Colloids and Surfaces

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Lecture-17

Theories of Vanderwaal Forces Based on Bulk Properties and Calculation of Hamaker Constant Using Bulk Properties

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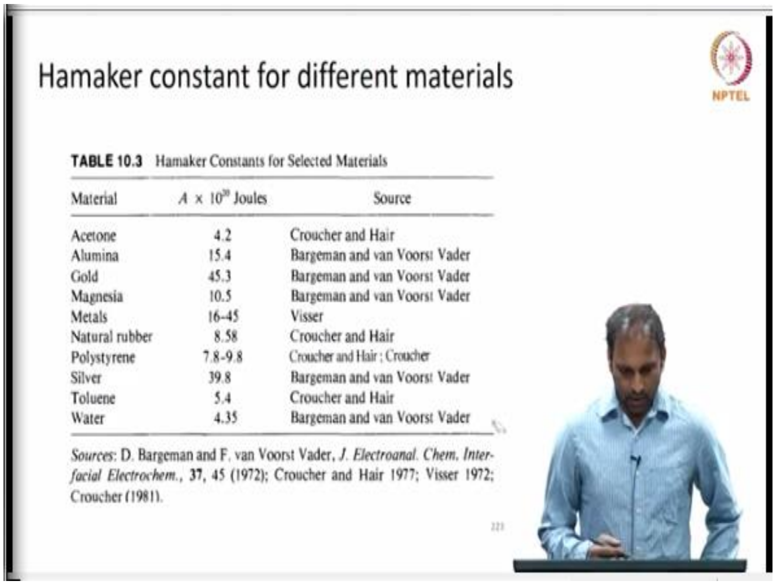

Hamaker constant for different materials

TABLE 10.3 Hamaker Constants for Selected Materials

Material	$A \times 10^{20}$ Joules	Source
Acetone	4.2	Croucher and Hair
Alumina	15.4	Bargeman and van Voorst Vader
Gold	45.3	Bargeman and van Voorst Vader
Magnesia	10.5	Bargeman and van Voorst Vader
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Toluene	5.4	Croucher and Hair
Water	4.35	Bargeman and van Voorst Vader

Sources: D. Bargeman and F. van Voorst Vader, *J. Electroanal. Chem. Interfacial Electrochem.*, **37**, 45 (1972); Croucher and Hair 1977; Visser 1972; Croucher (1981).

Ok, so in the last class we were talking about deriving an expression for van der Waals force of attraction between macroscopic bodies.

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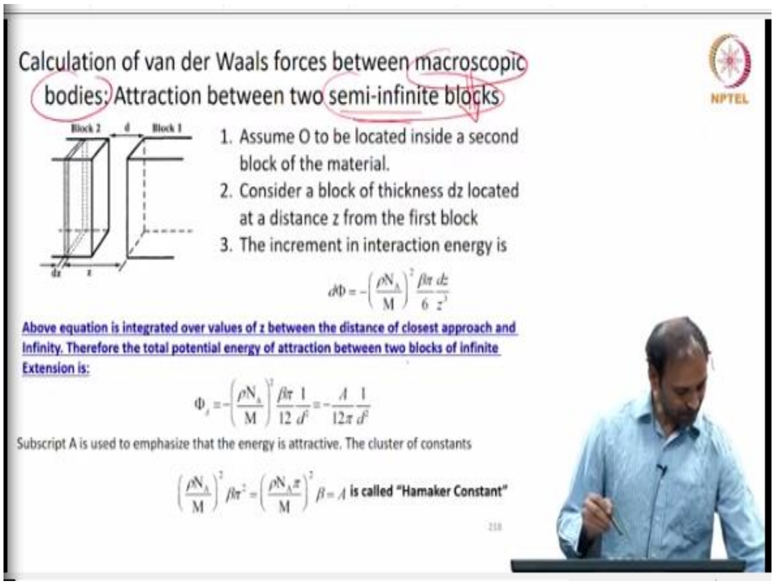

Calculation of van der Waals forces between macroscopic bodies: Attraction between two semi-infinite blocks

1. Assume O to be located inside a second block of the material.
2. Consider a block of thickness dz located at a distance z from the first block
3. The increment in interaction energy is

$$d\Phi = -\left(\frac{\rho N_A}{M}\right)^2 \frac{\beta\pi}{6}\frac{dz}{z^3}$$

Above equation is integrated over values of z between the distance of closest approach and Infinity. Therefore the total potential energy of attraction between two blocks of infinite Extension is:

$$\Phi_A = -\left(\frac{\rho N_A}{M}\right)^2 \frac{\beta\pi}{12}\frac{1}{d^2} = -\frac{A}{12\pi}\frac{1}{d^2}$$

Subscript A is used to emphasize that the energy is attractive. The cluster of constants

$$\left(\frac{\rho N_A}{M}\right)^2 \beta\pi^2 = \left(\frac{\rho N_A \pi}{M}\right)^2 \beta = A$$ **is called "Hamaker Constant"**

I just want to make a few points clear, one is that when you say between macroscopic bodies what it actually means is that these are not atoms or molecules, these are things that are much larger than that ok. And that means in this particular course this corresponds to the interaction between particles which are colloidal in size range ok.

You should not think macroscopic as really large bodies ok, this is what we are looking at is van der Waals interaction between semi infinite blocks where see the reason why you consider a semi infinite block is because when you do this integration, right. I do not have to you know I do not have to of course if I assume that there are finite blocks when I do this integration here right.

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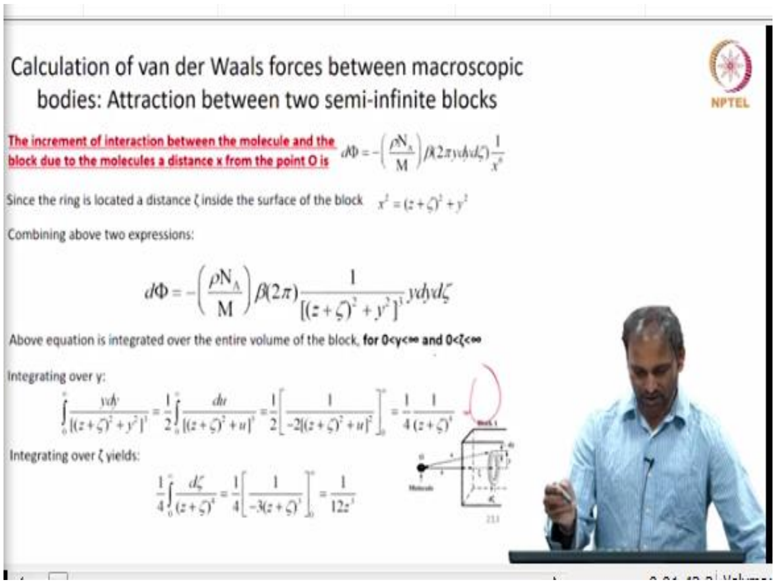

Calculation of van der Waals forces between macroscopic bodies: Attraction between two semi-infinite blocks

The increment of interaction between the molecule and the block due to the molecules a distance x from the point O is $d\Phi = -\left(\frac{\rho N_A}{M}\right)\beta(2\pi y\,dy\,d\zeta)\frac{1}{x^6}$

Since the ring is located a distance ζ inside the surface of the block $x^2 = (z+\zeta)^2 + y^2$

Combining above two expressions:

$$d\Phi = -\left(\frac{\rho N_A}{M}\right)\beta(2\pi)\frac{1}{[(z+\zeta)^2+y^2]^3}\,y\,dy\,d\zeta$$

Above equation is integrated over the entire volume of the block, **for $0<y<\infty$ and $0<\zeta<\infty$**

Integrating over y:

$$\int_0^\infty \frac{y\,dy}{[(z+\zeta)^2+y^2]^3} = \frac{1}{2}\int_0^\infty \frac{du}{[(z+\zeta)^2+u]^3} = \frac{1}{2}\left[\frac{1}{-2[(z+\zeta)^2+u]^2}\right]_0^\infty = \frac{1}{4}\frac{1}{(z+\zeta)^4}$$

Integrating over ζ yields:

$$\frac{1}{4}\int_0^\infty \frac{d\zeta}{(z+\zeta)^4} = \frac{1}{4}\left[\frac{1}{-3(z+\zeta)^3}\right]_0^\infty = \frac{1}{12z^3}$$

I would have another term which will come because of the finite size effects ok. So, to avoid you know these complications, so you have assume them to be semi infinite.

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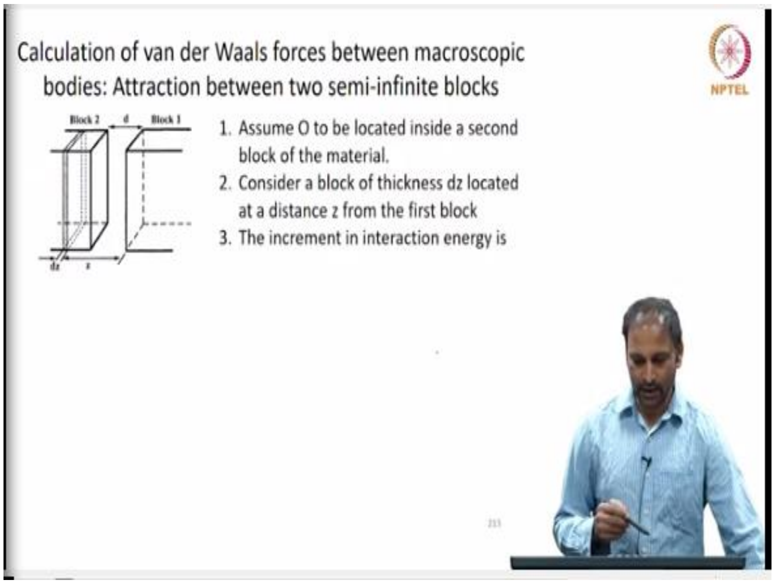

Calculation of van der Waals forces between macroscopic bodies: Attraction between two semi-infinite blocks

1. Assume O to be located inside a second block of the material.
2. Consider a block of thickness dz located at a distance z from the first block
3. The increment in interaction energy is

And the other question that was concerning you know some other discussion that we had is that.

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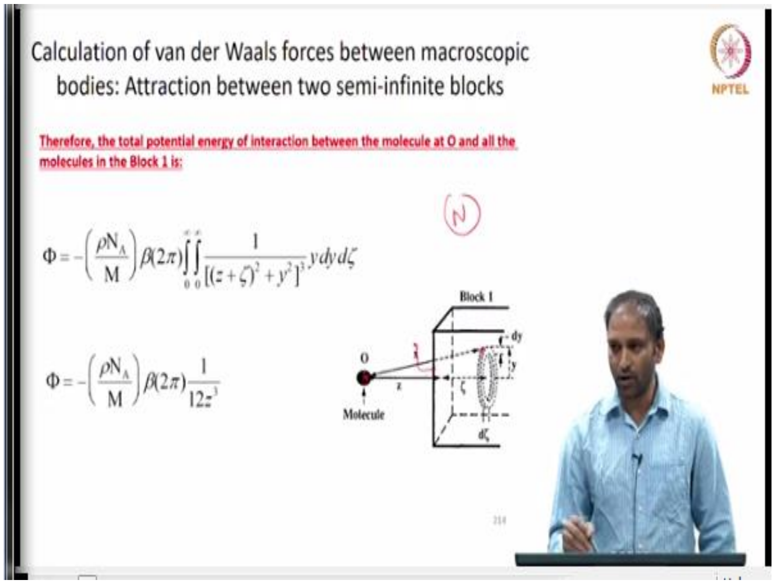

Calculation of van der Waals forces between macroscopic bodies: Attraction between two semi-infinite blocks

Therefore, the total potential energy of interaction between the molecule at O and all the molecules in the Block 1 is:

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$$\Phi = -\left(\frac{\rho N_A}{M}\right)\beta(2\pi)\int_0^\infty\int_0^\infty \frac{1}{[(z+\zeta)^2+y^2]^3} y\,dy\,d\zeta$$

$$\Phi = -\left(\frac{\rho N_A}{M}\right)\beta(2\pi)\frac{1}{12z^3}$$

See what we are doing here is the pair wise addition of interaction, ok. If I was doing the pair wise addition of you know the interaction forces, ok which will have you know in units of Newton. Then I would have to worry about resolving, ok because if we assume that the interactions act along the line that connects these 2 molecules, ok instead of interactions if I assume forces, then I would have to resolve that into 2 components one vertical and one horizontal.

And I would have to and I think because of the symmetry the vertical component would cancel each other. And the only you are goanna add only the horizontal component, right. You would have to do that if you are working with if you are derive an expression for the interaction force. But because we are doing you know we are working out the expression where the interaction energy, I do not have to worry about this, I just do the pair wise addition, ok.

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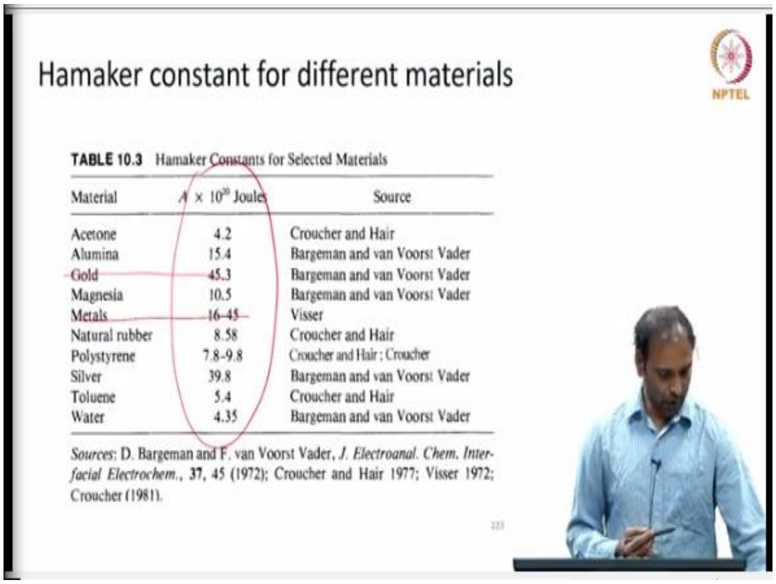

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Now, that is where we actually stopped right. So, we had listed down Hamaker constant for different materials. We mentioned that if you take a close look at you know these entries metals typically have a very high Hamaker constant, what essentially means is that if I have a dispersion of metallic particles, they are more prone to aggregation because of van der Waals forces compared to other materials that are listed here, ok, that is the ok.

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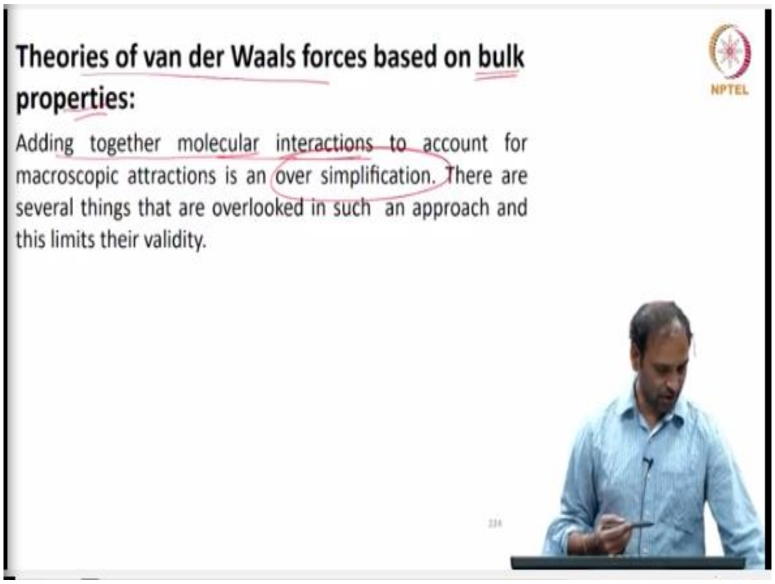

Theories of van der Waals forces based on bulk properties:

Adding together molecular interactions to account for macroscopic attractions is an over simplification. There are several things that are overlooked in such an approach and this limits their validity.

So, today what we will do is, we will try and look at what is called as theories for van der Waals forces based on bulk properties ok. And the reason why we want to do that is because the approach that we have followed so far there are some limitations ok. So, essentially the adding together of these molecular interaction that we have done so far it is an oversimplification, ok.

In this approach there are several things that are overlooked ok because of which this approach may not be applicable for all cases. That means you know there could be cases where we may have some limitation in terms of applying these theories, ok.

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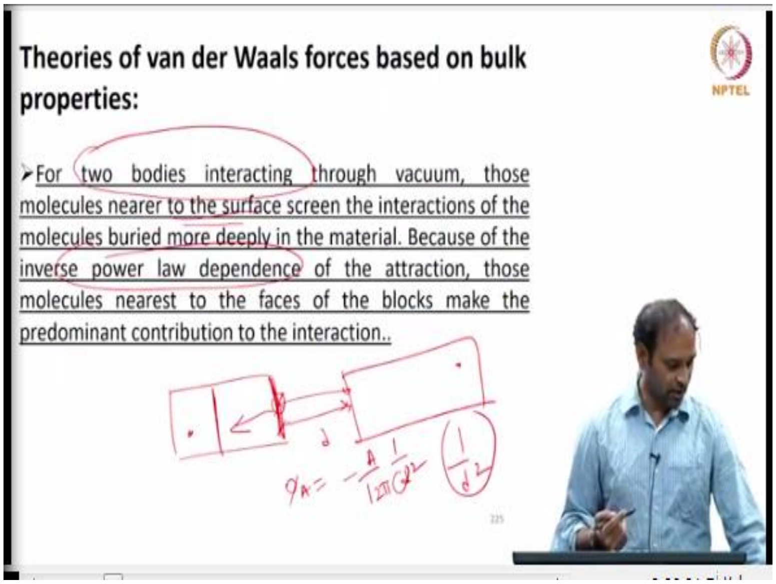

Theories of van der Waals forces based on bulk properties:

- For two bodies interacting through vacuum, those molecules nearer to the surface screen the interactions of the molecules buried more deeply in the material. Because of the inverse power law dependence of the attraction, those molecules nearest to the faces of the blocks make the predominant contribution to the interaction..

$\varphi_A = -\frac{A}{12\pi}\frac{1}{d^2}$ $\boxed{\frac{1}{d^2}}$

And again to give you a few indicators as to you know what we have kind of missed, ok. So, if you look at you know macroscopic bodies like this, right. And if it is semi infinite blocks, we said that you know this Vander Waals force of attraction goes as - 1 over 12 pi A into 1 over d square, right, that is what we derived, ok. Now, this d is the separation distance, right, that is the surface to surface separation distance ok.

However if you look at you know these blocks itself there are molecules that are close to the surface, ok. And there are molecules which are buried underneath ok, that is buried below the surface, ok. And we know that in this case of course you know the interaction goes is 1 over d square, right. That means the molecules that are closer to the surface ok. If I look at the interaction with the molecules on the surface of the 2 you know they will be more stronger.

However if I look at you know the molecular you know buried underneath ok they will have a weaker dependence ok what I mean by that is that if you have any 2 bodies interacting through vacuum ok. There is nothing in between these objects ok, the molecules near the surface ok will screen the interaction ok of the molecules that are you know buried underneath the material.

And because you have this inverse polar dependence ok, the molecules that are closer to the surface will contribute much more to the interaction than the molecule that are you know buried underneath ok. So, these kind of aspects were not considered in the derivation that we did ok.

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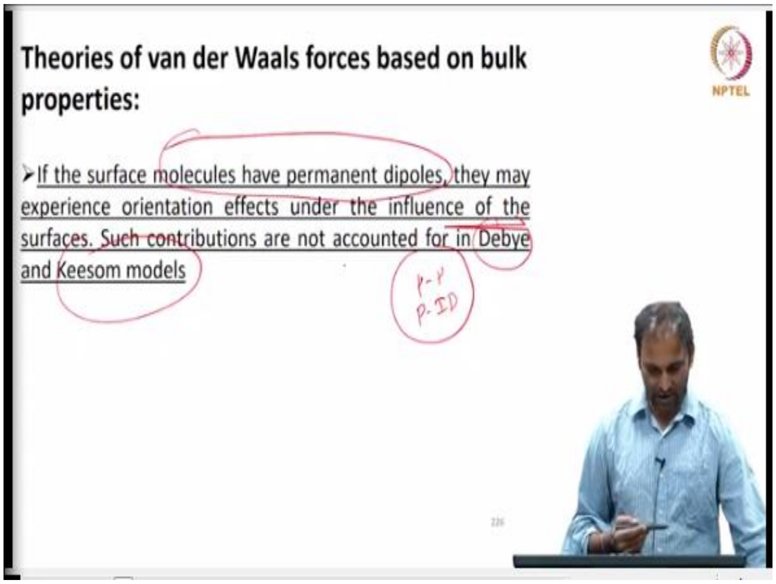

Theories of van der Waals forces based on bulk properties:

- If the surface molecules have permanent dipoles, they may experience orientation effects under the influence of the surfaces. Such contributions are not accounted for in Debye and Keesom models

The other effect that one may have to worry about is that you could have cases where you have particles and on the surface there could be molecules which have permanent dipole ok. Now if your particles like that when such particles are sufficiently close, there could be some orientation effect that may come into picture because of the presence of dipoles on the surface itself ok.

And if you look at you know Debye interactions and Keesom interactions which essentially deal with interaction between permanent dipole and permanent dipole and induced dipole ok. So, we kind of neglected such you know effects when we derived you know expression for when we talked about van der Waals force of interaction.

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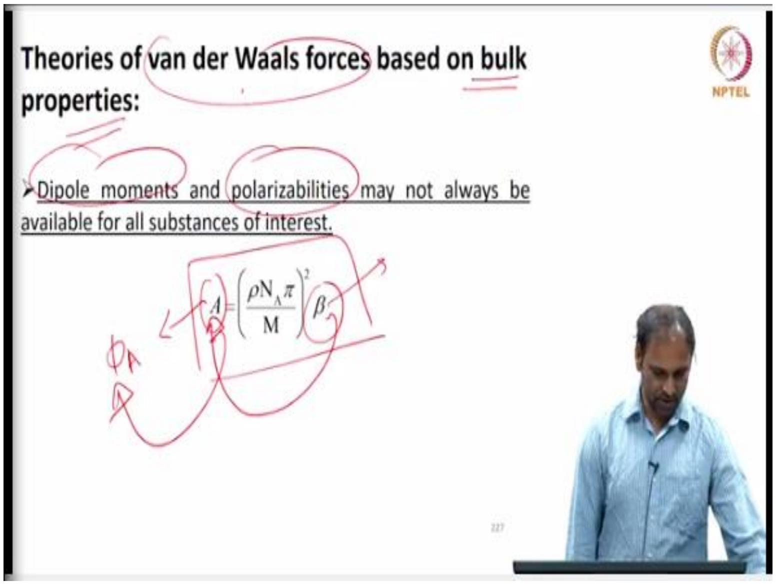

Theories of van der Waals forces based on bulk properties:

- Dipole moments and polarizabilities may not always be available for all substances of interest.

$$A = \left(\frac{\rho N_A \pi}{M}\right)^2 \beta$$

The other issue could be that I mentioned that this is a expression that you can use for calculating Hamaker constant, right. And if I know Hamaker constant I can actually calculate what is the van der Waals force of attraction, if I know the geometry of the 2 objects that are interacting right. And if I want to calculate Hamaker constant then I should know beta, ok and beta may or may not be available for all the materials, ok.

And we know that this beta again in turn will depend on the dipole moments and the polarizabilities right. If I do not have access to those values, I cannot calculate beta then further I cannot calculate A and then further I cannot calculate interaction potential, ok. So, therefore there is a need to look at theories in which I can kind of relate the van der Waals force of interaction to the bulk properties of the material itself ok.

If I have a material and if I am able to get hold of some physical property or some property that is specific to the material. And if I have a way of measuring it and if I am able to relate Vander Waals forces to those properties then you know I can have a way of assessing what is the Van der Waals force of interaction between the colloidal particles, right.

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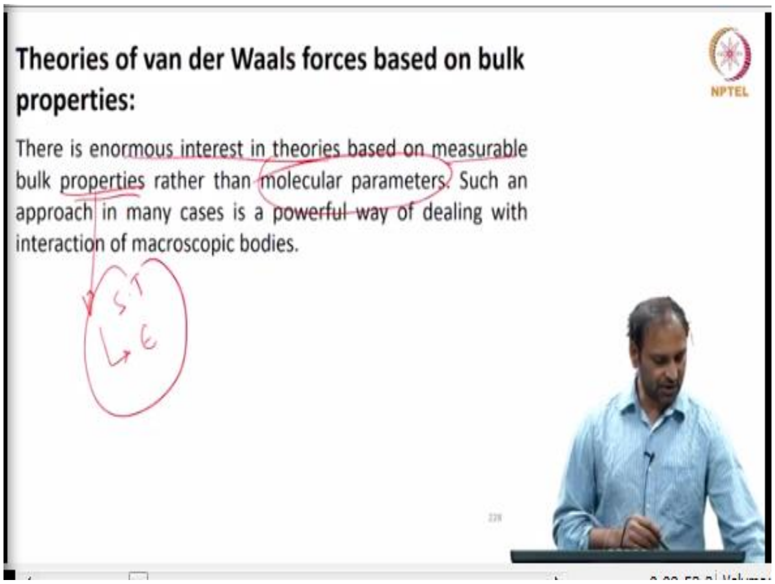

Theories of van der Waals forces based on bulk properties:

There is enormous interest in theories based on measurable bulk properties rather than molecular parameters. Such an approach in many cases is a powerful way of dealing with interaction of macroscopic bodies.

So, therefore there is enormous interest in theories based on measurable bulk properties, ok, when I say measurable properties I mean we are talking about properties like you know surface tension ok. There are properties like say dielectric constants and things like that, ok. If I can measure the certain bulk properties and if I have a way of relating these bulk properties to the Hamaker constant or the Vander Waals force of interaction rather than the molecular properties.

Then there is an interest in doing that because of the limitation that I have discussed so far, ok. So, we are going to look at some of these theories one by one.

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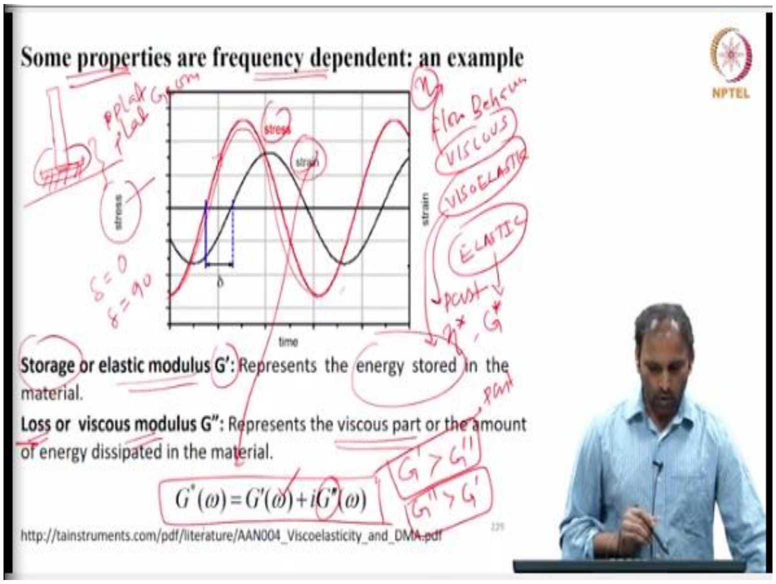

Some properties are frequency dependent: an example

Storage or elastic modulus G': Represents the energy stored in the material.

Loss or viscous modulus G": Represents the viscous part or the amount of energy dissipated in the material.

$$G^*(\omega) = G'(\omega) + iG''(\omega)$$

http://tainstruments.com/pdf/literature/AAN004_Viscoelasticity_and_DMA.pdf

Before I do that I would like to introduce a concept that certain properties of a material they are frequency dependent, ok. So, for that I have taken an example where see in materials right. You can classify materials into 3 classes in terms of their what is called the flow behavior ok, viscous materials ok and elastic materials, ok. These are more liquid like you know simple fluids that you can think of elastic materials are solids.

But there are materials which are in between they what are called as viscoelastic ok. And one of the common example of such material could be something like let us say paste for example or toothpaste that people use, ok, or ointment and things like that, ok. Now so while you can use for viscous materials you can use a property called viscosity right, to characterize it is flow behavior. If you have if one works with you know solids then you can talk about something like called elastic modulus ok.

But for materials which are viscoelastic people talk about something called as a complex viscosity ok or something called as a complex modulus, ok. And the way these measurements are done is ok, you take a we know that whenever you want to obtain any mechanical response of materials, you apply stress and measure the strain, right, that is what you do, right. Now if you take like say solids ok and if you apply some stress ok and look at what is the response that is strain in the material.

Then you will see that there is a phase shift between the stress and the strain. And then that phase shift is typically 0 this delta right I mean you know. That means if I have a stress it will you know essentially strain will also be something like that ok. However if you do a similar measurements when you apply a stress and then monitor what is the strain for a viscous material, you will see that you know the stress and the strain are completely out of phase, that means your delta is going to be 90, ok.

However for these viscoelastic materials you know your phase shift is going to be between 0 and 90. And depending upon the extent of phase shift you can say something about whether the material is closer to viscous behavior or the material is very close to the elastic kind of a material ok. And so therefore what people do is and you know I can apply this stress and strain in a sinusoidal way.

Then measure what is called as a frequency dependent you know material response ok. And that frequency dependent response it will have 2 terms one is what is called G prime or the elastic modulus also called as storage modulus ok, which represents something about the energy stored in a material. Because we know that you know when you take a solid ok if you are below the yield limit right, you can if I apply any stress to the material and if you release it right.

I mean you know say essentially it stores the energy that you know you apply right. And similarly you have G double prime which is what is called as a loss modulus or viscous modulus which represents the viscous component. Or it will tell you something about you know how much the energy is dissipated ok into the material, ok. And again there are ways of measuring it ok depending upon whether G prime is greater than G double prime or G double prime is greater than G prime you know one kind of tells you something about you know.

If G prime is greater than G double prime, then typically these materials are mostly like paste like for example, ok. Or if G double prime the viscous component is more than G double prime is going to be more liquid like and things like that, ok. So, therefore there are cases where people are interested to measure frequency dependent properties. I have given an example of a case where the frequency dependent properties are measured for particular material in which you wanted to assess their flow behavior, ok.

Now if yeah. So, typically the way these experiments are done is something like that ok. I have a like say there is a shaft ok. And then I have at the end there is a it could have a it is like say disk for example, ok. And then there is a bottom plate ok, you put your material here, ok, this is a classic example of what is called as a plate-plate geometry ok. And then what you do is I have a way of controlling the osil I mean what I can do is I can take the top plate and I can move it back and forth ok.

And I can do the back and forth movement either slowly or very fast ok, thereby I can actually change the frequency right, ok. So, then you look at you know if you are doing that in a stress control Rheometer what you do is you know what stress you applied, ok. And there are ways by which I can measure the strain, ok. And if I know the stress strain behavior, I can actually back calculate what is you know G, G prime, G double prime G star, there are ways to do that, ok.

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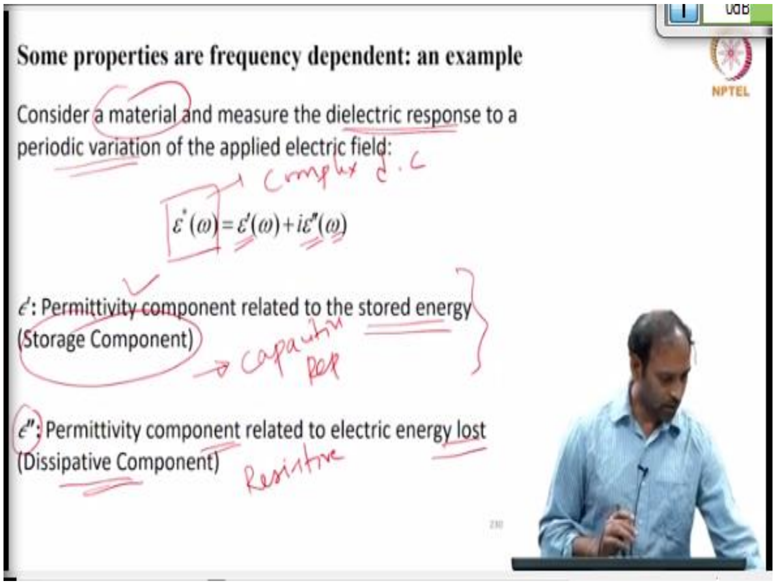

Some properties are frequency dependent: an example

Consider a material and measure the dielectric response to a periodic variation of the applied electric field:

complex d.c

$$\varepsilon^*(\omega)=\varepsilon'(\omega)+i\varepsilon''(\omega)$$

ε': Permittivity component related to the stored energy (Storage Component)

capacitive res

ε'': Permittivity component related to electric energy lost (Dissipative Component)

Resistive

Now another property which would be of interest for this particular you know lecture is a something called a complex dielectric constant ok. In which again what you do is you take a material of interest ok and then you measure the dielectric response ok to a periodic variation of the applied electric field ok. And I can of course change the frequency of the applied dielectric field ok.

And I can measure what it is called as a E star which is the complex dielectric constant which will again have 2 components you know epsilon prime and epsilon double prime are analogous to what I mentioned earlier. So, there is a storage component ok that is the permittivity component that is related to the energy storage ok. And there is a permittivity component, that is related to the energy loss ok.

And if you have a material where E prime dominates people typically call it as what is called as a capacitive response. Because we know that the capacitors are known to storage electric energy right, there are devices where you can store electric energy. And if E double prime is prominent people call it as what is called as a resistive response ok which is the dissipative component ok.

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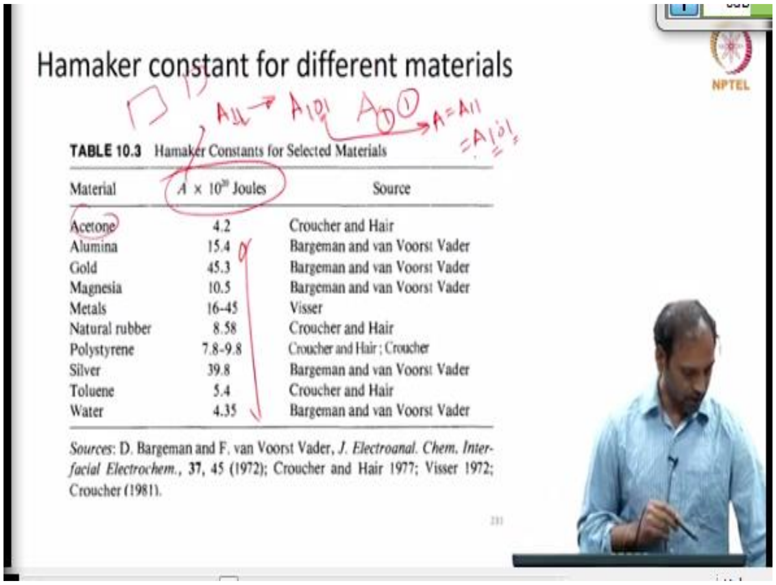

Hamaker constant for different materials

$A_{11} \rightarrow A_{101}$ $A_{0①0}$ $\rightarrow A = A_{11} = A_{101}$

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Acetone	4.2	Croucher and Hair
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So, with this background there is one particular theory which is ok. Before I do that I just want to mention one more you know important point. So, whenever you have table like this ok, when you say A is given you know there is list of tables, what this A essentially what it means is that this is the Hamaker constant for interaction between similar blocks ok or similar materials. This should actually be A_{11} ok, that means it is the energy of interaction between like say in this case acetone and acetone molecule ok or a block of acetone and a block of acetone ok, right.

But for more general convention is to write A_{11} with another number in between ok, this number tells you something about the medium in which these materials are placed ok, 0 if it is in vacuum ok. Therefore your A should actually be A_{11} or A_{101} ok, these are Hamaker constant for you know interaction of the same material interacting you know through vacuum ok.

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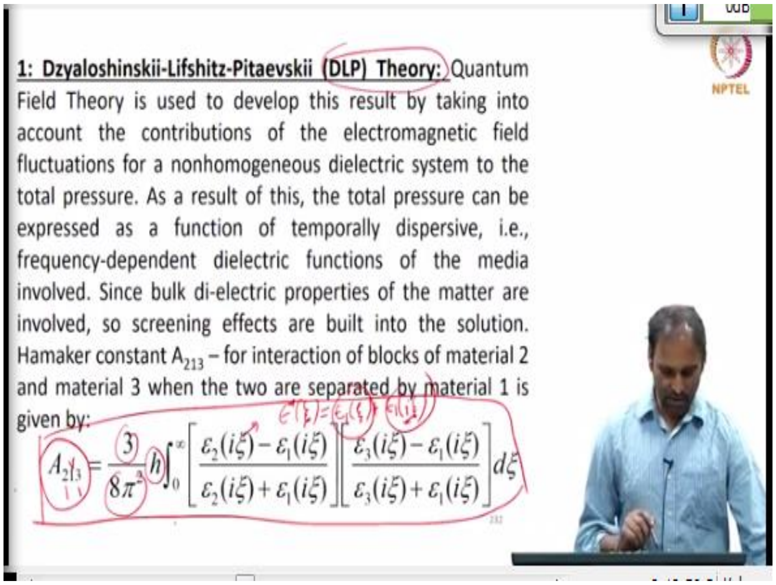

1: Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) Theory: Quantum Field Theory is used to develop this result by taking into account the contributions of the electromagnetic field fluctuations for a nonhomogeneous dielectric system to the total pressure. As a result of this, the total pressure can be expressed as a function of temporally dispersive, i.e., frequency-dependent dielectric functions of the media involved. Since bulk di-electric properties of the matter are involved, so screening effects are built into the solution. Hamaker constant A_{213} – for interaction of blocks of material 2 and material 3 when the two are separated by material 1 is given by:

$\epsilon^*(\xi) = \epsilon_1(\xi) + \epsilon_{11}(i\xi)$

$$A_{213} = \frac{3}{8\pi^2} h \int_0^\infty \left[\frac{\varepsilon_2(i\xi) - \varepsilon_1(i\xi)}{\varepsilon_2(i\xi) + \varepsilon_1(i\xi)}\right]\left[\frac{\varepsilon_3(i\xi) - \varepsilon_1(i\xi)}{\varepsilon_3(i\xi) + \varepsilon_1(i\xi)}\right] d\xi$$

So, there is the first theory is something called as a DLP theory ok. Again derivation is beyond the scope, but I would like to point to this particular expression because it tells us some nice things, ok. So, when you say A_{213} that is interact in a Hamaker constant for interaction of 2 with 3 and 1 is the medium in between them ok which goes as 3 divided by 8 pi square, h is a Planck's constant, ok, 0 infinity.

And so we have written, so this is the frequency right. So, we said that you know if you look at epsilon star ok is epsilon 1 in this case plus for some reason here this i is taken inside the. But anyway so there is a storage component and there is a loss component, ok. And, what you do is, so basically what is important in this case is that look, I should have measured the frequency dependent epsilon for all the 3 materials of interest, ok.

So, once I have access to that, I can substitute that in this expression and I can actually evaluate A_{212} that is all that is required at this point, ok.

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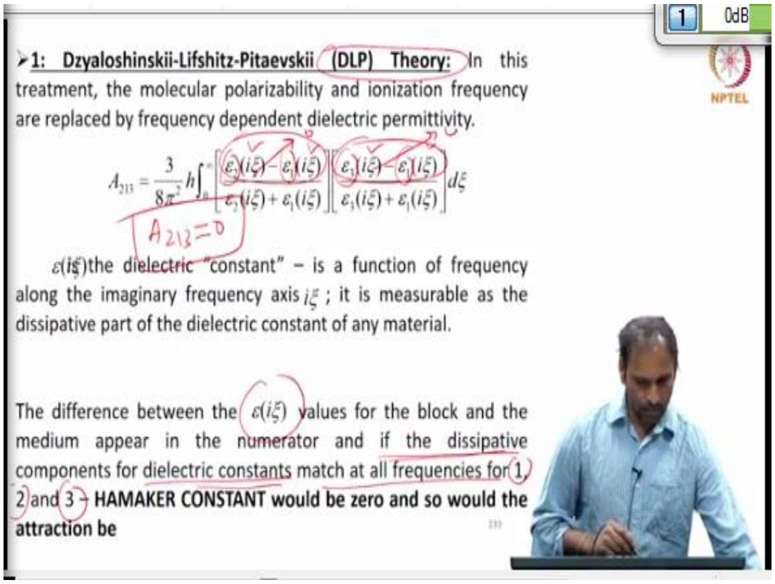

1: Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) Theory: In this treatment, the molecular polarizability and ionization frequency are replaced by frequency dependent dielectric permittivity.

$$A_{213} = \frac{3}{8\pi^2} h \int_0^\infty \left[\frac{\varepsilon_2(i\xi) - \varepsilon_1(i\xi)}{\varepsilon_2(i\xi) + \varepsilon_1(i\xi)}\right]\left[\frac{\varepsilon_3(i\xi) - \varepsilon_1(i\xi)}{\varepsilon_3(i\xi) + \varepsilon_1(i\xi)}\right] d\xi$$

$\boxed{A_{213} = 0}$

$\varepsilon(i\xi)$ the dielectric "constant" – is a function of frequency along the imaginary frequency axis $i\xi$; it is measurable as the dissipative part of the dielectric constant of any material.

The difference between the $\varepsilon(i\xi)$ values for the block and the medium appear in the numerator and if the dissipative components for dielectric constants match at all frequencies for 1, 2 and 3 → **HAMAKER CONSTANT would be zero and so would the attraction be**

Now the other nice things this tells you is that look at these numbers ok what you have is the you have the difference in the dissipative component of so they whatever is with i is the dissipative component of the dielectric constant. And what you have is a difference right, there is a difference in the dissipative component of the dielectric response between the particle 2 you know epsilon for the particle 2 and that for 1 and similarly that for 3 and that for 1 ok.

Now because you have the difference ok, if you have cases where if the dissipative component for a dielectric constants match for all the frequencies for 1, 2 and 3. Then this quantity can be 0, this quantity can be 0, therefore your A_{213} can indeed be 0 ok. If whenever you have A_{212} is 0 you know your Hamaker constant is 0. That means your van der Waals force of attraction would also be 0. So, therefore the knowledge that ok that van der Waals forces are always present ok, you can defy that ok.

If you are working in a with materials where for example, there are people who would be interested in look at experiments where the van der Waals forces can be switched off and then look at other kinds of interactions ok. So, in such cases you know something like this will help you know I can design an experiment where I choose a material 2, 1 and 3. Such that the frequency response you know are the same ok, the frequency response of the dissipative component are the same, therefore your A_{212} is going to be 0.

Therefore I can completely get rid of van der Waals force of in attraction, I can look at other effects that you may be interested to study, ok. So, that is about this DLP theory ok.

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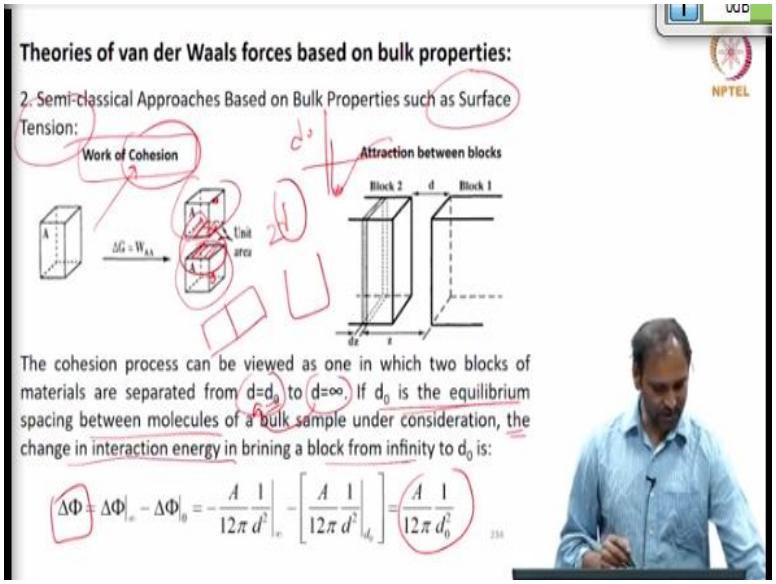

Theories of van der Waals forces based on bulk properties:

2. Semi-classical Approaches Based on Bulk Properties such as Surface Tension:

The cohesion process can be viewed as one in which two blocks of materials are separated from d=d$_0$ to d=∞. If d$_0$ is the equilibrium spacing between molecules of a bulk sample under consideration, the change in interaction energy in brining a block from infinity to d$_0$ is:

$$\Delta\Phi = \Delta\Phi\big|_{\infty} - \Delta\Phi\big|_{0} = -\frac{A}{12\pi}\frac{1}{d^2}\bigg|_{\infty} - \left[\frac{A}{12\pi}\frac{1}{d^2}\bigg|_{d_0}\right] = \frac{A}{12\pi}\frac{1}{d_0^2}$$

So, the other approach you know is to kind of relate you know this Hamaker constant or the van der Waals force of attraction. In turn that van der Waals force of attraction to surface tension, ok. So, we know we can talk about all of us know about work of cohesion, right. That means if I have 2 blocks, ok and if I just bring them together, ok. Then because you are people typical talk about the work of addition or cohesion as 2 times gamma, right, where.

Because you have 2 surfaces, you are joining them, ok, right, and this gamma is the surface tension, right. But other way of looking at cohesion process, ok, what do you mean by other way of looking at cohesion you know is that I have 2 blocks that are infinitely far apart. I bring them close and I join them, ok, when I joined them I can think about the distance between the molecules could be some value say let us say d$_0$, right.

So, we know that if you look at any material there is some equilibrium separation distance between the particles, right, ok. Let us think about an experiment, right, so I have you know this imaginary experiment. So, I have a let us say a block of water, ok, I have 2 blocks of water, initially they are far apart, I just bring them together and I make a single block ok. Now if I calculate what is the energy ok.

So, in this concept what is thought about is that I can think about the work of adhesion ok, as the van der Waals force of attraction between the 2 blocks, ok. In which what you do is, so you initially your materials are separated you know by like say very large distance what you do is, you kind of bring them close. And then join them such that the this is a separation between the molecules is now d_0 ok.

In this d_0 is the equilibrium spacing between the molecules of a bulk sample ok. So, if I do that you can actually calculate what is the change in the interaction energy to bring a block from infinity to d_0 ok. That essentially is - A divided by 2 pi 1 over d square because I am considering a case of 2 semi infinite blocks ok infinity - A by 2 pi 1 over d square d_0. Yeah, what do you mean by equilibrium spacing.

See in this case, if I am talking about block of water, ok. So, we know that because you have various interactions between water molecules the fact that they are still you know in the liquid state is because there is some overall interaction energy, ok. The balance of the attraction and repulsion all this will give you. So, if you look at like say Lenard-Jones potential, right, if you look at, ok, we talked about if you add the 2 components, so, you had something like this, right.

So, I am talking about that separation distance, that is a equilibrium separation distance between you know the atoms that constitute the bulk material. Yes, this is going to be in sub you know nanometer kind of ok, so, I mean maybe let us put it this way, right. When this cohesion happens, right ok, it is a process of bringing 2 blocks together and then joining them, ok. Now, if I were to think about what happens between the surface of the molecules that are on you know one block and the surface of the material on the other block.

When you are joining them you know in essence what it actually means is that they were very far apart initially. I am putting them together, so that the separation distant become d_0 ok and that separation distance is same as the separation distance that there and the separation distance there, ok that is the concept, right, yeah, ok. Therefore your the change in the interaction energy is A divided by 12 pi into 1 over d_0 square, where d_0 squared is the inter particle inter you know molecular spacing.

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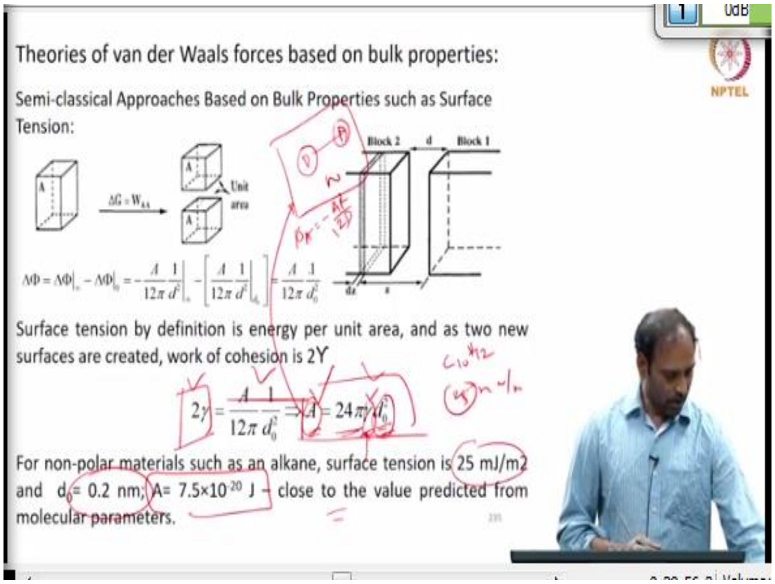

Theories of van der Waals forces based on bulk properties:

Semi-classical Approaches Based on Bulk Properties such as Surface Tension:

$$\Delta\Phi = \Delta\Phi|_{\infty} - \Delta\Phi|_{d_0} = -\frac{A}{12\pi}\frac{1}{d^2}\Big|_{\infty} - \left[\frac{A}{12\pi}\frac{1}{d^2}\Big|_{d_0}\right] = \frac{A}{12\pi}\frac{1}{d_0^2}$$

Surface tension by definition is energy per unit area, and as two new surfaces are created, work of cohesion is 2Y

$$2\gamma = \frac{A}{12\pi}\frac{1}{d_0^2} \Rightarrow A = 24\pi\gamma d_0^2$$

For non-polar materials such as an alkane, surface tension is 25 mJ/m2 and d_0= 0.2 nm; A= 7.5×10^{-20} J – close to the value predicted from molecular parameters.

And, the same as I said the work of cohesion is actually 2 times gamma, ok. Therefore I can equate the two and thereby I can get an expression which is a you know Hamaker constant A goes as 24 pi gamma into d_0 square, ok. And you can actually work a few things out, right. So, if you take, for example there is an example that is given here, if you take something like decane for example, ok, $C_{10}H_{12}$, right that is decane.

So, typical values of surface tension are about 25 you know milli joules per meter square or 25 milli newton per meter, ok, that is the surface tension, so I have that value. And d_0 is the spacing between the molecules, ok, typically you know 0.2 nanometer. If I put in these numbers, it turns out that you know the value that of A that I get is actually A is 7.5 into 10 power - 20 joules, ok, which is actually very close to what is been predicted.

So, at least for simple fluids, if you are working with dispersions which have like say emulsions for example, ok. If I have an emulsion of like say decane droplets in water, ok, if I want to calculate what is the interaction between the two. If you do not have access to the Hamaker constant, ok, then actually I can approach you know I can go with this approach wherein I know what will be the surface tension, ok.

And I know what is the equilibrium separation distance between the molecules that constitute you know the droplets. And I can actually get A from which in turn and if I assume that they are a spherical you know droplets, then I can actually go by and say that phi A goes something like - A times R divided by 12 D, right, that was a formula that we looked up, ok, I can actually calculate van der Waals interactions in this way, ok.

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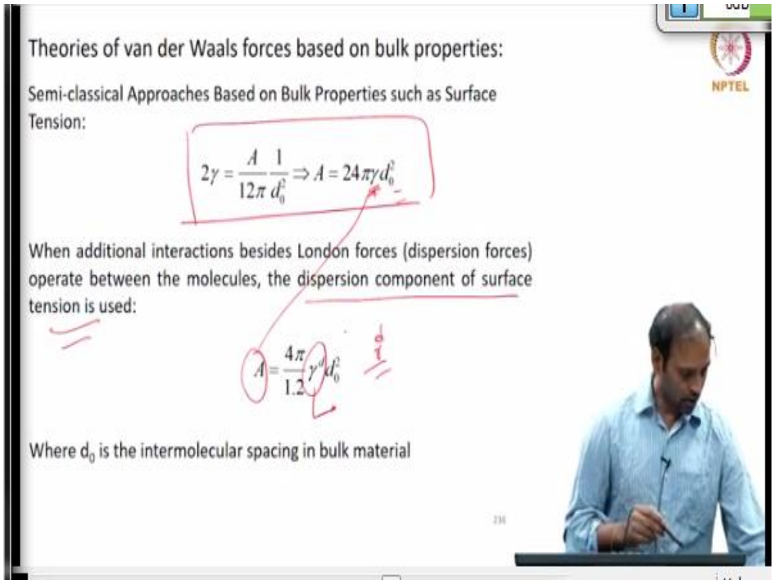

Theories of van der Waals forces based on bulk properties:

Semi-classical Approaches Based on Bulk Properties such as Surface Tension:

$$\boxed{2\gamma = \frac{A}{12\pi}\frac{1}{d_0^2} \Rightarrow A = 24\pi\gamma d_0^2}$$

When additional interactions besides London forces (dispersion forces) operate between the molecules, the dispersion component of surface tension is used:

$$A = \frac{4\pi}{1.2}\gamma^d d_0^2$$

Where d_0 is the intermolecular spacing in bulk material

So, there are I mean this is what we have just done right. So, you know 24 pi gamma d_0 square. There are also approaches where you relate A instead of to gamma you relate that to what is called as a gamma d ok. Where gamma d is what is called as it is the dispersion component of the surface tension ok, what it actually means is that.

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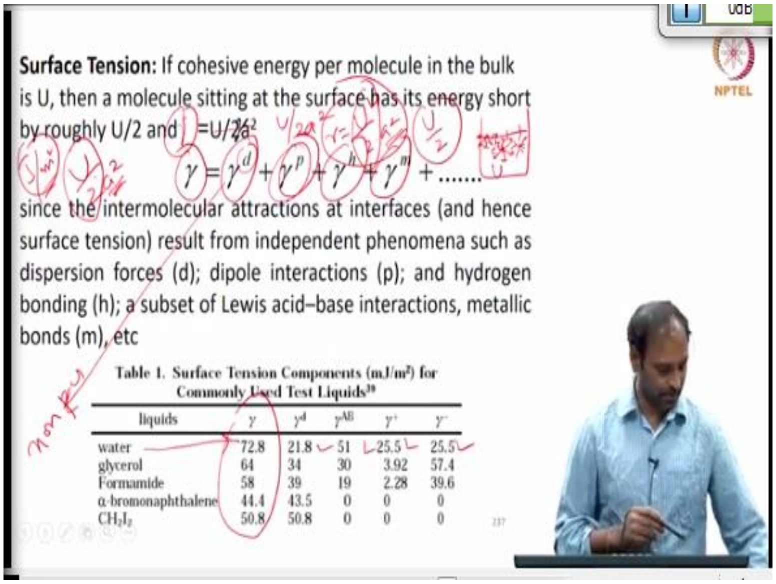

Surface Tension: If cohesive energy per molecule in the bulk is U, then a molecule sitting at the surface has its energy short by roughly U/2 and =U/2a^2

$$\gamma = \gamma^d + \gamma^p + \gamma^h + \gamma^m + \ldots\ldots$$

since the intermolecular attractions at interfaces (and hence surface tension) result from independent phenomena such as dispersion forces (d); dipole interactions (p); and hydrogen bonding (h); a subset of Lewis acid–base interactions, metallic bonds (m), etc

Table 1. Surface Tension Components (mJ/m^2) for Commonly Used Test Liquids[39]

liquids	γ	γ^d	γ^{AB}	γ^+	γ^-
water	72.8	21.8	51	25.5	25.5
glycerol	64	34	30	3.92	57.4
Formamide	58	39	19	2.28	39.6
α-bromonaphthalene	44.4	43.5	0	0	0
CH_2I_2	50.8	50.8	0	0	0

If you look at surface tension in general ok there seems to be some that should be gamma there ok, this is U divided by 2a square ok. So, whenever you talk about surface tension right, I mean the classic picture that you will see in the textbooks is that you know I have a container. If I look at a molecule in the bulk ok, it is being pulled in all direction you know by an equal you know force, right.

That means you know that the interactions are kind of isotropic right. However if you look at a molecular on the surface you know there is only interactions you know the you can think about the interaction being absent in the outer fluid, right. So, therefore you know I can define something like you know if the energy interaction between the molecules in the bulk is U, ok.

Now because of the fact that you know there if you look at a molecule at the surface, you can say that the on average the energy of interaction is going to be U by 2 because you know it is only interacting with maybe half the neighbors right. So, now if you know what is the area that the molecule occupies at the surface, I can actually calculate U divided by 2 times a square, where a square is the area that the molecules occupies to the surface, right ok.

So, you can kind of relate you know interfacial tension to the energy of interaction ok, where U is the energy of interaction between the molecules in the bulk ok. If I know that I can relate surface tension to the energy of interaction the bulk and the area that the molecules occupy, right.

Now by that concept what I can do is I can say that the overall contribution for the surface tension comes from the various intermolecular forces you know there is a dispersion component ok.

There could be some kind of a dipolar interaction, there could be hydrogen bonding interaction or metallic interaction, so on and so forth, ok. Therefore when we talk about the surface tension, ok one should understand that the surface tension the contribution to the surface tension comes from various types of interactions that are present for a between the molecules of a given substance.

And there could be various contribution and depending upon the nature of the material that we are trying to deal with you know gamma d could be dominant. If we look at as we said like for non polar species like decane and you know other material ok. Then gamma d would be the more dominant species of course if I goanna work with water then you know one has to worry about you know dipole interactions being important.

And you know, so people have kind of this is the you know this is for water, right, the overall surface tension and these are the different contributions that come from the different forces, ok. So, therefore, so you could actually relate A which is Hamaker constant you know if you are working with either a cases where several different forces contribute to you know surface tension.

Then you know you would have to consider the dispersion component of the contribution and then you can calculate what is the Hamaker constant.

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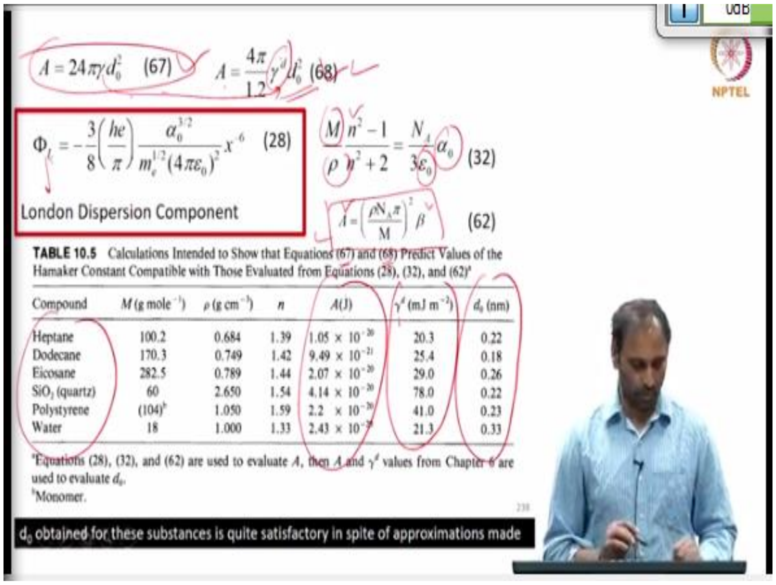

$A = 24\pi\gamma d_0^2$ (67) $A = \frac{4\pi}{1.2}\gamma^d d_0^2$ (68)

$$\Phi_L = -\frac{3}{8}\left(\frac{he}{\pi}\right)\frac{\alpha_0^{3/2}}{m_e^{1/2}(4\pi\varepsilon_0)^2}x^{-6} \quad (28)$$

London Dispersion Component

$$\frac{M}{\rho}\frac{n^2-1}{n^2+2} = \frac{N_A}{3\varepsilon_0}\alpha_0 \quad (32)$$

$$A = \left(\frac{\rho N_A \pi}{M}\right)^2 \beta \quad (62)$$

TABLE 10.5 Calculations Intended to Show that Equations (67) and (68) Predict Values of the Hamaker Constant Compatible with Those Evaluated from Equations (28), (32), and (62)[a]

Compound	M (g mole^{-1})	ρ (g cm^{-3})	n	A(J)	γ^d (mJ m^{-2})	d_0 (nm)
Heptane	100.2	0.684	1.39	1.05×10^{-20}	20.3	0.22
Dodecane	170.3	0.749	1.42	9.49×10^{-21}	25.4	0.18
Eicosane	282.5	0.789	1.44	2.07×10^{-20}	29.0	0.26
SiO_2 (quartz)	60	2.650	1.54	4.14×10^{-20}	78.0	0.22
Polystyrene	(104)[b]	1.050	1.59	2.2×10^{-20}	41.0	0.23
Water	18	1.000	1.33	2.43×10^{-20}	21.3	0.33

[a] Equations (28), (32), and (62) are used to evaluate A, then A and γ^d values from Chapter 6 are used to evaluate d_0.

[b] Monomer.

d_0 obtained for these substances is quite satisfactory in spite of approximations made

I just want to briefly now these are some tables in which so we have done this right. We know how to we got that, that is by equating the you know cohesion energy and the van der Waals interaction between the blocks, this were we considered you know instead of gamma, gamma d. This is one of the expressions that we would have looked up earlier, this is an expression for the London dispersion forces, ok.

And this we looked up earlier in which we relate Hamaker constant to beta and the other material properties ok. And there are also expressions where I can relate you know the polarizability you know and the permittivity to refractive index and you know the molar mass and you know stuffs like that, ok. So, what is been done here is they have calculated, so this is let me put it this way.

This is d_0, so calculations, so this is 67 and 68 that is these 2 ok**.** So, if you know the dispersion component, right gamma d. And if I know d_0, I can get A by this expression, right, because I know gamma d and d_0 square right. And of course if I, so the point that I want to make is that if the value is calculated from this, this you know or this they give comparable you know numbers ok.

And again you know for several materials is what is you know I wanted to mention, ok. So, you can the approach that I have mentioned you can use as approaches and wherever you do not have access to Hamaker constant you should be able to use one of these expressions and then calculate Hamaker constant for the material of interest ok, that is the point ok.

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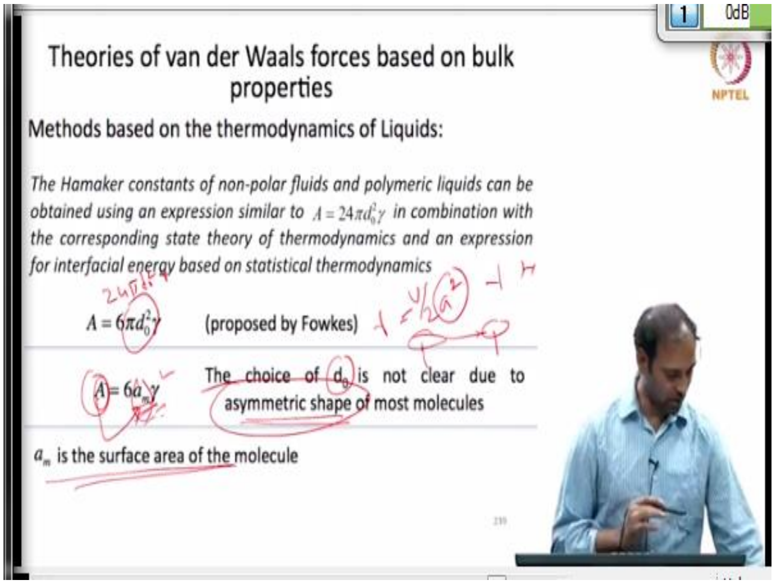

Theories of van der Waals forces based on bulk properties

Methods based on the thermodynamics of Liquids:

The Hamaker constants of non-polar fluids and polymeric liquids can be obtained using an expression similar to $A = 24\pi d_0^2\gamma$ *in combination with the corresponding state theory of thermodynamics and an expression for interfacial energy based on statistical thermodynamics*

$24\pi d_0^2\gamma$

$A = 6\pi d_0^2\gamma$ (proposed by Fowkes) $\frac{U}{2a^2}$

$A = 6a_m\gamma$ The choice of d_0 is not clear due to asymmetric shape of most molecules

a_m is the surface area of the molecule

So, there are so again people have proposed, so we had expression which is 24 pi d$_0$ square gamma, right, ok. There I mean if you look at this approach I mean one wanted to bring in what is called as a molecular anisotropy ok. If you have I said you know the U by 2 by a square ok is what gives you know in a way gamma, right. Now you know the a square is the area that the molecule occupies the interface.

Now you could have cases where you may be working with asymmetric shape molecules ok. If you look at molecular shapes, I mean there are objects which can be you know thought of very close to spherical shape and there are also cases where you know you have some non spherical or asymmetric shape molecules. Then you know what d do you consider? ok, what is the separation distance ok, is it the I mean if you have you know molecules like this you know whether the separation distance between this and this, center to center or this you know.

So, you will have issues you know finding out what is the actual d that you have to consider. Therefore there are approaches where I can relate A to the surface tension and a m, where a m is the surface area of the molecule itself. Then I know I do not have to worry about the separation distance, I can relate A to the surface area of the molecule directly ok.

So, this is one approach where A is kind of related to the surface area of the molecule and the surface tension of the material.

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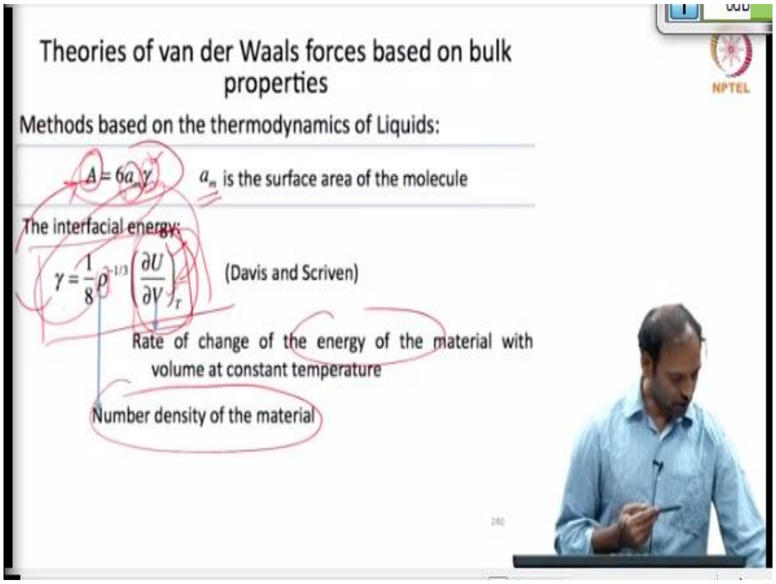

Theories of van der Waals forces based on bulk properties

Methods based on the thermodynamics of Liquids:

$A = 6a_m\gamma$ a_m is the surface area of the molecule

The interfacial energy:

$$\gamma = \frac{1}{8}\rho^{-1/3}\left(\frac{\partial U}{\partial V}\right)_T$$ (Davis and Scriven)

Rate of change of the energy of the material with volume at constant temperature

Number density of the material

Yeah, yeah that small a is the not that , a is the surface area of the molecule correct, correct. This A yeah oh then I have not made my point clear ok, this A that we are talking about what is this A will come back, will comeback, what is this a.

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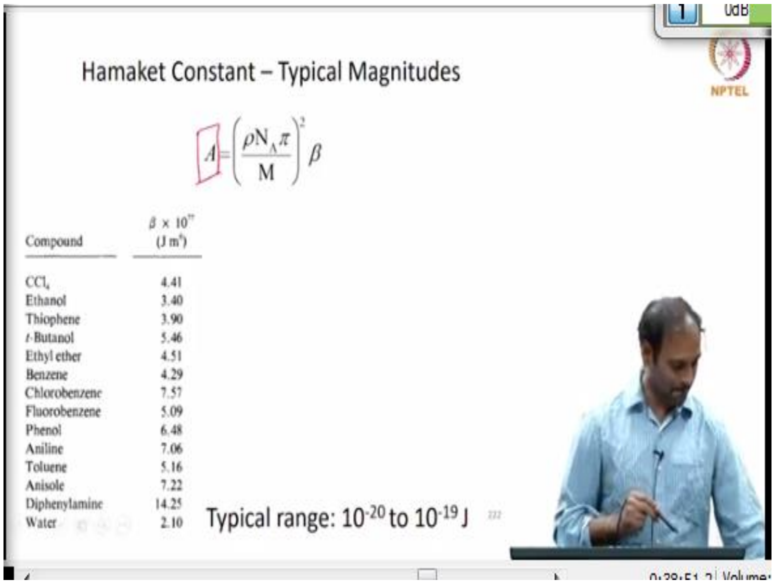

Hamaket Constant – Typical Magnitudes

$$A = \left(\frac{\rho N_A \pi}{M}\right)^2 \beta$$

Compound	$\beta \times 10^{77}$ (J m^6)
CCl_4	4.41
Ethanol	3.40
Thiophene	3.90
t-Butanol	5.46
Ethyl ether	4.51
Benzene	4.29
Chlorobenzene	7.57
Fluorobenzene	5.09
Phenol	6.48
Aniline	7.06
Toluene	5.16
Anisole	7.22
Diphenylamine	14.25
Water	2.10

Typical range: 10^{-20} to 10^{-19} J

Oh small a m, this one here, no here A Oh, this is ok let us say ok, here right, yeah. So, this a gamma is 2 a2 divided by sorry it is ok, U divided by 2 a square, ok. This is actually the area that the molecules occupy at the surface or at the interface one molecule, yeah. See, we are trying to think about like say we are trying to relate gamma which is the interfacial tension to the interaction energy ok.

Now if U is the interaction energy between the molecules in the bulk ok, U by 2, if you assume that you know there are only half neighbors, then you know U by 2 is what would the interaction energy for the molecules at the surface divided by a because you know surface tension is defined. You can think about this as energy per unit area right, this U will have units of energy and the area that it occupies a meter square right.

So, this essentially you know energy per unit area, right there are also approaches where you relate you know. Now this A goes as 6 a_m multiplied by gamma where a m is the surface area of the molecule and gamma I can relate it to again some thermodynamic properties, ok. If I know how the internal energy varies with in the volume of the material at a constant temperature.

And if rho is the then number density on the material, I can actually estimate gamma and I can plug that value of gamma into this expression. And in turn I can calculate a itself, ok, yeah, molecule yes. So, see this gamma was a surface tension, yeah right, gamma was the surface tension that we agree, right. So, if you have a cohesion process 2 times gamma will be the work of cohesion, ok.

So, this is the work of cohesion and you can think about this as a again work of cohesion will again have a units of energy, right. In this case again will be energy per unit area, right and you know we looked at right this again is a interaction energy between 2 blocks again this will also have units of again joules per meter square, right, ok. Now I am trying to relate gamma is the interfacial tension and I can relate interfacial tension to molecular properties, right.

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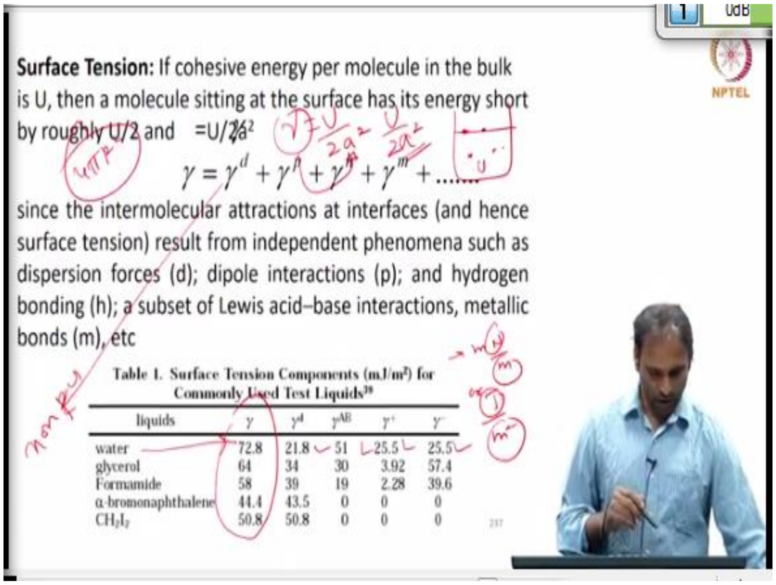

Surface Tension: If cohesive energy per molecule in the bulk is U, then a molecule sitting at the surface has its energy short by roughly U/2 and $=U/2a^2$

$$\gamma = \gamma^d + \gamma^p + \gamma^h + \gamma^m + \ldots\ldots$$

since the intermolecular attractions at interfaces (and hence surface tension) result from independent phenomena such as dispersion forces (d); dipole interactions (p); and hydrogen bonding (h); a subset of Lewis acid–base interactions, metallic bonds (m), etc

Table 1. Surface Tension Components (mJ/m²) for Commonly Used Test Liquids[29]

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glycerol	64	34	30	3.92	57.4
Formamide	58	39	19	2.28	39.6
α-bromonaphthalene	44.4	43.5	0	0	0
CH_2I_2	50.8	50.8	0	0	0

And that is how this was brought in, right, if you look at right, let's, ok, so to have here is gamma is U divided by 2 a square. So, all I am trying to say here is the gamma in a way is related to the area that the molecules occupy the surface, ok. So, let me put this way, right, now say that I have a container say that there are 2 molecules in the bulk and the interaction energy between them is U, right, ok.

Now I say that now these molecules are now at the surface, ok you know I can think about that now the energy of interaction would be not be the same, ok. I say it is going to be half, ok, that is U by 2, ok. Now surface tension you can it will have units of milli newtons per meter or joules per meter square either force per unit length or energy per unit area, ok. Now I know the interaction energy between the molecules at the surface at U by 2, ok, I want to get in the area you know into the picture.

And I say that this area that the molecules occupy the surface no, no I am yeah it will be proportional to some length square, ok. So, that it can be some time the a I mean the a_m is the yeah so it is some length square, ok. This some area right, ok and I am saying that this area is the area that the molecule occupies at the surface, is that ok. So, see no see the surface area so say that I have a spherical particle, say that the molecule that I am considering is spherical.

Now if these spherical molecule in the bulk then the surface area is going to be 4 pi R square, right. But what we are interested is the surface area that it occupies at the surface, the area that the molecule occupies at the surface, that is not pi R square, ok. It depends on the orientation of the, it depends on the shape of the you know molecule it depends on the orientation all of this, right. So, therefore, ok that is, ok, so in this case your A is related to gamma, ok times.

So, this in a way this a_m right, so I essentially have this pi d square, ok. That is an area term, right and all that is been done here is that look if you have cases w here you have you know some complex shape molecule. Instead of worrying about the distance of you know equilibrium separation distance you think about the surface area of the molecule, ok, that is what is done.

And now one of the way of getting gamma is to relate that to you know again some thermodynamic properties in this case how the internal energy of the material changes with volume at the constant temperatures. So, if you have this data, if I know what is rho I can plug this in this expression and I can get A, ok.

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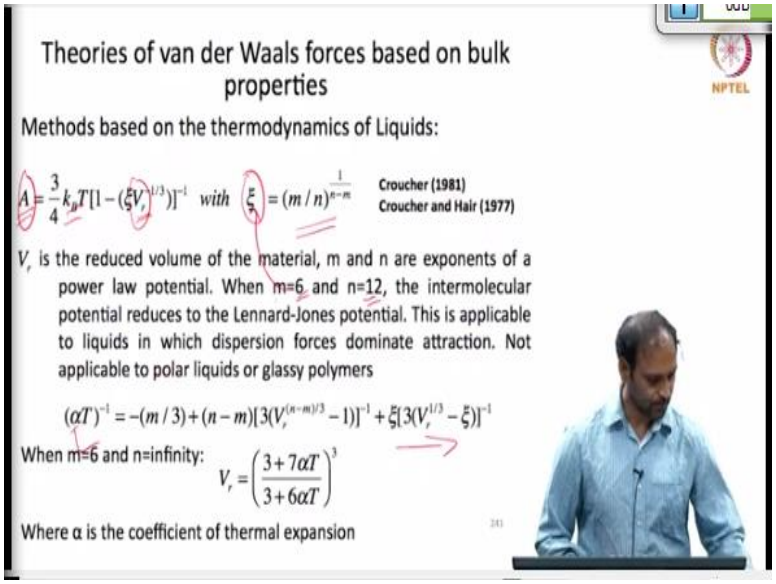

Theories of van der Waals forces based on bulk properties

Methods based on the thermodynamics of Liquids:

$$A = \frac{3}{4}k_BT[1-(\xi V_r)^{1/3})]^{-1} \quad with \quad \xi = (m/n)^{\frac{1}{n-m}}$$

Croucher (1981)
Croucher and Hair (1977)

V_r is the reduced volume of the material, m and n are exponents of a power law potential. When m=6 and n=12, the intermolecular potential reduces to the Lennard-Jones potential. This is applicable to liquids in which dispersion forces dominate attraction. Not applicable to polar liquids or glassy polymers

$$(\alpha T)^{-1} = -(m/3)+(n-m)[3(V_r^{(n-m)/3}-1)]^{-1}+\xi[3(V_r^{1/3}-\xi)]^{-1}$$

When m=6 and n=infinity:

$$V_r = \left(\frac{3+7\alpha T}{3+6\alpha T}\right)^3$$

Where α is the coefficient of thermal expansion

So, the other approaches there are cases where I can relate A which is the Hamaker constant to the thermal energy and Vr which is the reduce volume. And again there are expressions where I can relate if I know ok this essentially comes from the if you look at Lennard-Jones potential, right. So, typically Lenard Jones potential is an example of a 6, 12 potential, right.

So, where m equal to 6 and n is equal to 12 I can get you know from that I can get this parameter and there were also expressions where I can relate Vr which is the reduce volume to the you know the coefficient of thermal expansion you know. And other measurable properties, so therefore there are various theories available where I can relate Hamaker constant to measurable properties.

And depending upon the materials that I am working with I should be able to go back and of course some approaches are more suited for liquids, some are you know are more suited for polar liquids, some are more suited for other kind of materials. So, we have to think a little bit about which is the best theory that I should go to when applying them. However there are guidelines in the literature to look at appropriate you know theories to relate A to measurable quantities.

And you should be able to pick that up and then use them in your calculations to obtain what is the Hamaker constant, ok.

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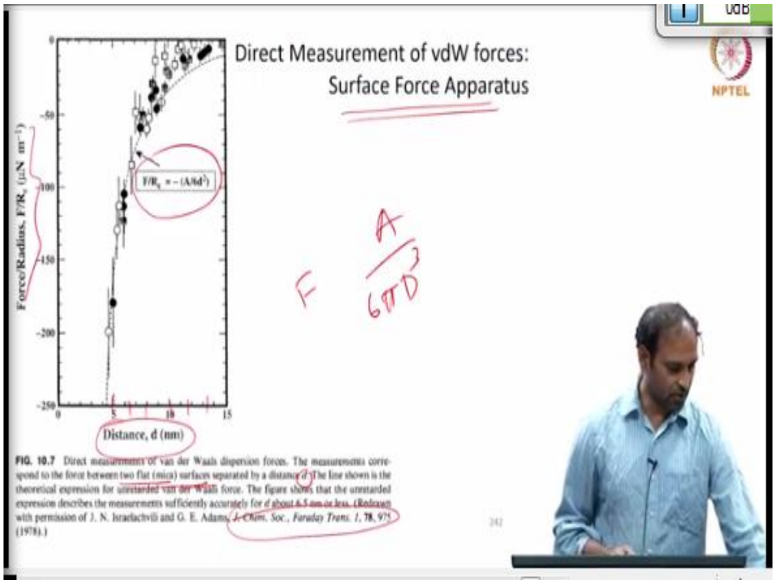

Direct Measurement of vdW forces:
Surface Force Apparatus

FIG. 10.7 Direct measurements of van der Waals dispersion forces. The measurements correspond to the force between two flat (mica) surfaces separated by a distance d. The line shown is the theoretical expression for unretarded van der Waals force. The figure shows that the unretarded expression describes the measurements sufficiently accurately for d about 6.5 nm or less. (Redrawn with permission of J. N. Israelachvili and G. E. Adams, *J. Chem. Soc., Faraday Trans. I*, **78**, 975 (1978).)

And just to end people have been able to measure van der Waals forces I would like you guys go back and read up some papers in the literature. That is something called as surface force apparatus, ok. And what is being measured here is force divided by radius as a function of distance, ok, force divided by radius. I will just go back to that expression, so we had that in one of the classes, right.

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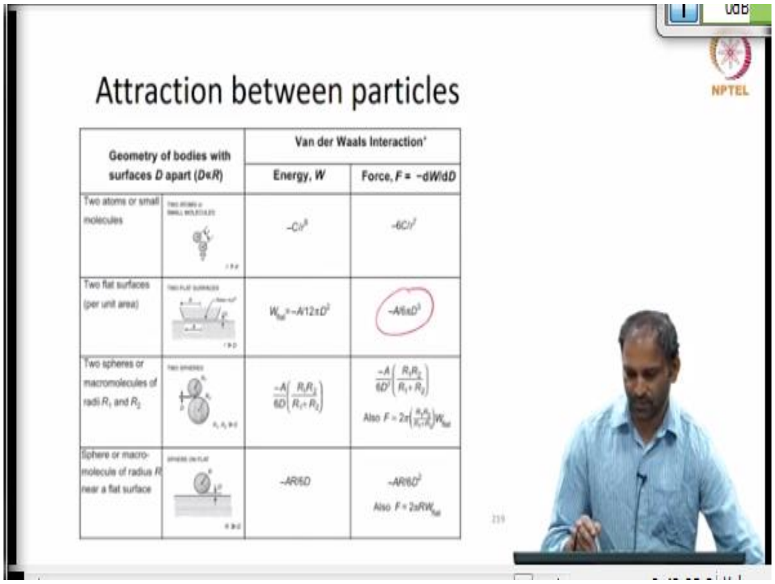

Attraction between particles

Geometry of bodies with surfaces D apart ($D \ll R$)		Van der Waals Interaction*	
		Energy, W	Force, $F = -dW/dD$
Two atoms or small molecules		$-C/r^6$	$-6C/r^7$
Two flat surfaces (per unit area)		$W_{flat} = -A/12\pi D^2$	$-A/6\pi D^3$
Two spheres or macromolecules of radii R_1 and R_2		$\frac{-A}{6D}\left(\frac{R_1R_2}{R_1+R_2}\right)$	$\frac{-A}{6D^2}\left(\frac{R_1R_2}{R_1+R_2}\right)$ Also $F = 2\pi\left(\frac{R_1R_2}{R_1+R_2}\right)W_{flat}$
Sphere or macromolecule of radius R near a flat surface		$-AR/6D$	$-AR/6D^2$ Also $F = 2\pi RW_{flat}$

So, if you look at this interaction force, ok between where is that, so that was here, ok. If you have 2 flat planes the interaction energy was A divided by 6 pi D cube, right. Now ok so that is your force, right, now I can so therefore , so if you look at this is the measurement, so the data point that you see that is the filled circles open circles and other experimental data that have been measured you have been able to measure force is a function of distance.

And that line is the fit, ok, so which, so there are direct measurements of van der Waals forces which people have been able to measure. And it kind of complies with you know this is actually done between 2 flat mica sheets, ok. And they are separate by a distance D for several distances you this will get these you know force divided by radius. And then plot that and it looks like it actually follows you know what is been predicted by theory, ok.

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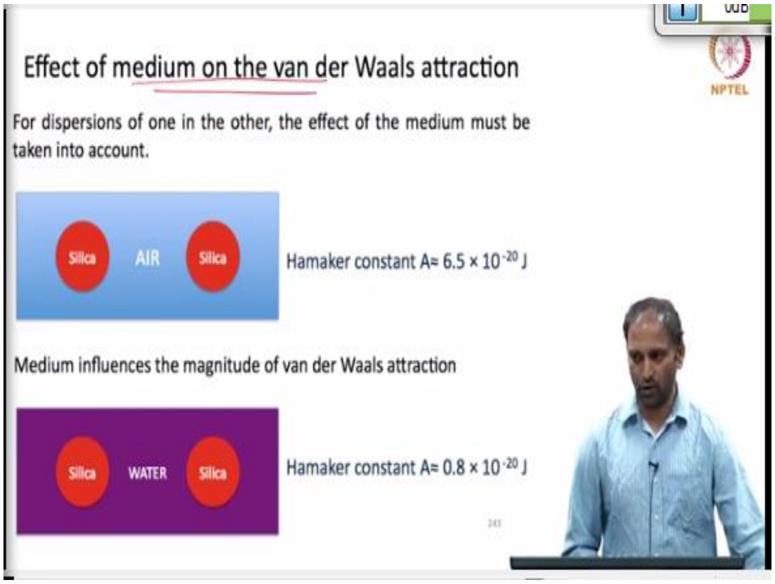

Effect of medium on the van der Waals attraction

For dispersions of one in the other, the effect of the medium must be taken into account.

Hamaker constant A≈ 6.5 × 10^{-20} J

Medium influences the magnitude of van der Waals attraction

Hamaker constant A≈ 0.8 × 10^{-20} J

So, I am stop here , so the next topic that I am going to do is to look at effect of medium on the van der Waals attraction, ok. So, instead of vacuum you know if you have air between the particles or if you have some other fluid between the particles how would van der Waals force of attraction be you know altered is what we goanna look at, so thanks.