Colloids and Surfaces
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Lecture-16
Calculation of Vanderwaal's Forces Between Semi-Infinite Blocks and Hamaker Constant-II

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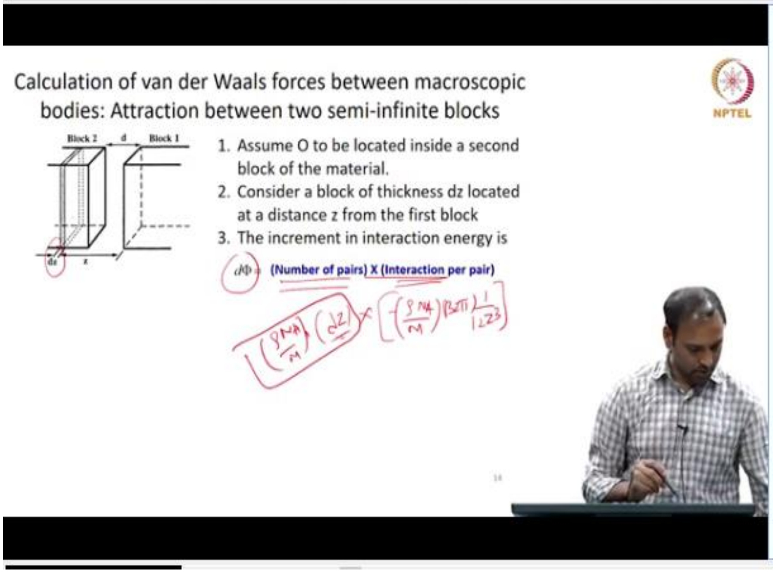

Calculation of van der Waals forces between macroscopic bodies: Attraction between two semi-infinite blocks

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

$d\Phi =$ (Number of pairs) X (Interaction per pair)

$$\left(\frac{\rho N_A}{M}\right)\left(dz\right)\times\left[-\left(\frac{\rho N_A}{M}\right)(\beta 2\pi)\frac{1}{12z^3}\right]$$

Now what we do is, we say that, I am going to say that this molecule O, it is now embedded in block 2 okay. And again, it is made up with the same material right. And we say if this is your molecule O and we are going to embed that in a small block of thickness dz okay. And that is located at a distance z from the surface of another block right. Now, again I can write up an expression for the increment in interaction okay. Exactly the way we wrote up okay.

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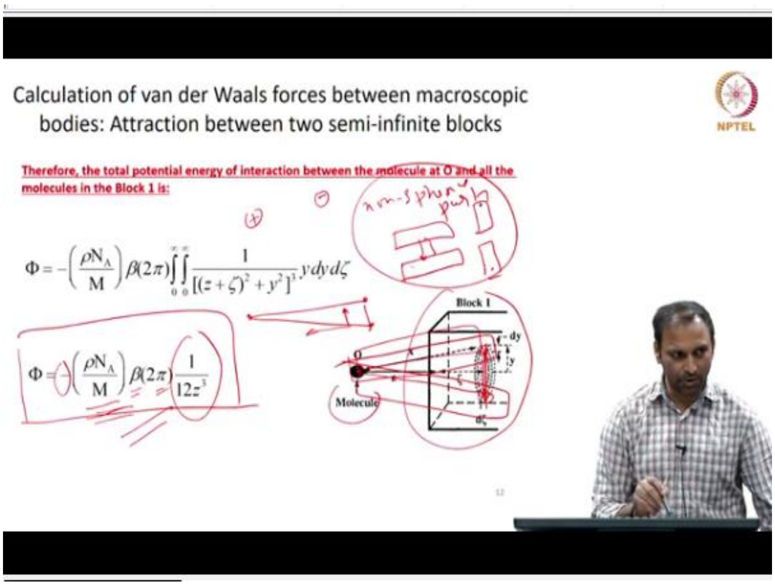

Calculation of van der Waals forces between macroscopic bodies: Attraction between two semi-infinite blocks

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

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

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

Let us go back and look at the expression right okay, it is I know that this is the interaction between every molecule that is in this small element and the entire block right. Now my interaction per. So, I will again, the same concept right. The number of pairs multiplied by interaction per pair. Now, the interaction per pair now is actually it is - rho NA by M into beta into 2 pi, right into 1 over 12 z cube, you guys agree, right.

There is the interaction per pair, now multiply by the number of, you know, pairs. So, I am going to multiply this only by dz okay. And I am going to say that the interaction that I am going to calculate is interaction per unit area okay, ideally, I should multiply this by the number of molecules in this small strip, dz, okay, which is dz times rho NA by M, into some area, right.

Because that is the volume. So, this will give me the number of atoms or molecules in their small thin section, dz right. That is area times dz will be the volume that multiplied by number per unit volume. But I am going to say that the d phi, or the phi that I am going to calculate, it is actually energy per unit area. And then I am going to multiply this interaction pair only by rho NA by M multiplied by the dz okay.

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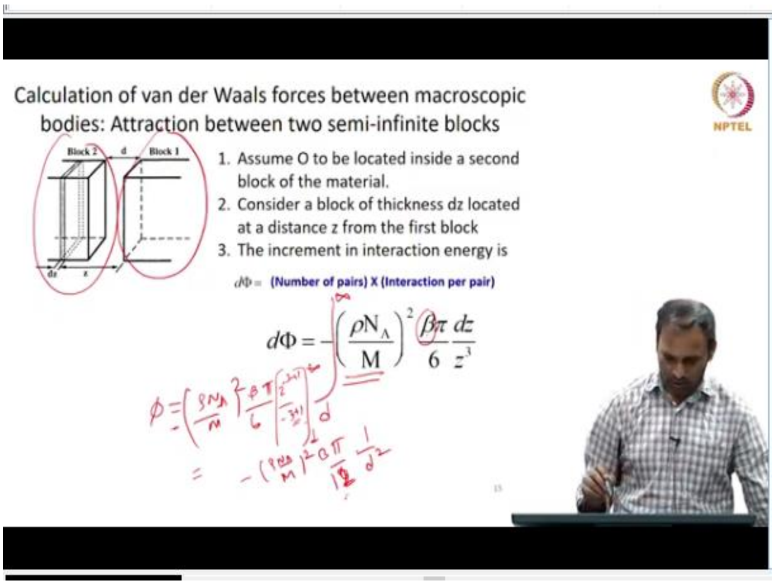

Calculation of van der Waals forces between macroscopic bodies: Attraction between two semi-infinite blocks

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

$d\Phi$ = (Number of pairs) X (Interaction per pair)

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

$$\phi = -\left(\frac{\rho N_A}{M}\right)^2 \frac{\beta\pi}{6}\left[\frac{z^{-3+1}}{-3+1}\right]_d^\infty$$

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

Therefore, I have rho NA by M whole square, I had 2 beta and there was 12 there. So, there is a you know factor of 2 I have removed. So, beta pi into dz divided by 6 z cube is what you get. Yeah, so this is yeah, yeah. I mean, this is the area of the surface area of the block if you want to consider yeah okay. So, now, what I can I want to do is if I want to now get the overall interaction between block 2 and block 1.

What do I do, I again have to do an integration and this integration is going to be from d which is the distance of closest separation to again, infinity right, I could have them really far apart, the separation distance is going to be infinite. And then I can bring them to any distance d, okay. So, if you do that, your phi is going to be rho NA divided by M whole square beta pi divided by 6 okay, again, z power - 3 + 1 divide by - 3 + 1 okay, 0 d 2 infinite okay.

I have a negative sign here, right okay. So, therefore, this becomes - rho NA by M whole square into beta pi by 6 into 1 over d square okay and there was 2 there right, there was a 2 here this becomes well right, because the - 2 right - 3 + 1 is 2. Therefore, 6 2 is 12 okay.

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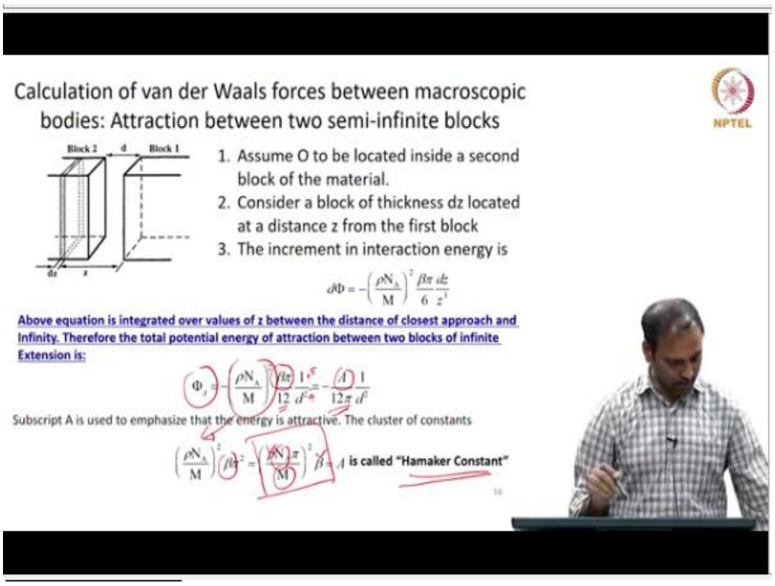

Calculation of van der Waals forces between macroscopic bodies: Attraction between two semi-infinite blocks

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"

So, therefore, what you actually end up is the overall interaction phi A okay is going to be row NA by M whole square beta times pi divided by 12 into 1 over d square, there are a cluster of constants, this rho NA by M is a constant for a given material that you consider and you have B okay, that is again beta, again constant for a given material okay, you can multiply this by pi and divide by pi you know to get a particular form okay.

And then you know your phi A essentially goes as - A divided by 12 pi into 1 over d square and this A actually is a cluster of constants which is what is called Hamaker constant okay, which has all the material properties, right. It has what is beta, the density of the material that you are considering Avogadro number and this is the molar mass right.

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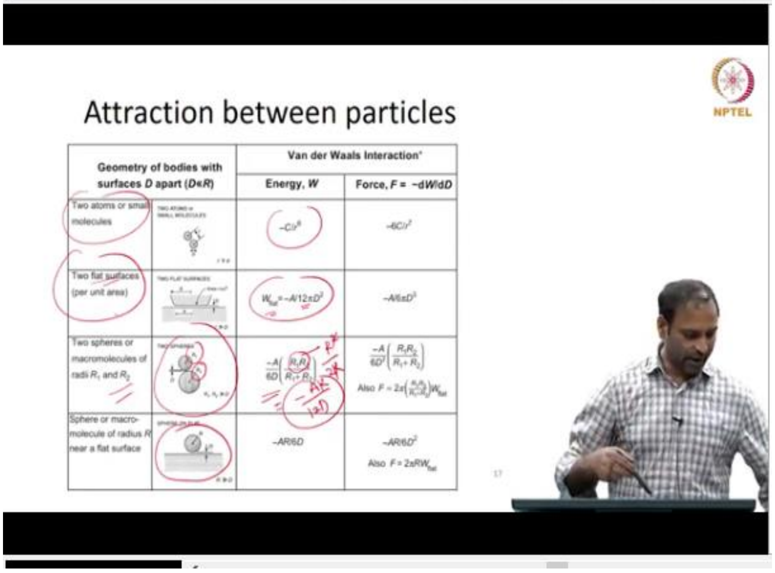

Attraction between particles

Geometry of bodies with surfaces D apart (D≪R)		Van der Waals Interaction*	
		Energy, W	Force, F = −dW/dD
Two atoms or small molecules	TWO ATOMS or SMALL MOLECULES	$-C/r^6$	$-6C/r^7$
Two flat surfaces (per unit area)	TWO FLAT SURFACES	$W_{flat} = -A/12\pi D^2$	$-A/6\pi D^3$
Two spheres or macromolecules of radii R_1 and R_2	TWO SPHERES	$\frac{-A}{6D}\left(\frac{R_1R_2}{R_1+R_2}\right)$	$\frac{-A}{6D^2}\left(\frac{R_1R_2}{R_1+R_2}\right)$ 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	SPHERE ON FLAT	$-AR/6D$	$-AR/6D^2$ Also $F = 2\pi RW_{flat}$

So, now, that is the interaction between 2 you know blocks right. Now, in fact, that is what we derived here, okay, - A divided by 12 pi into 1 over distance square okay, that is for 2 flat surfaces. And that is what I mentioned right, this interaction if you calculate I will come back to this point little later, okay. Now, if you had 2 atoms or small molecules, you know your energy of interaction goes as 1 over distance power 6.

Now, if you have 2 flat plates, the energy of interaction goes is 1 over distance square okay. Similarly, you have expression for different you know, types of particles that you are going to deal with okay, if you have 2 spherical particles of you know different radii R 1 and R 2 and if they are again this you know separated by a distance d, then the energy of interaction goes as - A divided by 60 times R 1 R 2 divided by R 1 + R 2.

If the particles are of same size this becomes R square divided by 2 times R right, if you have particles of same size, then this gets cancelled. Therefore, regimentation will be - A divided by 12 times my AR divided by 12 times d right, that is if you are working with 2 spherical particles and if you would like to calculate what is the van der Waals force of interaction between 2 identical spheres of same radius.

Then the energy of interaction is going to be - AR divided by 12 d okay. So, therefore and this is the interaction between 12 a spherical particle under a flat surface the energy of interaction goes as - AR divided by 6 times d.

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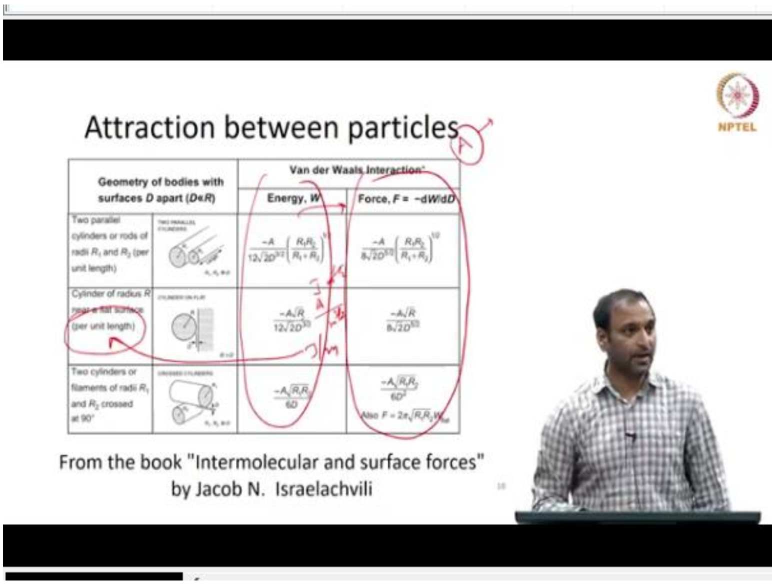

Attraction between particles

Geometry of bodies with surfaces D apart ($D \ll R$)		Van der Waals Interaction	
		Energy, W	Force, $F = -dW/dD$
Two parallel cylinders or rods of radii R_1 and R_2 (per unit length)	TWO PARALLEL CYLINDERS	$\frac{-A}{12\sqrt{2}D^{3/2}}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/2}$	$\frac{-A}{8\sqrt{2}D^{5/2}}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/2}$
Cylinder of radius R near a flat surface (per unit length)	CYLINDER ON FLAT	$\frac{-A\sqrt{R}}{12\sqrt{2}D^{3/2}}$	$\frac{-A\sqrt{R}}{8\sqrt{2}D^{5/2}}$
Two cylinders or filaments of radii R_1 and R_2 crossed at 90°	CROSSED CYLINDERS	$\frac{-A\sqrt{R_1R_2}}{6D}$	$\frac{-A\sqrt{R_1R_2}}{6D^2}$ Also $F = 2\pi\sqrt{R_1R_2}W_{flat}$

From the book "Intermolecular and surface forces" by Jacob N. Israelachvili

So, there are expressions like this which are available in the literature, which you could use, okay. So, this is, so this column is for the energy of interaction. And of course, as I said, if you know the energy of interaction, I can also calculate what is the force of interaction just by - dW by you know if you differentiate this with respect to distance, okay, that is when you get the force of interaction right.

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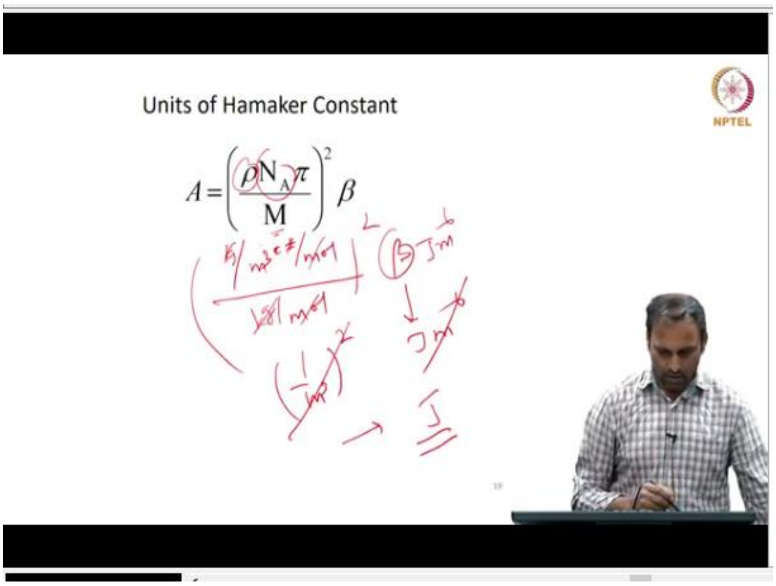

Units of Hamaker Constant

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

Now, before I would like to make a point, but before that, I would think about what is the units of Hamaker constant, right. Let us, so this is the expression for Hamaker constant, right, that is what we derived. So, rho has units of kg per metre cube, right. That is your density. N_A is number per mole right divided by and you have M is a molecular weight that is, you know grams per mole right or kg per mole or grams per mole, right.

What is that, Yeah, yeah so that is finite. So, right, everything is cancel. So a beta was in your beta**.**

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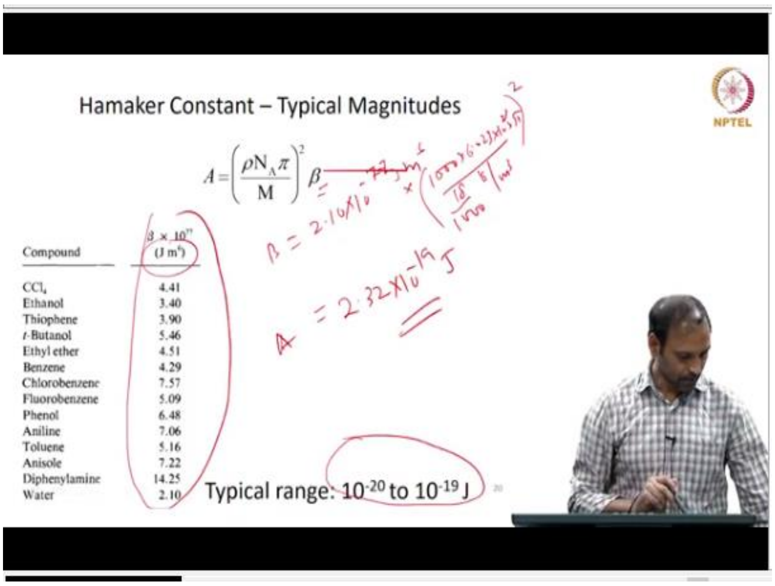

Hamaker Constant – Typical Magnitudes

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

$$\beta = 2.10\times10^{-77}\ \mathrm{J\,m^6} \times \left(\frac{1000\times6.023\times10^{23}\times3.14}{\frac{18}{1000}\ \mathrm{kg/mol}}\right)^2$$

$$A = 2.32\times10^{-19}\ \mathrm{J}$$

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

I do not know if you pay attention beta actually has units of joules metre per 6 okay, it has units of okay joules, okay metre per 6 right, this unit is joules metre per 6 and you have 1 over metre cube okay again whole square. So, therefore this metre power 6 metre power 6 gets canceled. Therefore, Hamaker constant will have a unit of joules right. Then let us think about typical values for Hamaker constant okay.

I know the magnitude of beta for several materials, let us take a simple case of water, beta is okay 2.10 into 10 power - 77 joules metre per 6 right this beta okay multiply that by density of water is 1000 okay let us say some number typical number kg per metre cube Avogadro number is 6.023 10 power 23, you have pi divided by molecular weight of water it is 18 grams per mole okay.

That is 18 divided by 1000 okay, that is kg per metre cube whole square right, if you put in all the number that I get is about 2.32 okay that is A is going to be 2.32 into 10 power - 19 joules is what you get okay. If you put in the typical values you know for the constants right. So, this for water or typical number that you get is 2.3 to 10 power - 19. So, typical range of Hamaker constant for any material is in the range from 10 power - 20 to 10 power - 19 joules okay.

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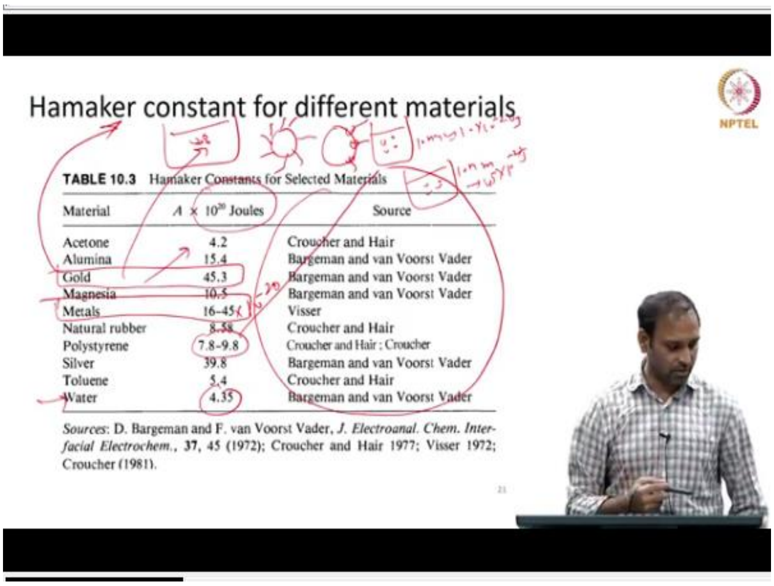

Hamaker constant for different materials

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
Metals	16–45	Visser
Natural rubber	8.58	Croucher and Hair
Polystyrene	7.8–9.8	Croucher and Hair ; Croucher
Silver	39.8	Bargeman and van Voorst Vader
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).

Now, this is a list of Hamaker constant for different materials taken from different sources , what is interesting to note would be that this is water if you look at this number right 4.35 is very close to what we calculated right of course, this is an approximation right, it is very close to what we calculated. Now, if you look at metals okay, the numbers are I know about 16 to 45 you know 10 per - 20 okay.

This is 10 power - 20. This is when you say is 10 power 20 there is going to be - 20 right. Now, and if you look at gold. So, what it means is that if I have a polystyrene particles okay of some size say 10 nanometer for example, okay whose Hamaker constant is about say 10 okay 10 power - 20 joules or if I take gold particles of again exactly the same size whose Hamaker constant is about 45 okay into 10 power - 20 okay.

The gold particles would experience a greater van der Waals force of attraction compared to the polystyrene particles because the Hamaker constant for gold particles are much larger than the Hamaker constant for polystyrene, okay, that is the implications. Therefore, you go back and look at literature, whenever you people talk about gold nanoparticles, you will always see that the moment you may gold particles they cluster together.

And they form large aggregates because of the large magnitude of van der Waals force of attraction, if you want to keep particles of metals, okay in a dispersed state, what people typically do is they make particles and then they typically put a stabilizing layer. It could be grafting, okay, it could be putting a surfactant layer on the top okay, something like that there is always done.

If you do not do that, the van der Waals interactions are going to dominate and they will lead the particles could aggregate a cluster because of van der Waals forces, okay. So, before we finished just one point one thing that you should watch out is whenever you have an expression for energy, in some cases, the energy is expressed as energy per unit length. If you look at this, right, A has units of joules.

This is metre per half right, there is R right and you have metre power 3 by 2, okay, this gets cancelled therefore, energy is going to be in okay, joules per unit length. And of course, you had a case where you know the energy was expressed in terms of energy per unit area, okay or if you can take cases like this energy is expressed just in terms of joules itself, okay, one thing that you should worry about whenever you get an expression, you can have an expression in which you calculate the interaction energy.

Or interaction energy per unit area, or interaction energy per unit length, you have to be careful, that is all okay, so with that we will stop. So, what we will do tomorrow is we will talk a little bit about the limitation of the approach that we followed, okay. And then we are going to come up with some simple methods by which I can relate a Hamaker constant to some measurable properties of the materials, okay, it is what we are going to look at in the next class. Thanks.