bodies

Consider configuration shown in Figure (a). Objective is to calculate the total potential energy of attraction between the two particles shown in (a)

1. Every atom in sphere 1 attracts every atom in sphere 2 with an attractive potential is given by

$$\Phi_a = -\frac{1}{(4\pi\varepsilon_0)^2}\left(2\alpha_{0,1}\mu_1^2 + \frac{2}{3}\frac{\mu_1^4}{k_BT} + 3h\frac{1}{v}\alpha_{0,1}^2\right)x^{-6} = -\beta_{11}x^{-6}$$

To add interactions corresponding to all the atoms in each particles, we have to calculate total number of atoms in each

2. If $N_A$ is the total number of atoms, number of atoms per unit volume is $N_A$/Volume=$\rho N_A/M$

3. Total atoms in a volume element $dV_{1a}$ (sphere 1) and $dV_{2a}$ (sphere 2) is $(\rho N_A/M)dV_{1a}$ and $(\rho N_A/M)dV_{2a}$ respectively

4. The total number of pair-wise interactions between volume elements is

$(\rho N_A/M)^2 dV_{1a}dV_{2a}$

So we will take configuration a that is given here okay. Now if I consider one atom in a and one atom in particle 1 and one atom in the particle 2 okay we know that there is a attractive van der Waals force of interaction okay, that means every atom in sphere 1 attracts every atom in sphere 2 with an attractive potential or energy which is given by phi a is equal to okay - beta 11 x power - 6 okay.

So, we know where that comes from okay. Now because we want to calculate the total interaction okay, before that what we have to do is we should calculate the number of atoms in particle 1 or sphere 1 and the number of you know atoms in particle 2 or sphere 2 right. If you define NA as the total number of atoms okay, if you define NA is the total number of atoms in the particle the number of atoms per unit volume is NA divided by volume.

I can you know relate volume to the density and the mass, therefore the number of atoms per unit volume okay is given by rho N A divided by M, is it ok right. N A is the total number of atoms divided by the volume of the particle will give you the number per unit volume right, number of atoms per unit volume right and that number is going to be same for both the particles right.

In fact whether I take because these are made up of same composition their same composition whether I take N A into rho divided by M, that is the number of atoms per unit volume whether I take particle 1 here, particle 2 here, or particle 1 here, particle 2 here, that number is going to be exactly same right, because their composition is same okay. Now if you take some differential volume element okay dV is a differential volume element in sphere 1 in configuration a okay.

This dV 1 a corresponds to a differential volume dV in sphere 1 in case a right, that is here, that is your case a. Similarly if dV 2 a is the differential volume that you consider in sphere 2 okay and again corresponding to case a, then this term and this term will give you the total number of atoms right, it will give you the total number of atoms that you have in the differential volumes d V 1 a and d V 2 a is it okay.

Yeah N is the total number of atoms you know yeah, in fact but the cases are different. Now so you are considering both have the same number of atoms in both the cases is the same, you see if I take a colloidal particle right I am saying that I have a colloidal particle okay. If it is a chemically homogeneous okay, if it is say gold nanoparticle for example, whether I take a very small fraction of the particle.

And I calculate what is the number per unit volume by considering this or I take another small volume and I calculate or I calculate for the entire particle itself it will be the same number right. So, therefore this rho N A by M, that is what I was trying to say right, whether I take case a or case b okay or any particle this number is going to be same because they are of same composition okay.

The total number of pairwise interactions are essentially the product of the total number of you know atoms that we have in the differential volume d V1 a and in the differential volume d V 2 a okay, that is the total number of pairwise interactions okay one of the way to think about this would be that imagine that I have 2 particles okay. There is a colloidal particle, just for the sake of simplicity.

There is a colloidal particle which has only 2 atoms okay. So, the number of pairwise interactions are interaction of this with this and this with this that makes it 2 okay and the interaction of this with this and this with this that makes it another 2 okay, therefore the total number of pairs interactions are 4**,** therefore the number of atoms in this multiplied by the number of atoms in this will give you the total number of pairwise interaction that you should consider right. That is this.

So, yeah I mean okay so N A is defined as the total number of atoms okay. Now okay, so do you guys have a confusion that why is this rho N A by M same for both the cases, is that your confusion, I mean okay let me put this way okay. So, say that I have gold nanoparticles okay and say that they are prepared say that you know I have made particles of different dimensions okay by a same technique for example.

I have used identical you know reaction to make these particles but I have a way of tuning the size okay, maybe you know we define this aspect ratio right, this is l divided by d is aspect ratio and aspect ratio is different in the 3 cases. Now if the reaction chemistry that is involved in the preparation of all of these are the same, then I would expect particles of same chemistry right, same composition right.

Now if the particles are of same composition whether I take this particle or this particle calculate the number of atoms per unit volume okay will be same for all of them right. So, all I am trying to do is define a quantity called number of atoms per unit volume okay, let us not say that you can say that N A is the number of atoms right okay in a given volume right. Therefore you can define number of atoms per unit volume that will be this quantity.

And because the compositions are the same this is going to be same for all the particles if you considered, is that okay. Therefore the total number of pairwise interactions okay between the volume elements that we have considered okay is this.

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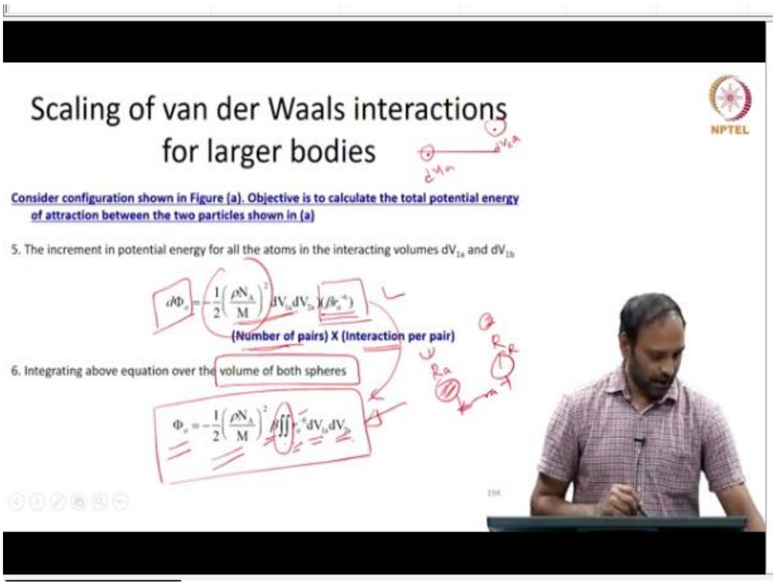

Scaling of van der Waals interactions for larger bodies

Consider configuration shown in Figure (a). Objective is to calculate the total potential energy of attraction between the two particles shown in (a)

5. The increment in potential energy for all the atoms in the interacting volumes $dV_{1a}$ and $dV_{1b}$

$$d\Phi_a = -\frac{1}{2}\left(\frac{\rho N_A}{M}\right)^2 dV_{1a}dV_{2a}(\beta r_a^{-6})$$

(Number of pairs) X (Interaction per pair)

6. Integrating above equation over the volume of both spheres

$$\Phi_a = -\frac{1}{2}\left(\frac{\rho N_A}{M}\right)^2 \beta\iint r_a^{-6}dV_{1a}dV_{2a}$$

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So, now instead of considering individual atoms or molecules, if I taken a differential volume now okay dV 1 a and dV 2 a right, then I can think about what is called as a the increment in the so they were interacting by some energy earlier, now because I am considering a large number of atoms right in each of these differential volumes. Then the increment in the interaction is given by, this is the this term that we had for interaction per pair right.

So, let us go back right this okay is a interaction per pair right multiplied by the number of pairs okay, the number of pairs multiplied by the interaction per pair okay will give you the increment in the interaction potential, if I want I can integrate that okay over the entire volume of the spheres, then I would get the total van der Waals you know force of attraction between every atom you know between the 2 particles now right.

Because I have considered all the atoms now, that is going to be a double integral right is going to be a volume integral right okay. So, I just have to integrate this okay because this is constant I have taken it out, beta is also constant because once the material that you are considering is fixed, beta is fixed therefore double integral of r a power - 6 because r a is the separation distance here right.

That is a separation distance now multiplied by the 2 differential volumes right. So, that is the total interaction potential between all the atoms in particle 1 which has a radius R a and the particle 2 which also has you know radius R and they are separated by a distance r a right.

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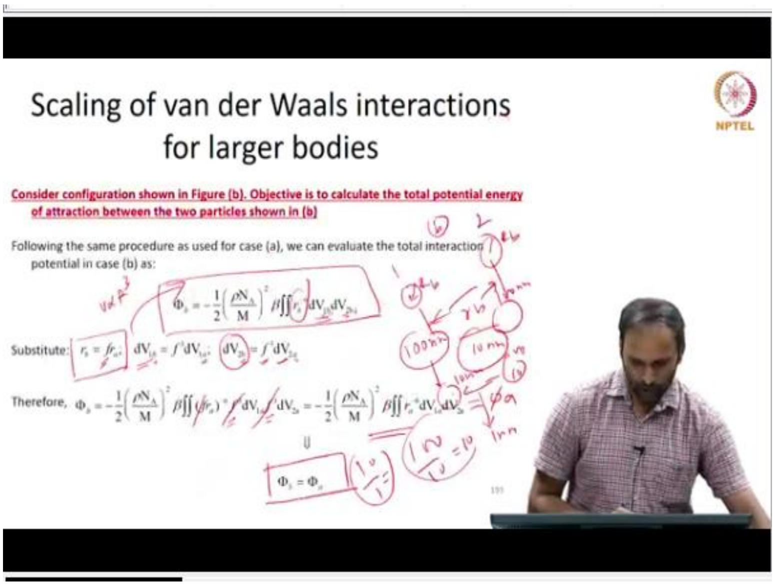

Scaling of van der Waals interactions for larger bodies

Consider configuration shown in Figure (b). Objective is to calculate the total potential energy of attraction between the two particles shown in (b)

Following the same procedure as used for case (a), we can evaluate the total interaction potential in case (b) as:

$$\Phi_b = -\frac{1}{2}\left(\frac{\rho N_A}{M}\right)^2 \beta \iint r_b^{-6}\, dV_{1b}\, dV_{2b}$$

Substitute: $r_b = f r_a$; $dV_{1b} = f^3 dV_{1a}$; $dV_{2b} = f^3 dV_{2a}$

Therefore, $\Phi_b = -\frac{1}{2}\left(\frac{\rho N_A}{M}\right)^2 \beta \iint (f r_a)^{-6} f^3 dV_{1a} f^3 dV_{2a} = -\frac{1}{2}\left(\frac{\rho N_A}{M}\right)^2 \beta \iint r_a^{-6}\, dV_{1a}\, dV_{2a}$

$$\Downarrow$$

$$\boxed{\Phi_b = \Phi_a}$$

I can do a similar exercise okay, what do you mean which are not related yeah I mean I could have in fact you know you know you do not have to go through this concept of differential volumes okay, you can also take the entire sphere and I can do it okay. Then it will be a much simpler you know exercise as well okay you can do that as well yeah. Now I can do a similar exercise okay and I can calculate the van der Waals force of interaction for the case 2 right.

For the case 2 we had again sphere 1 and sphere 2, they are separated by a distance R b right and of course there radius were also R b right and if I do that I will get a similar expression okay only thing is instead of r a I would have r b to the power of - 6 and you will have differential volume 1 in the case b, this is case b right. And the differential volume 2 in the case b.

Now we know that R a and R b are related right. R b is larger than R a by a factor f okay and because the volume goes as R to the power of 3 okay I can relate differential volume in the case of b to the differential volume in the case of a okay as dV 1 b is f cube times dV 1 a right. Similarly I can say dV 2 b that is the volume of the differential volume v 2 that I have considered in the case b is a factor f cube times differential volume in a right.

If I put them back into this expression. So, I have f R a power – 6, there is f 3, f 3 okay, this essentially gets cancelled what you end up with is whatever that you had for phi a, therefore this tells you that the van der Waals force of interaction in the case b is same as the van der Waals force of attraction in the case a okay. So, the implications of this is that if I take like say 100 nanometer particles okay.

And if I am talking about the van der Waals force of interaction between them like say at 10 nanometer okay or I take 10 nanometer particle and I am asking a question as to what is the van der Waals force of interaction at a separation distance 1 nanometer right. So, 100 divided by 10 is the scaling of the size okay, that is by a factor of 10. Let us look at scaling the distance 10 divided by 1 again there is a factor of 10.

In cases like this 100 nanometer particles at a separation distance of 10 nanometer will experience the same van der Waals force of attraction as the case where you have 10 nanometer particles separated by a distance of 1 nanometer okay. So, that is the implication of this result okay yeah. So, that is all I wanted to say today.

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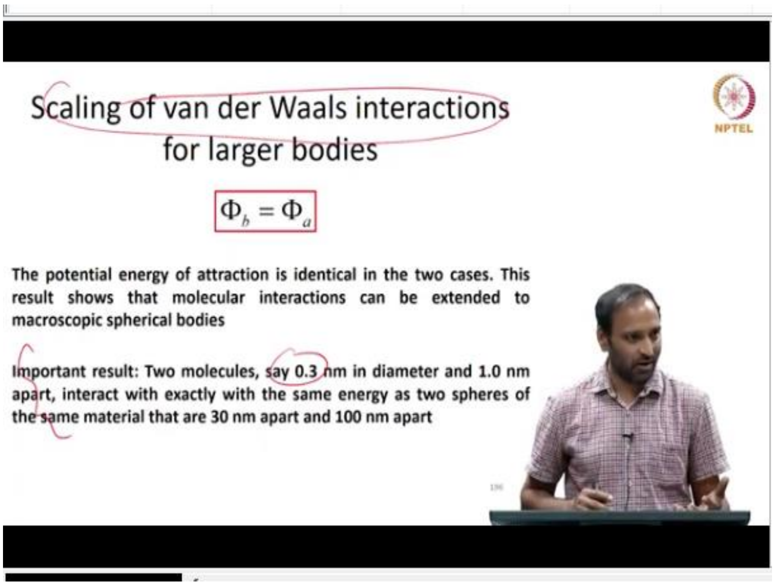

Scaling of van der Waals interactions for larger bodies

$$\boxed{\Phi_b = \Phi_a}$$

The potential energy of attraction is identical in the two cases. This result shows that molecular interactions can be extended to macroscopic spherical bodies

Important result: Two molecules, say 0.3 nm in diameter and 1.0 nm apart, interact with exactly with the same energy as two spheres of the same material that are 30 nm apart and 100 nm apart

And then what we will do is so yeah, so this is again I have kind of a similar thing that I mentioned right, if you take 0.3 yeah basically the same concept that I mentioned right, yeah.

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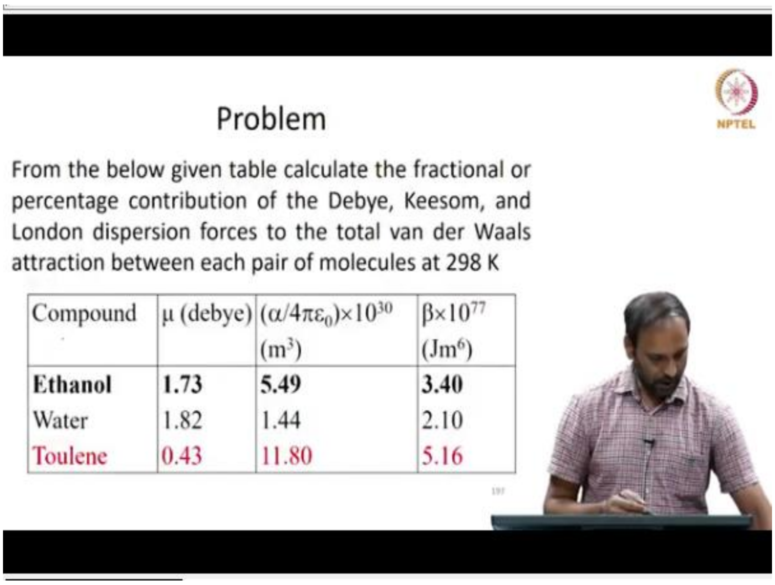

## Problem

From the below given table calculate the fractional or percentage contribution of the Debye, Keesom, and London dispersion forces to the total van der Waals attraction between each pair of molecules at 298 K

| Compound | μ (debye) | $(\alpha/4\pi\varepsilon_0)\times10^{30}$ ($m^3$) | $\beta\times10^{77}$ ($Jm^6$) |
|---|---|---|---|
| **Ethanol** | **1.73** | **5.49** | **3.40** |
| Water | 1.82 | 1.44 | 2.10 |
| Toulene | 0.43 | 11.80 | 5.16 |

Yeah, yeah that is why right I mean we were saying the scaling of van der Waals interaction right, that is what you know so that means if I take 2 cases where both the dimensions of the particles and the separation distance scale in the same way okay in 2 cases, in such cases the van der Waals force of attraction in the 2 cases will be identical okay, that is the you know crux of the result.